

DFT Calculation on the Electron Affinity of Polychlorinated Dibenzo-*p*-dioxins

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Polychlorinated dibenzo-*p*-dioxins (PCDDs) are extremely toxic and persistent environmental pollutants. Their chemical reactivities and other physicochemical/biological properties show a strong dependence on the chlorination pattern. With increasing the number of chlorines, dioxin congeners become more electronegative and gain higher electron affinities. The vertical electron affinities (VEA) are related with the LUMO energies of neutral molecules. LUMO energies of all PCDD congeners were calculated at the B3LYP/6-31G** level and those of some selected congeners at the level of B3LYP/6-311G**/B3LYP/6-31G** and B3LYP/cc-pvtz/B3LYP/6-31G**. The total energies of neutral and anionic species for dibenzo-*p*-dioxins (DD), 1469-TCDD, 2378-TCDD, and OCDD were calculated at the level of B3LYP/6-31G**, B3LYP/aug-cc-pvdz, and B3LYP/aug-cc-pvtz/B3LYP/6-31G**. By using the four congeners with D_{2h} symmetry as reference molecules, we could estimate VEA (B3LYP/aug-cc-pvdz) of 75 PCDD congeners based on the linear correlations between LUMO energy and VEA (B3LYP/6-31G**) and between VEA (B3LYP/6-31G**) and VEA (B3LYP/aug-cc-pvtz/B3LYP/6-31G**). Results show that all PCDDs with the number of Cl ≥ 3 have positive electron affinities. The PCDD electron affinity values provided in this work can be a useful data set in understanding the congener-specific reactivities of dioxins in various environmental media.

Key Words : Polychlorinated dibenzo-*p*-dioxin, DFT, Electron affinity

Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) have attracted public interests due to their toxicity and persistency.^{1,2} A large quantity of PCDDs has been emitted into the atmosphere from various incineration sources of chlorine-containing wastes,³⁻⁶ transported through a long distance, and distributed globally.⁷⁻⁹ PCDDs have very low water solubility and accumulate in lipids of biological organisms.

Physical, chemical, and biological properties of PCDDs strongly depend on the number and position of substituted chlorines in general. In particular, it is widely recognized that the biological toxicities of PCDDs are extremely congener specific.^{10,11} Recently, Mhin *et al.*¹² have shown that the molecular quadrupole moments as a surrogate parameter for molecular charge distribution change sensitively and systematically with the chlorination pattern and that all toxic congeners share a unique charge distribution pattern. The ring vibrational IR frequencies of PCDDs are also very sensitive to the chlorination pattern.¹³ Lee *et al.*¹⁴ recently calculated the heat of formation for 75 PCDD congeners using a DFT method and demonstrated that the intramolecular chlorine repulsion energies critically affect their thermodynamic properties in a systematic way. While many other physicochemical properties of PCDDs are expected to be highly congener-specific, experimental data on PCDDs are scarce due to their toxicity and experimental difficulties in dealing with them.¹⁵⁻¹⁷ Therefore, computational methods are ideal for predicting their properties and in other dioxin-

related research.¹⁸⁻²¹

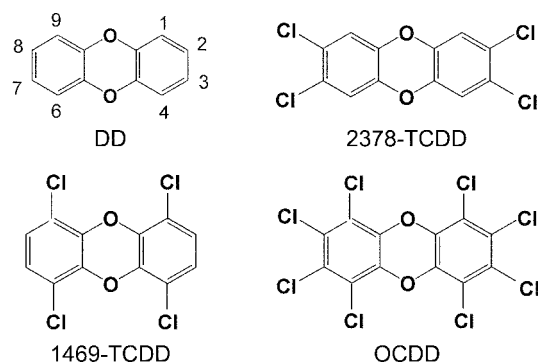
Frontier orbitals and the gap energy between HOMO and LUMO can be employed to explain reactivities of PCDDs as well as their thermodynamic properties.^{19,22,23} Koester *et al.*¹⁹ reported MNDO calculation results for LUMO energies of PCDDs with the number of Cl ≥ 4 . However, semi-empirical calculations on electronic properties such as an electron affinity are not reliable. Berkout *et al.*²⁴ reported that an electron attachment energy obtained from electron capture negative ion mass spectrometry was well correlated with the virtual orbital energy calculated at DFT level. In a previous study,²⁵ the electronic energy required for the transition from a neutral ground state to a lowest excited anionic state was assumed to be a vertical electronic affinity (VEA). They calculated VEA of 1368-TCDD, 2378-TCDD, and 1234-TCDD at the level of B3LYP/aug-cc-pvdz to be 0.232, 0.152, and 0.116 eV, respectively. DFT calculation gave reasonable estimations for VEA.

