

Theoretical Study of 1,4,6,9-Tetra chlorinated dibenzo-*p*-dioxin anion

Byung Jin Mhin^{*}, Srinivas Odde, and Kang-Hyun Han

Department of Chemistry, PaiChai University, 493-6 Doma-dong, Seoku, Daejeon 302-735, Korea

Jung Eun Lee and Wonyong Choi

School of Environmental Science and Engineering, Pohang University of Science and Technology,
Pohang 790-784, Korea

ABSTRACT

The equilibrium geometry, adiabatic electron affinity, harmonic vibrational frequencies, and infrared intensities of 1,4,6,9-Tetra chlorinated dibenzo-*p*-dioxin anion have been studied using B3LYP method. The local minimum conformation is found to be twisted form with D_2 symmetry. The predicted adiabatic electron affinity is 0.54 eV. The predicted inversion barrier between twisted and planar conformers was 0.9 kcal/mol, thus we expect that experimentally observed structure seems to be planar. The characteristic IR band of 1,4,6,9-TCDD anion appears at 1510 cm^{-1} , which is a benzene ring skeleton vibration mode related with CaCb and C2C3 bond. This characteristic band could be used for identification of 1,4,6,9-TCDD anion.

1. Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) are highly toxic and widespread pollutants, which are generated from various incomplete combustion processes (e.g., municipal solid waste incinerators) and chemical processes dealing with chlorinated aromatic compounds (*1-3*). There are 76 PCDD congeners (75 PCDD congeners with one to eight chlorines and non-chlorinated dibenzo-*p*-dioxin

Corresponding Author : Byung-Jin Mhin, Department of Chemistry, PaiChai University, Daejeon, 302-735, Korea. Tel. : +82-42-520-5611, E-mail : mhin@pcu.ac.kr

(DD)), and their physicochemical properties and biological toxicities are highly congener specific in general (4-9). Four D_{2h} symmetric congeners (DD, 1,4,6,9-Tetrachlorinated dibenzo-p-dioxins (1,4,6,9-TCDD), 2,3,7,8-Tetrachlorinated dibenzo-p-dioxins (2,3,7,8-TCDD), and Octachlorinated dibenzo-p-dioxins (OCDD)) are reference compounds among all 76 PCDD congeners for the congener specificity: Charge distributions of PCDDs change very sensitively and systematically with the chlorination patterns. The ring vibrational frequencies of PCDDs also change systematically with the chlorination patterns. The vertical electron affinities of PCDDs increase with increasing the number of chlorines. The thermodynamic stability of PCDDs increase with increasing the number of chlorines, but the stability of isomers was determined by the Cl-Cl intramolecular repulsion.

Since PCDDs are chemically stable and accumulate in various media of natural environments and living organisms, the development of effective PCDDs destruction methods and understanding their degradation mechanisms in the environment are of significant importance. Many degradation methods of PCDDs, which include incineration (10), catalytic degradation (11, 12), radiolysis (13), ozonation (14), ozonation-photolysis (15), photo-Fenton reaction (16), direct photolysis (17-19), and photocatalysis (20-23), have been investigated. Among them, photolysis has been intensively investigated since it is the most important degradation pathway in environmental media where solar light can reach. PCDDs can absorb near-UV light that is contained in sunlight and subsequently undergo a series of photochemical processes to induce their transformation or degradation. The photochemistry and photolytic properties of PCDDs have been studied in various media such as organic solvents (22, 24, 25), acetonitrile/water mixture (26-30), and on solid surfaces (25, 31-33).

