Electron affinity and inversion distortion of dibenzo-p-dioxin

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Received 8 April 2005
Available online 13 June 2005

Abstract

The photochemical fate of polychlorinated dibenzo-p-dioxins, ubiquitous environmental pollutants, could be highly influenced by electron-donors such as triethylamine. Therefore, it is essential to have electron affinities of these species. We have performed density functional calculations for neutral and anion of dibenzo-p-dioxin (DD) to obtain the adiabatic electron affinity. We find that the order of $D_2$ and $D_{2h}$ structures varies with the level of theory. The $D_{2h}$ neutral DD undergoes inversion distortion into less symmetric $D_2$ anion upon electron attachment due to C–O–C bond cleavage.

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1. Introduction

It is well known that polychlorinated dibenzo-p-dioxins (PCDDs), one of the most persistent organic pollutants, are extremely toxic to biosphere [1]. Physicochemical properties of PCDDs are very sensitive to the chlorination pattern, namely, the number and position of the chlorine atom. There have been a number of studies on the reaction mechanisms for the formation or decomposition of PCDDs theoretically and experimentally [2–5]. Scheme 1 shows a molecular structure and substitution position of dibenzo-p-dioxin (DD) with the molecule oriented on the $yz$ plane. According to the chlorination pattern, DD can have 75 chlorinated congeners. We have recently reported that electronic charge distributions of PCDDs are very sensitive to the chlorination pattern [6], that the vertical electron affinities of PCDDs increase with the chlorination level [7], and that thermodynamic stabilities of PCDDs depend on the Cl–Cl intramolecular repulsions and thus the chlorination pattern [8].

PCDDs are formed in various combustion processes such as municipal incinerators and are dispersed widely through the atmosphere. Photolytic decompositions or transformations take place in the troposphere [9–11]. Polyhalogenated aromatic hydrocarbons (PHAs) in organic solvent could be degraded effectively in the presence of electron-donor compound such as alkyl amine [11–14]. PHA seems to be partially negative-charged by accepting electron charge from electron-rich compounds under the UV irradiation. Therefore, it is important to understand molecular properties of PCDDs and their anions [6–9,15]. Moreover, toxicity [16] and properties [17] of such aromatic derivatives have been the topic of many studies. It is difficult to measure the molecular properties of PCDDs due to the toxicity and large number
of isomers. In a previous work [7], the vertical electron affinities (VEA) of DD, 1,4,6,9-TCDD, 2,3,7,8-TCDD, and OCDD were computed. We have found that the results were sensitive to the basis sets and methods.

In this Letter, we have carried out the density functional calculations (B3LYP) for the DD anion as well as neutral species to estimate the adiabatic electron affinity of DD. We have calculated adiabatic electron affinities of DD and investigated the basis set effects.

2. Computational method

We have performed the density functional calculations (B3LYP) with the 6-31G**, 6-31+G*, 6-311++G**, and aug-cc-pvdz basis sets for the neutral and anionic DD with the $D_{2h}$ and $D_2$ symmetries. We find that the molecular properties are very sensitive to the addition of polarization functions. The addition of polarization function on second-row atoms are absolutely required to estimate more accurate structures because s and p functions cannot describe correctly flexibility of multi-nuclear molecule. In this Letter, at least the d functions were added on heavy atoms. Moreover, the highest energy MOs of anions, highly excited electronic states, and loose supermolecular complexes, tend to be much more spatially diffused [18]. Therefore, in this Letter diffuse functions are added to the basis sets to compare the basis set effect.

The anion of DD, calculated using augmented basis set of Dunning and co-workers, has no imaginary frequency at the $D_{2h}$ symmetry while the optimized anions obtained by the basis sets of 6-31+G* and 6-311++G** have imaginary frequencies. Therefore, we have done further calculations for less symmetric anion, namely, $D_2$ symmetric anion. The AEA of DD, which is calculated as the negative of the reaction energy for a neutral to be an anion. The AEA and zero point energy (ZPE) corrected AEA are evaluated as Eqs. (1) and (2), respectively [19,20]

$$\text{AEA (eV)} = E_{\text{neutral}} - E_{\text{anion}}$$  \hspace{1cm} (1)

$$\text{AEA}^{\text{ZPE}} (\text{eV}) = E_{\text{neutral}}^{\text{ZPE}} - E_{\text{anion}}^{\text{ZPE}}$$ \hspace{1cm} (2)

which $E_{\text{neutral}}$ is the total energy of neutral DD from the optimized geometry with the $D_{2h}$ symmetry and $E_{\text{anion}}$ is the total energy at the optimized structure of DD anion with $D_{2h}$ symmetry. AEA$^{\text{ZPE}}$ is obtained from the optimized neutral and anion in terms of ZPE-corrected energy. $E_{\text{neutral}}^{\text{ZPE}}$ is the ZPE-corrected energy of neutral with the $D_{2h}$ symmetry and $E_{\text{anion}}^{\text{ZPE}}$ is the ZPE-corrected energy of anion from the structures with $D_{2h}$ or $D_2$ symmetries. All calculations were carried out using Gaussian’98 codes [21].