In this work, we carried out DFT calculation to estimate VEA for all 75 PCDD congeners by using the calculated vertical electron affinities of highly symmetric congeners as references: dibenzo-*p*-dioxin (DD), 1,4,6,9-tetrachlorinated dibenzo-*p*-dioxin (1469-TCDD), 2,3,7,8-tetrachlorinated dibenzo-*p*-dioxin (2378-TCDD), and octachlorinated dibenzo-*p*-dioxin (OCDD). The calculated results show that mono- and some dichlorinated dioxins have negative electron affinities while all other congeners with the number of Cl ≥ 3 have positive electron affinities.

Computational Methods

We have carried out DFT calculation using a Gaussian 98

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Scheme 1. Structure of four dioxin congeners with D_{2h} symmetry for which the vertical electron affinities (VEA) were directly calculated in this work.

suit of programs²⁶ for DD and 75 PCDDs at the B3LYP/6-31G** level to obtain their LUMO energies. Vertical electron affinities (VEA) were obtained for DD, 1469-TCDD, 2378-TCDD, OCDD (Scheme 1) based upon the calculation for the neutral and anionic species at the level of B3LYP/6-31G**, B3LYP/aug-cc-pvdz, and B3LYP/aug-cc-pvtz//B3LYP/6-31G**. VEA²⁵ was evaluated from eq 1:

$$\text{VEA (eV)} = E_{\text{neutral}} - E_{\text{anion}} \quad (1)$$

where E_{neutral} is the total energy of neutral dioxin species at an optimized geometry and E_{anion} is the total energy of the corresponding dioxin anion calculated at the optimized geometry of the neutral species. DFT calculation for open-shell systems such as the anionic species reduces spin contamination.^{27,28} MP2 level calculation was not performed due to spin contamination. In our calculation the S^2 value for anionic radical value is less than 0.76.

Results and Discussion

The total energies of neutral and anionic species for DD, 1469-TCDD, 2378-TCDD, and OCDD are calculated at the level of B3LYP/6-31G**, B3LYP/aug-cc-pvdz, and B3LYP/aug-cc-pvtz//B3LYP/6-31G** are listed in Table 1. Based on the total electronic energies of neutral and anionic dioxin species, VEA for the four D_{2h} congeners are obtained from eq 1. The nuclear geometry of anions is assumed to be the same to that of neutral dioxin molecules. It was reported that VEA values calculated at the DFT level was reliable and consistent with experimental results: the previously reported VEA value of 1234-TCDD calculated at the B3LYP/aug-cc-

pvdz level was 0.116 eV,²⁵ which is agreeable with the experimental value of 0.11 eV.²⁴

LUMO energies of DD and 75 PCDDs calculated at the B3LYP/6-31G** level are listed in Table 2. LUMO energies calculated using different basis sets are compared in Figure 1, which shows that they monotonously decrease with increasing the number of chlorines. DD has the highest LUMO energy and OCDD, the lowest among all. Electron affinity is proportional to negative LUMO energy. We obtain good linear correlations between LUMO and VEA at the B3LYP/6-31G** ($R^2 = 0.9960$), the B3LYP/aug-cc-pvdz, ($R^2 = 0.9906$) and B3LYP/aug-cc-pvtz//B3LYP/6-31G** ($R^2 = 0.9664$) level as shown in Figure 2. LUMO and VEA at the B3LYP/6-31G**, B3LYP/aug-cc-pvdz, and B3LYP/aug-cc-pvtz//B3LYP/6-31G** level can be related through eqs 2, 3, and 4, respectively.