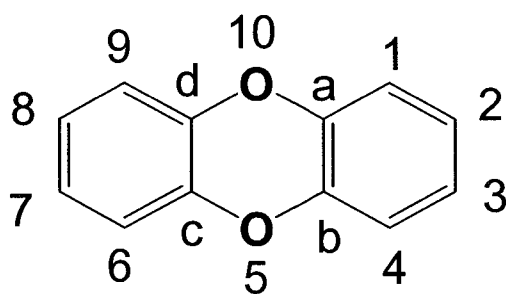
Photolysis of PCDDs has been a subject of intensive studies but it has exhibited complex behaviors that have never been explained clearly. The photolytic degradation of PCDDs leads to less chlorinated congeners or other degradation products. The photolysis of PCDDs seems to be related with the number and position of chlorines, the kind of surrounding media in complex ways. Most photoreactions of PCDDs were carried out in organic solvents because their water solubility is extremely low. From our recent study on the solvent specific photolysis of OCDD, it has been proposed that the solvent specificity in OCDD photolysis is mainly ascribed to the difference in the electron donating (or accepting) tendency among various solvents (20-33). Therefore it is important to understand molecular properties of PCDDs and their anions.

In a previous work (34) about dibenzo-p-dioxin (DD) as the first reference molecule, the adiabatic electron affinities (AEA) were computed. We have found that the DD anion's geometry is very

sensitive to the diffuse functions, and the D_{2h} neutral DD undergoes inversion distortion into less symmetric D_2 anion upon electron attachment due to COC bond cleavage (34). The ring inversion process of DD anion between the twisted and planar conformers investigated using DFT method at the level of B3LYP/6-311++G**: The twisted form was local minimum, and planar form was the second order saddle point. In this work we have carried out the density functional calculations (B3LYP) for the 1,4,6,9-TCDD anion as well as neutral species to investigate the effects of non-lateral position chlorination. The characteristic IR band of 1,4,6,9-TCDD anion appears at 1510 cm^{-1} , which is a benzene ring skeleton vibration mode related with CaCb and C2C3 bond. This characteristic band could be used for identification of 1,4,6,9-TCDD anion.

2. Computational Method

We have performed the density functional calculations (B3LYP) with the 6-311++G** basis sets for the neutral and anionic 1,4,6,9-TCDD with the D_{2h} and D_2 symmetries. Neutral PCDD has a planar structure with two benzene rings linked by a pair of oxygen atoms. For the analysis of vibrational modes, we defined the coordinated as follows: x, y, and z refer to the direction perpendicular to the molecular plane (the yz plane), the non-lateral direction (parallel to the O-O direction), and the lateral direction in D_{2h} symmetry, respectively, as shown below.



Scheme 1

1,4,6,9-TCDD molecule is composed of 12 carbons but these highly symmetric molecule have only three kinds of carbon sites: oxygen-bonded carbon, Ca, Cb, Cc, Cd (ν carbon); α -position carbon, C1, C4, C6, C9 (α carbon); C2, C3, C7, C8 (β carbon) as shown in scheme 1. Dioxin molecule has torsional modes of two benzene rings: Central six-membered ring has three out-of-plane motion: in-phase twisting (b_{2g}), out-of-phase twisting (a_u), and ring-puckering modes (b_{3u}). There are

60 vibrational modes: The vibrations of D_{2h} 1,4,6,9-TCDD are distributed as $11a_g + 4b_{1g} + 5b_{2g} + 10b_{3g} + 5a_u + 10b_{1u} + 10b_{2u} + 5b_{3u}$, and for the twisted form with D_2 symmetry, the vibrations fall into $16a+14b_1+15b_2+15b_3$. The anion of 1,4,6,9-TCDD with the D_{2h} symmetry has one imaginary mode of out-of-phase twisting (a_u). Therefore, we have done further calculations for less symmetric anion, namely, D_2 symmetric anion. The AEA of 1,4,6,9-TCDD 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 (34)

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

$$\text{AEA}_0 \text{ (eV)} = E^{\text{ZPE}}_{\text{anion}} - E^{\text{ZPE}}_{\text{neutral}} \quad (2)$$

E_{neutral} is the total energy of neutral 1,4,6,9-TCDD from the optimized geometry with the D_{2h} symmetry and E_{anion} is the total energy at the optimized structure of 1,4,6,9-TCDD anion with D_{2h} and D_2 symmetry. AEA_0 is obtained from the optimized neutral and anion in terms of ZPE-corrected energy. $E^{\text{ZPE}}_{\text{neutral}}$ is the ZPE-corrected energy of neutral with the D_{2h} symmetry and $E^{\text{ZPE}}_{\text{anion}}$ 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 (37).