3. Results and discussion

3.1. Adiabatic electron affinity

The AEAs and ZPE-corrected AEAs (AEA$^{\text{ZPE}}$) of DD calculated in the B3LYP method with four different basis sets are negative, as shown in Table 1. The AEA and AEA$^{\text{ZPE}}$ calculated by the B3LYP/6-31G** level is the lowest, $-1.164$ and $-0.951$ eV, respectively. Among the AEA$^{\text{ZPE}}$ values, the AEA$^{\text{ZPE}}$ ($-0.368$ eV) calculated by the 6-311++G** basis set is higher than the values of other basis sets. The AEA calculated by the B3LYP/aug-cc-pvdz level has the highest value. ($-0.385$ eV) Also, the AEA$^{\text{ZPE}}$ ($-0.368$ eV) evaluated

<table>
<thead>
<tr>
<th>Basis set</th>
<th>Symmetry</th>
<th>Species</th>
<th>Energy (Hartree)</th>
<th>AEA (eV)</th>
<th>AEA$^{\text{ZPE}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-31G**</td>
<td>$D_{2h}$</td>
<td>Neutral</td>
<td>−612.54018</td>
<td>−1.164</td>
<td>−0.951</td>
</tr>
<tr>
<td>6-31G**</td>
<td>$D_{2h}$</td>
<td>Anion</td>
<td>−612.49740</td>
<td>−0.796</td>
<td>−0.490</td>
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<td>6-31+G*</td>
<td>$D_{2h}$</td>
<td>Neutral</td>
<td>−612.54832</td>
<td>−0.796</td>
<td>−0.531</td>
</tr>
<tr>
<td>6-31+G*</td>
<td>$D_{2h}$</td>
<td>Anion</td>
<td>−612.51906</td>
<td>−0.796</td>
<td>−0.531</td>
</tr>
<tr>
<td>6-311++G**</td>
<td>$D_{2h}$</td>
<td>Neutral</td>
<td>−612.51908</td>
<td>−0.796</td>
<td>−0.531</td>
</tr>
<tr>
<td>6-311++G**</td>
<td>$D_{2h}$</td>
<td>Anion</td>
<td>−612.51906</td>
<td>−0.796</td>
<td>−0.531</td>
</tr>
<tr>
<td>aug-cc-pvdz</td>
<td>$D_{2h}$</td>
<td>Neutral</td>
<td>−612.68492</td>
<td>−0.452</td>
<td>−0.368</td>
</tr>
<tr>
<td>aug-cc-pvdz</td>
<td>$D_{2h}$</td>
<td>Anion</td>
<td>−612.66833</td>
<td>−0.450</td>
<td>−0.409</td>
</tr>
</tbody>
</table>

Table 1
DFT (B3LYP) calculated AEA and ZPE-corrected AEA (AEA$^{\text{ZPE}}$) of DD

![Scheme 1. Structure and chlorine substitution numbering of dibenzo-p-dioxin.](image-url)
The vibrations of neutral DD are shown in Table 2 and for the anion DD we contrast the frequencies relative to the neutral. There are frequencies for the anion in the 6-31 + G* and 6-311++G** calculations. There are 60 vibrational modes for the D_{2h} DD that correlate into 11 a_u + 4 b_1g + 5 b_2g + 10 b_3g + 5 a_g + 10 b_{1u} + 10 b_{2u} + 5 b_{3u}. The vibrational modes with imaginary frequencies are depicted in Fig. 1. The D_{2h} symmetric anion of the B3LYP/6-31+G* level has three imaginary frequencies, 1449 cm\(^{-1}\) (b_3g), 5401 cm\(^{-1}\) (a_u), 561 cm\(^{-1}\) (b_{1u}). The D_{2} symmetric anion has two imaginary frequencies, 14881 cm\(^{-1}\) (b_3g) and 501 cm\(^{-1}\) (b_1) at the B3LYP/6-31+G* level. Figs. 1a and d are in-plane ring vibrations. The vibrational mode (b) corresponds to the C–O–C symmetric stretching out of plane while modes (c) and (e) correspond to C–O–C bending, namely, butterfly vibration out of plane. The imaginary frequencies (b), (c), (e) are related with C–O–C bonding, namely, butterfly vibration out of plane. The imaginary frequencies (b_3u) and (b_1u) or (b_2u) due to symmetric stretching of C–O–C group, 2691i cm\(^{-1}\) (a_u) and 951 cm\(^{-1}\) (a_u). The D_{2} symmetric anion is the global minimal structure, which has no imaginary frequency. The DD anion with the D_{2h} symmetry undergoes inversion distortion into less symmetric D_{2} anion upon electron attachment as