$$\text{VEA (B3LYP/6-31G**)} = -1.953 - 38.211 E_{\text{LUMO}} \quad (2)$$

$$\text{VEA (B3LYP/aug-cc-pvdz)} = -0.685 - 19.018 E_{\text{LUMO}} \quad (3)$$

$$\text{VEA (B3LYP/aug-cc-pvtz//B3LYP/6-31G**)} = -0.623 - 19.099 E_{\text{LUMO}} \quad (4)$$

We performed similar calculations at the level of B3LYP/aug-cc-pvdz and B3LYP/aug-cc-pvtz//B3LYP/6-31G** for

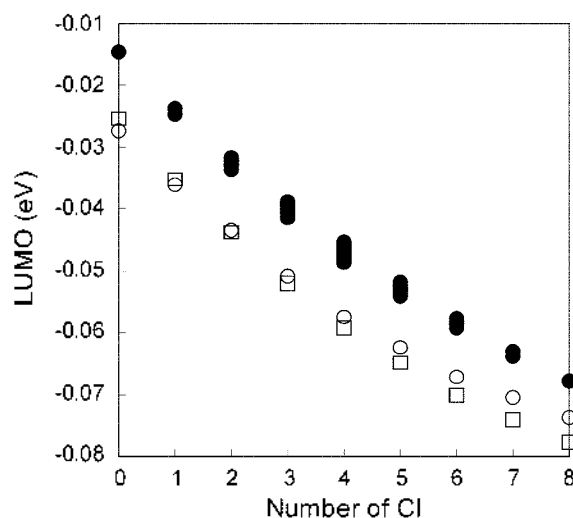


Figure 1. LUMO energies of PCDDs calculated at the level of B3LYP/6-31G** (filled circle) for all congeners, B3LYP/cc-pvtz//B3LYP/6-31G** (open circle), and B3LYP/6-31G**//B3LYP/6-31G** (open square) for the most stable congeners within the homologues (DD, 2-MCDD, 27-DCDD, 137-TrCDD, 1369-TCDD, 12479-PCDD, 124689-HxCDD, 1234679-HpCDD, OCDD).

Table 1. Total Energies (Hartree) of Neutral and Anionic Dioxin Species and VEA (eV) Calculated at the level of B3LYP/6-31G**, B3LYP/aug-cc-pvdz, and B3LYP/aug-cc-pvtz//B3LYP/6-31G**

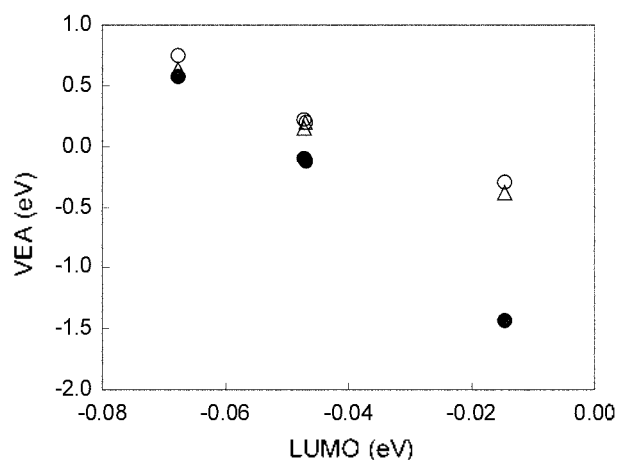
	B3LYP/6-31G**			B3LYP/aug-cc-pvdz			B3LYP/aug-cc-pvtz//B3LYP/6-31G**		
	Neutral	Anion	VEA	Neutral	Anion	VEA	Neutral	Anion	VEA
DD	-612.54018	-612.48758	-1.431	-612.59925	-612.58510	-0.385	-612.74844	-612.73765	-0.294
2378-TCDD	-2450.90069	-2450.89710	-0.098	-2451.06196	-2451.06772	0.157	-2451.25833	-2451.26656	0.224
1469-TCDD	-2450.89662	-2450.89240	-0.115	-2451.05704	-2451.06465	0.207	-2451.25564	-2451.26288	0.197
OCDD	-4289.23236	-4289.25368	0.580	-4289.49543	-4289.51893	0.640	-4289.74513	-4289.77276	0.752