Table 1. B3LYP/6-311++G** predicted relative energies (adiabatic electron affinity: AEA, AEA_0 , Vertical electron affinity (VEA) in eV), E_c (Hartree), and ZPE (kcal/mol) of the 1,4,6,9 TCDD.

Conf.	Symm	Img	State	Ee	ZPE (Kcal/mol)	Eo			
							AEA	AEA_0	VEA
DD									
Neutral	D_{2h}	0	1A_g	-612.68492	111.92	-612.51850	0.00	0.00	-0.68
Anion	D_{2h}	2	2A_g	-612.66833	109.91	-612.50488	-0.45	-0.37	
Anion	D_2	0	4A	-612.66839	110.98	-612.50336	-0.45	-0.41	
1469-TCDD									
Neutral	D_{2h}	0	1A_g	-2451.15463	86.63	-2451.02581	0.00	0.00	0.18
Anion	D_{2h}	1	2A_u	-2451.16623	81.16	-2451.04559	0.32	0.54	
Anion	D_2	0	4A	-2451.16756	82.02	-2451.04560	0.35	0.54	

3. Results and Discussion

The electronic energy (E_e), zero-point energy corrected electronic energy (E_0), VEAs, AEAs and ZPE-corrected AEAs (AEAo) of 1,4,6,9-TCDD are calculated in the B3LYP method listed in Table 1. The twisted form with D_2 symmetry was a local minimum, and there was almost no barrier (0.09 kcal/mol) for the inversion. All VEA, AEA, and AEAo had the positive values. The electron affinity successively increases with the chlorination for the PCDDs. Our results calculated here are similar trends to their electron affinities (8) which accounts for the anion stability. This means that this radical anion is more stable than the corresponding neutral molecule. The AEA and (AEAo) calculated for D_{2h} and D_2 symmetric systems are 0.32 (0.54) and 0.35 (0.54) eV, respectively. The vertical electron affinity of -0.18 eV is much lower compare to the adiabatic electron affinity.

The structural parameters of both the neutral and anion 1,4,6,9-TCDD are shown in Table 2. The neutral species are optimized at the D_{2h} symmetry with no imaginary frequency. The brief look at the table reveals that benzene rings remain the planarity, and Ca-Cb (Cc-Cd), C2-C3 (C7-C8) bond lengths elongated by the added electron. The distortion from D_{2h} symmetry to D_2 symmetry slightly decreases these bond lengths. In going from 1A_g to 2A_u and 2A states, the C-Cl bond length is 1.744, 1.766, and 1.772 Å. The local minimal structure of DD and 1,4,6,9-TCDD anions had the same symmetry, but the out-of-phase twisting angle showed quite difference: -17° in 1,4,6,9-TCDD and 0.6° in DD.

Table 2. Structural parameters for 1,4,6,9 TCDD (${}^1A_{1g}$: neutral with the D_{2h} symmetry, 2A_u : anion with the D_{2h} symmetry, 2A : anion with the D_2 symmetry)