\begin{table}[h]
\centering
\begin{tabular}{cccc}
\hline
Neutral & Anion (D_{2h}) & Anion (D_{2}) \\
\hline
\begin{tabular}{c}
a_u \ 117 \\
\end{tabular} & \begin{tabular}{c}
a_u \ 951 \\
\end{tabular} & \begin{tabular}{c}
a \ 119 \\
\end{tabular} \\
\begin{tabular}{c}
a_g \ 396 \\
\end{tabular} & \begin{tabular}{c}
a_g \ 394 \\
\end{tabular} & \begin{tabular}{c}
a \ 391 \\
\end{tabular} \\
\begin{tabular}{c}
a_g \ 465 \\
\end{tabular} & \begin{tabular}{c}
a_g \ 2691i \\
\end{tabular} & \begin{tabular}{c}
a \ 513 \\
\end{tabular} \\
\begin{tabular}{c}
a_g \ 575 \\
\end{tabular} & \begin{tabular}{c}
a_g \ 575 \\
\end{tabular} & \begin{tabular}{c}
a \ 572 \\
\end{tabular} \\
\begin{tabular}{c}
a_g \ 676 \\
\end{tabular} & \begin{tabular}{c}
a_g \ 418 \\
\end{tabular} & \begin{tabular}{c}
a \ 707 \\
\end{tabular} \\
\begin{tabular}{c}
a_g \ 738 \\
\end{tabular} & \begin{tabular}{c}
a_g \ 737 \\
\end{tabular} & \begin{tabular}{c}
a \ 730 \\
\end{tabular} \\
\begin{tabular}{c}
a_g \ 852 \\
\end{tabular} & \begin{tabular}{c}
a_g \ 795 \\
\end{tabular} & \begin{tabular}{c}
a \ 863 \\
\end{tabular} \\
\begin{tabular}{c}
a_g \ 953 \\
\end{tabular} & \begin{tabular}{c}
a_g \ 952 \\
\end{tabular} & \begin{tabular}{c}
a \ 958 \\
\end{tabular} \\
\begin{tabular}{c}
a_g \ 1050 \\
\end{tabular} & \begin{tabular}{c}
a_g \ 1048 \\
\end{tabular} & \begin{tabular}{c}
a \ 1016 \\
\end{tabular} \\
\begin{tabular}{c}
a_g \ 1176 \\
\end{tabular} & \begin{tabular}{c}
a_g \ 1168 \\
\end{tabular} & \begin{tabular}{c}
a \ 1155 \\
\end{tabular} \\
\begin{tabular}{c}
a_g \ 1241 \\
\end{tabular} & \begin{tabular}{c}
a_g \ 1238 \\
\end{tabular} & \begin{tabular}{c}
a \ 1229 \\
\end{tabular} \\
\begin{tabular}{c}
a_g \ 1352 \\
\end{tabular} & \begin{tabular}{c}
a_g \ 1352 \\
\end{tabular} & \begin{tabular}{c}
a \ 1354 \\
\end{tabular} \\
\begin{tabular}{c}
a_g \ 1531 \\
\end{tabular} & \begin{tabular}{c}
a_g \ 1527 \\
\end{tabular} & \begin{tabular}{c}
a \ 1516 \\
\end{tabular} \\
\begin{tabular}{c}
a_g \ 1655 \\
\end{tabular} & \begin{tabular}{c}
a_g \ 1654 \\
\end{tabular} & \begin{tabular}{c}
a \ 1548 \\
\end{tabular} \\
\begin{tabular}{c}
a_g \ 3187 \\
\end{tabular} & \begin{tabular}{c}
a_g \ 3145 \\
\end{tabular} & \begin{tabular}{c}
a \ 3145 \\
\end{tabular} \\
\begin{tabular}{c}
a_g \ 3202 \\
\end{tabular} & \begin{tabular}{c}
a_g \ 3164 \\
\end{tabular} & \begin{tabular}{c}
a \ 3164 \\
\end{tabular} \\
\hline
\end{tabular}
\caption{Vibrational frequencies (cm\(^{-1}\)) of DD at the level of B3LYP/6-311++G**}
\end{table}
result of the C–O–C bond cleavage. In Table 2, the vibrational frequencies calculated from the B3LYP/6-311++G** are listed to compare frequency change from neutral to anion. According to the DFT results, the vibrational frequencies with the a_u symmetry shift much more than the other mode. Fig. 2 which contains frequency correlations, shows that the DD anion with the D_2 symmetry has similar frequencies to the DD neutral.