Table 2. Calculated Total Energy (E_{rot})^a (Hartree), -LUMO (eV)^b at the B3LYP/6-31G**, and VEA (eV)^{c,d} Estimated at the Level of B3LYP/aug-cc-pvdz and B3LYP/aug-cc-pvtz//B3LYP/6-31G** for PCDDs

	E_{rot}^a	-LUMO ^b	VEA ^c	VEA ^d
	B3LYP/6-31G**	B3LYP/6-31G**	B3LYP/aug-cc-pvdz	B3LYP/aug-cc-pvtz//B3LYP/6-31G**
DD	-612.54018	0.015	-0.403	-0.336
2-MCDD	-1072.13315	0.025	-0.215	-0.149
1-MCDD	-1072.13034	0.024	-0.232	-0.166
27-DCDD	-1531.72563	0.034	-0.044	0.022
28-DCDD	-1531.72563	0.034	-0.044	0.022
17-DCDD	-1531.72290	0.033	-0.059	0.007
18-DCDD	-1531.72280	0.033	-0.060	0.006
13-DCDD	-1531.72191	0.033	-0.056	0.010
23-DCDD	-1531.72104	0.032	-0.070	-0.004
16-DCDD	-1531.72021	0.032	-0.074	-0.008
14-DCDD	-1531.71960	0.032	-0.066	0.000
19-DCDD	-1531.71956	0.032	-0.082	-0.016
12-DCDD	-1531.71836	0.032	-0.084	-0.018
137-TrCDD	-1991.31407	0.041	0.104	0.169
138-TrCDD	-1991.31405	0.041	0.102	0.168
237-TrCDD	-1991.31327	0.041	0.089	0.155
147-TrCDD	-1991.31176	0.041	0.093	0.159
136-TrCDD	-1991.31138	0.041	0.089	0.154
139-TrCDD	-1991.31083	0.040	0.082	0.148
127-TrCDD	-1991.31063	0.040	0.076	0.142
128-TrCDD	-1991.31053	0.040	0.076	0.141
178-TrCDD	-1991.31050	0.040	0.074	0.140
146-TrCDD	-1991.30851	0.040	0.073	0.138
126-TrCDD	-1991.30798	0.039	0.063	0.128
129-TrCDD	-1991.30729	0.039	0.055	0.120
124-TrCDD	-1991.30646	0.040	0.073	0.139
123-TrCDD	-1991.30502	0.039	0.055	0.120
1368-TCDD	-2450.90225	0.049	0.239	0.304
1379-TCDD	-2450.90181	0.048	0.234	0.299
1378-TCDD	-2450.90145	0.048	0.225	0.290
2378-TCDD	-2450.90069	0.047	0.212	0.277
1369-TCDD	-2450.89942	0.048	0.225	0.290
1478-TCDD	-2450.89911	0.047	0.216	0.281
1268-TCDD	-2450.89889	0.047	0.215	0.280
1247-TCDD	-2450.89849	0.048	0.222	0.287
1248-TCDD	-2450.89841	0.048	0.222	0.287
1279-TCDD	-2450.89837	0.047	0.207	0.273
1278-TCDD	-2450.89801	0.047	0.200	0.265
1237-TCDD	-2450.89702	0.047	0.204	0.269
1238-TCDD	-2450.89699	0.047	0.203	0.268
1469-TCDD	-2450.89662	0.047	0.210	0.275
1269-TCDD	-2450.89605	0.047	0.199	0.265
1267-TCDD	-2450.89559	0.046	0.189	0.255
1249-TCDD	-2450.89518	0.047	0.202	0.267
1246-TCDD	-2450.89517	0.047	0.203	0.268
1289-TCDD	-2450.89486	0.046	0.182	0.247
1236-TCDD	-2450.89435	0.046	0.190	0.255

Table 2. Continued.