Parameter	B3LYP/6-311++G**		
	${}^1A_{1g}$	2A_u	2A
$r(O_{10}C_a)$	1.372	1.367	1.373
$r(C_aC_b)$	1.397	1.435	1.431
$r(C_aC_1)$	1.393	1.392	1.392
$r(C_1C_2)$	1.393	1.389	1.388
$r(C_2C_3)$	1.388	1.420	1.413
$r(C_1Cl_{15})$	1.744	1.766	1.772
$r(C_2H_2)$	1.082	1.081	1.082
$\angle C_dO_{10}C_a$	117.3	117.9	116.5
$\angle O_{10}C_aC_b$	121.4	121.0	120.6
$\angle C_1C_aC_b$	119.9	118.6	118.6
$\angle C_aC_1C_2$	120.1	122.3	122.2
$\angle C_1C_2C_3$	120.1	119.1	119.1
$\angle C_aC_1Cl_{15}$	119.5	118.5	118.8
$\angle C_1C_2H_2$	119.4	119.9	120.0
Benzene ring			
$\tau(C_1C_aC_bC_4)$	0.	0.	0.
$\tau(C_bC_aC_1C_2)$	0.	0.	1.
$\tau(C_aC_1C_2C_3)$	0.	0.	-2.
Central Dioxin ring			
$\tau(O_{10}C_aC_bO_5)$	0.	0.	21.
$\tau(O_5C_bC_aC_1)$	180.	-180.	-170.
$\tau(O_{10}C_aC_1C_2)$	0.	0.	170.
$\tau(O_{10}C_aC_1Cl_{15})$	0.	0.	-10.
$\tau(C_aC_1C_2H_2)$	-180.	-180.	176.
$\tau(Cl_{15}C_1C_2H_2)$	0.	0.	-3.
$\tau(C_dC_cC_aC_b)$	0.	0.	-17.

$\tau(C_dC_cC_aC_b)$ for the Dibenzo-*p*-dioxin (DD) : D_{2h} (0.0); $D_{2h}(0.0)$; D_2 (-0.6)

Table 3. Vibrational frequencies (cm⁻¹) of 1,4,6,9-TCDD at the level of B3LYP/6-311++G**

¹ A _g			² A _u			² A		
a _u	39	0	a _u	31	0	a	30	0
a _u	298	0	a _u	287	0	a	292	0
a _u	552	0	a _u	516	0	a	458	0
a _u	804	0	a _u	373i	0	a	645	0
a _u	936	0	a _u	687	0	a	786	0
a _g	154	0	a _g	151	0	a	149	0
a _g	331	0	a _g	322	0	a	316	0
a _g	437	0	a _g	437	0	a	417	0
a _g	620	0	a _g	611	0	a	611	0
a _g	901	0	a _g	869	0	a	856	0
a _g	1152	0	a _g	1099	0	a	1095	0
a _g	1234	0	a _g	1233	0	a	1217	0
a _g	1340	0	a _g	1345	0	a	1342	0
a _g	1468	0	a _g	1446	0	a	1425	0
a _g	1637	0	a _g	1568	0	a	1555	0
a _g	3215	0	a _g	3213	0	a	3198	0
b _{1u}	100	0	b _{1u}	97	0	b ₁	100	0
b _{1u}	415	0	b _{1u}	407	0	b ₁	405	1
b _{1u}	521	33	b _{1u}	502	34	b ₁	482	73
b _{1u}	692	6	b _{1u}	672	5	b ₁	670	32
b _{1u}	952	235	b _{1u}	899	317	b ₁	911	360
b _{1u}	1197	52	b _{1u}	1155	46	b ₁	1209	4
b _{1u}	1233	7	b _{1u}	1192	14	b ₁	1165	71
b _{1u}	1500	143	b _{1u}	1490	105	b ₁	1481	160
b _{1u}	1641	8	b _{1u}	1357	1	b ₁	1458	11
b _{1u}	3202	0	b _{1u}	3196	6	b ₁	3186	11
b _{1g}	96	0	b _{1g}	94	0	b ₁	83	1
b _{1g}	274	0	b _{1g}	230	0	b ₁	195	5
b _{1g}	586	0	b _{1g}	510	0	b ₁	514	8
b _{1g}	799	0	b _{1g}	652	0	b ₁	683	14

(continue)