3.3. Structural parameters

The structural parameters of both the neutral and anion DD are shown in Table 3. The neutral species are optimized at the D_2h symmetry with no imaginary frequency. The geometrical changes to be an anion are more at the 6-31G** level, especially the r_Ca-Cb bond lengths increase by 0.036 Å. The bond lengths of the center ring are elongated as being an anion. However, the geometrical changes are negligible at both 6-311++G** and aug-cc-pvdz levels. The dihedral angles of the D_2 symmetric anion are not greatly different from the planar D_2h symmetric structure. The D_2 anion tilts towards the molecular plane or relative to the perpendicular axis at the B3LYP/6-311++G** level. The dihedral angle variation is less than 3° and the τ(C_1C_aC_bC_4) dihedral angle changes by only 2.2°.

4. Conclusion

The DD anion’s geometry is very sensitive to the diffuse functions while the neutral DD exhibits the D_2h structure at all levels. At the B3LYP/aug-cc-pvdz level, the optimized DD anion exhibits D_2h symmetry while the D_2 structure is favored at the B3LYP/6-311++G** level. The atomic charge distributions of neutral DD and anion DD show that for the anion, the atomic charges at C_a and C_2 sites increase substantially in both D_2h and D_2 anions relative to the neutral. For the D_2h anion the repulsive interactions between C_a and C_b or C_2 and C_3 are expected to be much greater than the other bonds. The inversion distortion from D_2h to D_2 can reduce anion’s positive charges at C_a and C_2 sites and repulsive interaction between C_a and C_b or C_2 and C_3, consistent with the geometrical changes τ(C_aC_bC_4) and imaginary frequencies of meta-stable anion due to the C–O–C bond cleavage. The AEs of DD are very close at B3LYP/6-311++G** and B3LYP/aug-cc-pvdz levels.
Acknowledgments

This work was supported by KOSEF through the Center for Integrated Molecular Systems (CIMS), the KOSEF Grant (No. R-14-2002-004-01001-0), and the Brain Korea 21 Project. The Research at UC Davis was supported by the National Science Foundation under Grant No. CHE-0236434. The work at LLNL was performed in part under the auspices of the US Department of Energy by the University of California, LLNL under Contract No. W-7405-Eng-48.

References


Table 3
Structural parameters for DD (N: neutral with the $D_{2h}$ symmetry, $A_1$: anion with the $D_{2h}$ symmetry, $A_2$: anion with the $D_2$ symmetry)

<table>
<thead>
<tr>
<th></th>
<th>6-31G**</th>
<th>6-31+G*</th>
<th>6-31++G**</th>
<th>aug-cc-pvdz</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N</td>
<td>A_1</td>
<td>N</td>
<td>A_1</td>
</tr>
<tr>
<td>r(O10Ca)</td>
<td>1.381</td>
<td>1.378</td>
<td>1.382</td>
<td>1.391</td>
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<tr>
<td>r(C_Ca)</td>
<td>1.400</td>
<td>1.436</td>
<td>1.399</td>
<td>1.386</td>
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<tr>
<td>r(C_Ca)</td>
<td>1.390</td>
<td>1.393</td>
<td>1.392</td>
<td>1.412</td>
</tr>
<tr>
<td>r(C_Ca)</td>
<td>1.397</td>
<td>1.396</td>
<td>1.398</td>
<td>1.414</td>
</tr>
<tr>
<td>r(C_Ca)</td>
<td>1.394</td>
<td>1.426</td>
<td>1.397</td>
<td>1.393</td>
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<tr>
<td>r(C_Ca)</td>
<td>1.085</td>
<td>1.088</td>
<td>1.086</td>
<td>1.086</td>
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<tr>
<td>r(C_Ca)</td>
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<td>1.087</td>
<td>1.086</td>
<td>1.089</td>
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<td>r(C_Ca)</td>
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<td>r(C_Ca)</td>
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<td>tau(O_Ca_CO)</td>
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<td>0.0</td>
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</table>
| Bond length in Å.