	E_{rot}^a	-LUMO ^b	VEA ^c	VEA ^d
	B3LYP/6-31G**	B3LYP/6-31G**	B3LYP/aug-cc-pvdz	B3LYP/aug-cc-pvtz//B3LYP/6-31G**
1239-TCDD	-2450.89376	0.046	0.183	0.249
1234-TCDD	-2450.88835	0.045	0.178	0.243
12479-PCDD	-2910.48591	0.054	0.343	0.408
12468-PCDD	-2910.48586	0.054	0.344	0.409
12478-PCDD	-2910.48558	0.054	0.336	0.400
12368-PCDD	-2910.48498	0.054	0.331	0.396
12379-PCDD	-2910.48456	0.053	0.325	0.390
12378-PCDD	-2910.48422	0.053	0.318	0.383
12469-PCDD	-2910.48306	0.053	0.330	0.395
12467-PCDD	-2910.48262	0.053	0.320	0.385
12489-PCDD	-2910.48250	0.053	0.320	0.385
12369-PCDD	-2910.48225	0.053	0.321	0.386
12367-PCDD	-2910.48168	0.052	0.308	0.373
12389-PCDD	-2910.48115	0.052	0.301	0.366
12347-PCDD	-2910.48011	0.053	0.317	0.382
12346-PCDD	-2910.47689	0.052	0.299	0.364
124689-HxCDD	-3370.06947	0.059	0.442	0.506
124679-HxCDD	-3370.06945	0.059	0.441	0.506
123679-HxCDD	-3370.06860	0.059	0.429	0.494
123689-HxCDD	-3370.06854	0.059	0.429	0.493
123678-HxCDD	-3370.06774	0.058	0.417	0.482
123468-HxCDD	-3370.06752	0.059	0.431	0.496
123789-HxCDD	-3370.06725	0.058	0.412	0.476
123478-HxCDD	-3370.06714	0.058	0.424	0.489
123469-HxCDD	-3370.06471	0.058	0.418	0.483
123467-HxCDD	-3370.06415	0.058	0.409	0.474
1234679-HpCDD	-3829.65089	0.064	0.523	0.588
1234678-HpCDD	-3829.65007	0.063	0.511	0.576
OCDD	-4289.23236	0.068	0.599	0.664

**Figure 2.** Correlation between LUMO calculated at the B3LYP/6-31G** level and VEA (B3LYP/6-31G**) (filled circle), VEA (B3LYP/aug-cc-pvdz) (open triangle), and VEA (B3LYP/aug-cc-pvtz//B3LYP/6-31G**) (open circle) for DD, 1469-TCDD, 2378-TCDD, OCDD.

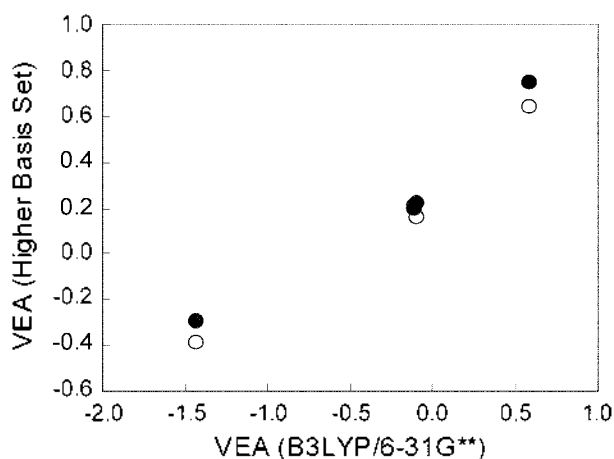


Figure 3. Correlation between VEA (B3LYP/6-31G**) and VEA (B3LYP/aug-cc-pvdz) (open symbol) or VEA (B3LYP/aug-cc-pvtz//B3LYP/6-31G**) (filled symbol) for DD, 1469-TCDD, 2378-TCDD, OCDD.