1A_g			4A_u			2A		
b_{2U}	220	0	b_{2U}	216	2	b_2	215	1
b_{2U}	332	0	b_{2U}	318	20	b_2	318	6
b_{2U}	716	1	b_{2U}	688	393	b_2	692	147
b_{2U}	975	194	b_{2U}	905	235	b_2	905	4
b_{2U}	1154	4	b_{2U}	1082	563	b_2	1099	213
b_{2U}	1287	152	b_{2U}	1250	138	b_2	1233	104
b_{2U}	1311	52	b_{2U}	1327	21	b_2	1316	47
b_{2U}	1469	1034	b_{2U}	1418	1335	b_2	1416	565
b_{2U}	1605	40	b_{2U}	1515	772	b_2	1510	910
b_{2U}	3215	0	b_{2U}	3212	8	b_2	3198	27
b_{2g}	187	0	b_{2g}	79	0	b_2	32	284
b_{2g}	307	0	b_{2g}	277	0	b_2	276	153
b_{2g}	544	0	b_{2g}	430	0	b_2	423	286
b_{2g}	701	0	b_{2g}	585	0	b_2	607	399
b_{2g}	936	0	b_{2g}	707	0	b_2	775	202
b_{3U}	25	1	b_{3U}	60	0	b_3	25	0
b_{3U}	99	1	b_{3U}	97	0	b_3	84	1
b_{3U}	294	1	b_{3U}	266	0	b_3	141	5
b_{3U}	581	20	b_{3U}	527	24	b_3	501	2
b_{3U}	798	64	b_{3U}	654	100	b_3	684	100
b_{3g}	175	0	b_{3g}	171	0	b_3	174	0
b_{3g}	447	0	b_{3g}	429	0	b_3	426	0
b_{3g}	584	0	b_{3g}	558	0	b_3	563	5
b_{3g}	644	0	b_{3g}	625	0	b_3	618	1
b_{3g}	928	0	b_{3g}	905	0	b_3	907	7
b_{3g}	1163	0	b_{3g}	1104	0	b_3	1118	1
b_{3g}	1248	0	b_{3g}	1178	0	b_3	1215	4
b_{3g}	1477	0	b_{3g}	1445	0	b_3	1485	19
b_{3g}	1594	0	b_{3g}	1476	0	b_3	1454	0
b_{3g}	3202	0	b_{3g}	3197	0	b_3	3186	2

The vibrational frequencies of neutral 1,4,6,9-TCDD are shown in Table 3 and for the anion 1,4,6,9-TCDD we contrast the frequencies relative to the neutral. The D_{2h} symmetric anion at the B3LYP/6-311++G** level have one imaginary frequency modes. This vibrational mode are depicted in Fig. 1: This vibrational modes is out-of-phase twisting mode of central dioxin ring (an asymmetric bending of Ca and Cb or Cc and Cd due to symmetric stretching of COC group, $372i$ cm^{-1} (a_u)). The D_2 symmetric anion is the local minimal structure, which has no imaginary frequency. As shown in Fig.2, the vibrational frequencies pattern of neutral and anion are quite different. It should be noted that the benzene ring skeleton vibration modes (a_g , b_{2u}) is drastically shifted from 1637, and 1605 at neutral molecule to 1555 and 1510 cm^{-1} at twisted form (Fig. 3). Furthermore, since the b_{2u} mode has very strong IR band, this band can be used as a characteristic signal for identification of the 1,4,6,9-TCDD anion, which is useful for the photolysis mechanism study.

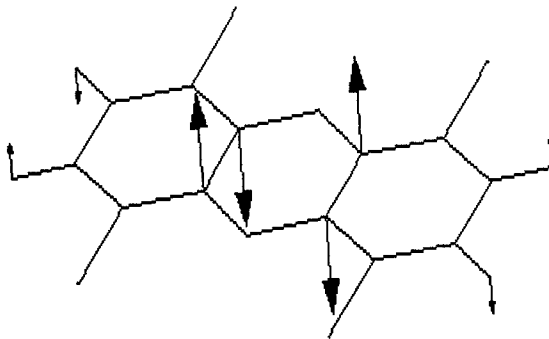


Fig1. Imaginary Frequency Mode of 1469-TCDD Anion with D_{2h} symmetry ($i372.58$ cm^{-1}).

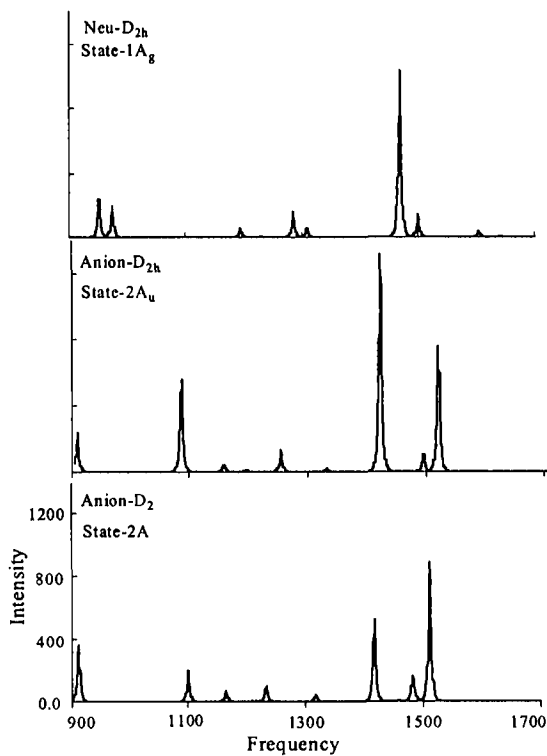


Fig 2. IR spectrum of 1,4,6,9-TCDD molecule (1A_g), and anion(2A_u , 2A).

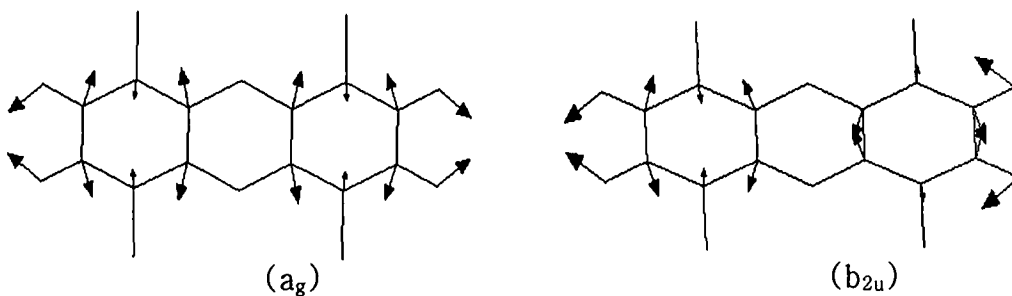


Fig 3. The a_g (a), b_{2u} (b_2) normal vibrational modes of 1,4,6,9-TCDD. The b_{2u} (b_2) normal vibrational mode is a characteristic IR band of 1,4,6,9-TCDD anion.

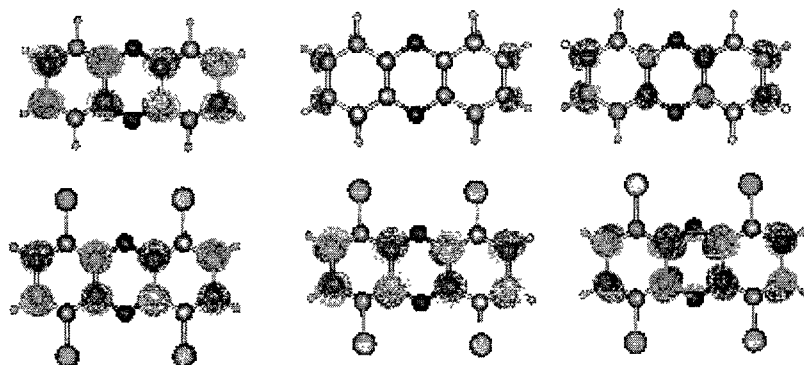


Fig 4. Neutral state LUMO, anion state SOMOs of DD and 1,4,6,9-TCDD.