D_{2h} congeners to get more reliable electron affinities, which are listed in Table 1. VEA calculated at the B3LYP/6-31G** level are well correlated with VEA obtained at the B3LYP/aug-cc-pvdz level and B3LYP/aug-cc-pvtz//B3LYP/6-31G** for D_{2h} congeners as shown in Figure 3. The linear relation between these two VEA values can be represented by eq 5 and eq 6, respectively.

$$\text{VEA (B3LYP/aug-cc-pvdz)} = 0.286 + 0.493 \text{ VEA (B3LYP/6-31G**)} \quad (5)$$

$$\text{VEA (B3LYP/aug-cc-pvtz//B3LYP/6-31G**)} = 0.351 + 0.492 \text{ VEA (B3LYP/6-31G**)} \quad (6)$$

We estimate VEA values for all PCDD congeners by using eqs 5 and 6, which are also listed in Table 2. The experimental electron attachment energies obtained from electron capture negative ion mass spectrometry were 0.11 and 0.2 eV for 1234-TCDD and 12378-PCDD, respectively,²⁴ which could be compared with the estimated electron affinities. VEA (1234-TCDD) = 0.178 eV and VEA (12378-PCDD) = 0.318 eV in Table 2.

Figure 4 shows the variation of the estimated VEA (B3LYP/aug-cc-pvtz//B3LYP/6-31G**) as a function of Cl numbers. VEA steadily increases with the number of chlorines. On the other hand, dioxin congeners with the same number of chlorines are all similar in their VEA values (*i.e.*, no position effect). It is compared with the fact that molecular charge distribution and IR frequencies of dioxins are highly sensitive to the position of substituted chlorines.^{12,13} The difference between VEA (B3LYP/aug-cc-pvdz) and VEA (B3LYP/6-31G**) in Table 1 is 1.046 eV for DD, but only 0.060 eV for OCDD, which indicates that VEA values calculated from small and large basis sets converge with increasing the chlorine numbers. PCDDs with the number of Cl ≥ 3 have positive VEA whereas DD, MCDD, and DCDD congeners show negative VEA values.

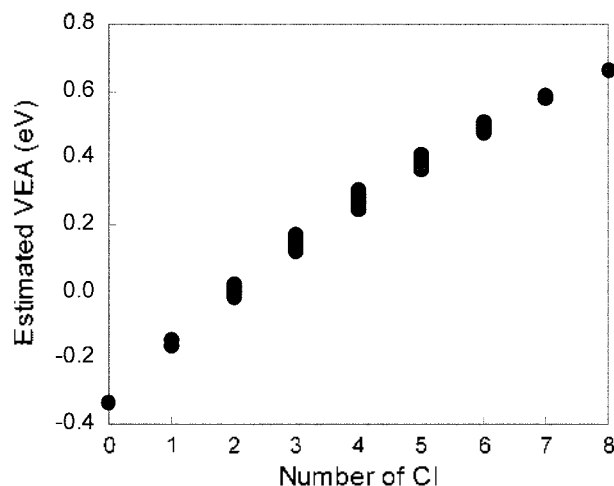


Figure 4. Estimated VEA (B3LYP/aug-cc-pvtz//B3LYP/6-31G**) of PCDDs as a function of Cl numbers.

Therefore, anionic forms of highly chlorinated congeners are energetically more stable than neutral species.

Molecules carrying higher EA could be more reactive under reductive conditions. The chemical and biological reactivities of highly chlorinated dioxin congeners in various environmental media should be dependent on the electron donating tendency of the surrounding media.²⁹⁻³¹ For example, the photolytic degradation of OCDD in organic solvent was markedly enhanced in the presence of triethylamine (TEA).³² In photolytic degradation of halogenated aromatic compounds,^{33,34} TEA can play the role of an electron donor to form an excited charge-transfer complex upon photon absorption and induce the formation of anionic species. In general, excited anionic species as an intermediate could be involved in the photolytic degradation of PCDDs in reductive media. Therefore, the vertical electron affinities calculated in this work could be valuable in understanding the congener-specific reactivities of PCDDs and their fate in environmental media.

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