To observe the charge transfer phenomena in 1,4,6,9-TCDD the atomic charge distributions and spin populations were obtained using the Mullikan population analysis for the anions have reported in Table 4. The added electron was mainly in the α - and ν -carbon. Structural distortion seems to move β electron from ν position carbon to β position carbon atoms. Thus, charge increases from 0.21e- to 0.62 e- in the β position carbon, and more spin locates in the ν -position. The neutral state lowest unoccupied molecular orbital (LUMO) and anion state singly occupied molecular orbital (SOMO) for the DD, and 1,4,6,9-TCDD are reported in Fig. 4. In case of the 1,4,6,9-TCDD anion (D_{2h} and D_2), SOMO orbital has shown that the added

Table 4. Atomic charge distributions (e) and atomic spin densities (ρ) of 1,4,6,9-TCDD at the B3LYP/6-311++G** level by using Mullikan Population Analysis.^a

Atom	Neutral	Anion D_{2h}	Anion D_2
O ₅	0.04	0.06 (-0.03)	0.07 (-0.02)
C _a	-0.78	-1.03 (0.12)	-0.96 (0.48)
C ₁	0.16	0.56 (-0.03)	0.85 (-0.31)
C ₂	0.06	-0.21 (0.18)	-0.62 (0.13)
Cl ₁₅	0.34	0.27 (0.00)	0.29 (-0.03)
H ₁₆	0.19	0.14 (-0.01)	0.14 (-0.01)

^a The values in parenthesis are spin densities.

electron populates in the γ - and β -position carbons, and this one occupies antibonding orbital between γ carbons and β carbons. Thus, CaCb and C₂C₃ bond orders decrease and these bonds elongate.

Conclusion

We have studied 1,4,6,9-TCDD anion using B3LYP method and compared the results with the DD anion. The twisted conformer with D₂ symmetry was found to be the local minimum such as DD anion. The predicted inversion barrier between twisted and planar conformers was 0.9 kcal/mol, thus we expect that experimentally observed structure seems to be planar. The characteristic IR band of 1,4,6,9-TCDD anion appears at 1510 cm⁻¹, which is a benzene ring skeleton vibration mode related with CaCb and C₂C₃ bond. This characteristic band could be used for identification of 1,4,6,9-TCDD anion. The β electron moves from γ -position carbons to β -position carbons along with the out-of-phase twisting mode. The high reactivity of the γ -carbons further supports the COC bond cleavage (34) mechanism when it undergoes inversion distortion into less symmetric D₂ anion upon electron attachment to the neutral state D_{2h}.

Acknowledgment.

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References:

- (1) Addink, R.; Olie, K. *Environ. Sci. Technol.* **1995**, *29*, 1425.
- (2) Dickson, L. C.; Lenoir, D.; Hutzinger, O. *Environ. Sci. Technol.* **1992**, *26*, 1822.
- (3) Paasivirta, J. *Water Sci. Technol.* **1988**, *20*, 119.
- (4) Choudhary, G. *Chlorinated Dioxins and Dibenzofurans in the Total Environment* Choudhary, G., Keith, L. H., Rappe, C., Eds.; Butterworth: Boston, 1983; Chapter 19.
- (5) Mhin, B. J.; Choi, J.; Choi, W. *J. Am. Chem. Soc.* **2001**, *123*, 3584.
- (6) Mhin, B. J.; Lee, J. E.; Choi, W. *J. Am. Chem. Soc.* **2002**, *124*, 144.
- (7) Lee, J. E.; Choi, W.; Mhin, B. J. *J. Phys. Chem. A* **2003**, *107*, 2693.
- (8) Lee, J. E.; Choi, W.; Mhin, B. J. *Bull. Korean Chem. Soc.* **2003**, *24*, 792.
- (9) Safe, S. *Crit. Rev. Toxicol.* **1990**, *21*, 51.

- (10) Kasai, E.; Harjanto, S.; Terui, T.; Nakamura, T.; Waseda, Y. *Chemosphere* **2000**, *41*, 857.
- (11) Ide, Y.; Kashiwabara, K.; Okada, S.; Mori, T.; Hara, M. *Chemosphere* **1996**, *32*, 189.
- (12) Hiraoka, M.; Takeda, N.; Kasakura, T.; Imoto, Y.; Tsuboi, H.; Iwasaki, T. *Chemosphere* **1991**, *23*, 1445.
- (13) Hilarides, R. J.; Gray, K. A.; Guzzetta, J.; Cortellucci, N.; Sommer, C. *Environ. Sci. Technol.* **1994**, *28*, 2249.
- (14) Palauschek N.; Scholz, B. *Chemosphere* **1987**, *16*, 1857.
- (15) Muto, H.; Shinada, M.; Takizawa, Y. *Environ. Sci. Technol.* **1991**, *25*, 316.
- (16) Pignatello, J. J.; Huang, L. Q. *Water Res.* **1993**, *27*, 1731.
- (17) Botre, C.; Memoli, A.; Alhaiqui, F. *Environ. Sci. Technol.* **1978**, *12*, 335.
- (18) Dobbs, A. J.; Grant, C. *Nature* **1979**, *278*, 163.
- (19) Colombini, M. P.; Francesco, F. D.; Fuoco, F. *Microchem. J.* **1996**, *54*, 331.
- (20) Choi, J.; Choi, W Mhin, B. J. *Environ. Sci. Technol.* **2004**, *38*, 2082-2088.
- (21) Pelizzetti, E.; Borgarello, M. *Chemosphere* **1988**, *17*, 499.
- (22) Pelizzetti, E.; Minero, C.; Carlin, V.; Borgarello, E. *Chemosphere* **1992**, *25*, 343.
- (23) Choi, W.; Hong, S. J.; Chang, Y. S.; Cho, Y. *Environ. Sci. Technol.* **2000**, *34*, 4810.
- (24) Dung, M. H.; O'Keefe, P. W. *Environ. Sci. Technol.* **1994**, *28*, 549.
- (25) Kieatiwong, S.; Nguyen, L. V.; Hebert, V. R.; Hackett, M.; Miller, G. C. *Environ. Sci. Technol.* **1990**, *24*, 1575.
- (26) Desideri, A. *Boll. Chim. Farm.* **1979**, *118*, 274.
- (27) Choudhary, G. G. *J. Agric. Food Chem.* **1989**, *37*, 254.
- (28) Kim, M.; O'Keefe, P. W. *Chemosphere* **2000**, *41*, 793.
- (29) Friesen, K. J.; Muir, D. C. G.; Webster, G. R. B. *Environ. Sci. Technol.* **1990**, *24*, 1739.
- (30) Dulin, D.; Drossman, H.; Mill, T. *Environ. Sci. Technol.* **1986**, *20*, 72.
- (31) Crosby, D. G.; Wong, A. S. *Science* **1977**, *195*, 1337.
- (32) Miller, G. C.; Hebert, V. R.; Miille, M. J.; Mitzel, R.; Zepp, R. G. *Chemosphere* **1989**, *18*, 1265.
- (33) Koester, C. J.; Hites, R. A. *Environ. Sci. Technol.* **1992**, *26*, 502.
- (34) Lee, J.E.; Choi, W.; Odde, S; Mhin, B J.; Balasubramanian, K. *Chem. Phys. Letters* **2005**, *410*, 142146
- (35) Arulmozhiraja, S.; Fujii, T; Tokiwa, H.; *J. Phys. Chem. A* **2000**, *104*, 7068.
- (36) S. Arulmozhiraja, M. Morita, *J. Phys. Chem. A* **2004**, *108*, 3499.
- (37) M.J. Frisch, G.W. Trucks, H.B. Schlegel, et al., GAUSSIAN 98, Revision-A.9, Gaussian, Inc., Pittsburgh, PA, 2000.