

## **4. Other Research**

# Structure, Energy, Vibrational Frequencies and Potential Energy Curve of 2,3,7,8-Tetrachlorinated Dibenzo-p-Dioxin: ab initio MO studies

Contact Person

Toshihiro Fujii  
Environmental Chemistry Division  
National Institute for Environmental Studies

Research Organization; Special Research Projects

Theme Studies on exposure to halogenated organic compounds and its human health effects

Researchers H. Tokiwa (Guest Scientist from Rikkyo University)  
H. Ichikawa (Guest Scientist from Hoshi College of Pharmacy)  
Y. Soma (Regional Environmental Division)

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Optimized geometries and total energies for the 2,3,7,8-tetrachlorinated dibenzo-p-dioxin (TCDD) molecules (Fig. 1) were calculated using the Gaussian 92 system of programs at two ab initio MO levels: RHF/6-31G and RHF/6-31G\*. In addition to the above levels, the corresponding basis sets, including diffuse function, were also used. The fully-optimized geometry is given for the TCDD molecule. The results were compared and agree closely with the observed structures, which were obtained by X-ray spectrometry.

Harmonic vibrational frequencies are calculated at the above-mentioned levels of theory on the basis of the optimized geometries. Comparison with experimental IR results is discussed. It is predicted from vibrational analyses that the butterfly flapping motion of two benzo-planes is a motion having a very low fundamental frequency ( $3.6\text{ cm}^{-1}$ ). For those modes which are IR inactive, the predicted Raman frequencies are reported.

Some ambiguity concerning the dynamic behavior has also been investigated in terms of the potential energy curve (PEC) as a function of the

folding angle ( $\theta$ ), to specify the butterfly flapping motion of two benzo-planes. It is shown that the potential has little curvature near the minimum. The small curvature of the PEC appears to be consistent with the far-infrared  $3.6\text{ cm}^{-1}$  frequency of the flapping motion.

Highly toxic polychlorinated dibenzo-p-dioxins (PCDDs) have been detected as trace contaminants in incinerator fly ash [1], herbicide formulations and the synthesis of several important commercial chlorophenolic compounds [2]. As a result, a number of poisoning fears have occurred in recent years due to release of these substances into the environment [3].

Among 75 possible PCDDs having from one to eight chlorine atoms, 2,3,7,8-tetrachlorinated dibenzo-p-dioxin (2,3,7,8-TCDD) shows the highest degrees of toxicity [4]. This has triggered a large number of scientific studies [5] aimed at elucidating the chemical and biological properties of TCDD-related compounds.

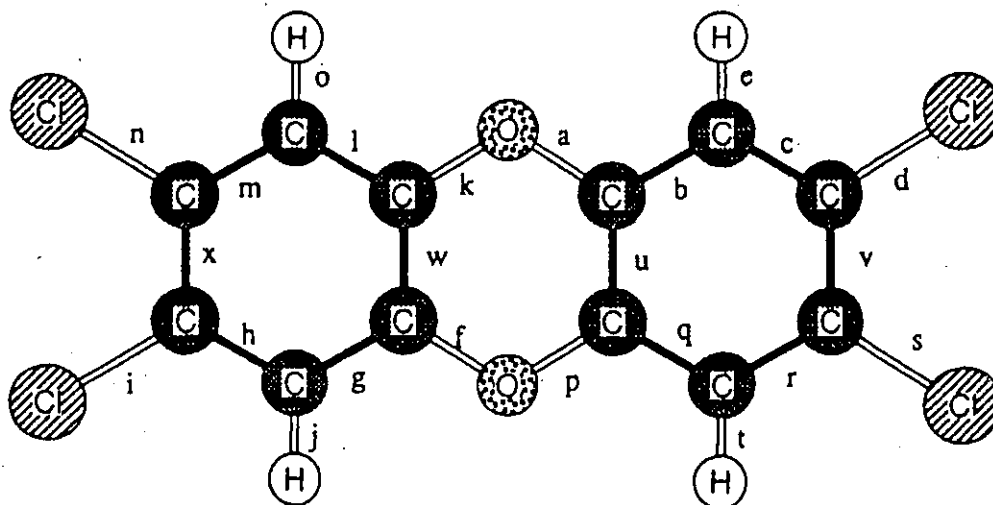


Fig. 1. Structure of the TCDD molecule and its notation with bonding scheme. Refer to Table I, for definition of structural parameters for the TCDD molecule.

Table I. Optimized geometries of the TCDD molecule from various ab initio RHF levels.

	6-31G	6-31G*	6-31G*(+O,Cl)	exptl
a, (f, k, p)	1.385	1.360	1.361	1.379
b, (g, l, q)	1.375	1.375	1.376	1.377
c, (h, m, r)	1.384	1.386	1.386	1.384
d, (i, n, s)	1.791	1.731	1.732	1.728
e, (j, o, t)	1.069	1.072	1.072	1.01
u, (w)	1.383	1.384	1.384	1.387
v, (x)	1.380	1.385	1.386	1.385
ab (=fg, kl, pq)	118.7	118.4	118.4	117.6
bc (=gh, lm, qr)	119.4	120.2	120.2	121
cd (=hi, mn, rs)	117.9	118.2	118.2	118.9
be (=gj, lo, qt)	119.5	119.2	119.3	119
au (=fw, kw, pu)	120.7	121.6	121.6	122.2
bu (=gw, jw, qu)	120.4	120.0	120.1	
cv (=hx, mx, rv)	120.2	119.8	119.8	
ak (=fp)	118.2	116.8	116.9	115.7
aub (fwg, kwl, puq)	180.0			
bec (gjh, lom, qtr)	180.0			
ecd (ihj, omn, srt)	180.0			
cdv (rsv, mnx, hix)	180.0			
dvs (nxi)	180.0			

Research into the behavior of PCDDs requires a data base of molecular properties. Unfortunately, due to the great number of chlorinated dioxins and the high toxicity of certain isomers, experimental information about these molecular parameters is hard to obtain. In the absence of experimental data, molecular orbital calculations may be used to provide vital information about these molecules.

We have performed ab initio calculations for 2,3,7,8-TCDD at a relatively high level of theory because only semi-empirical studies were previously done and no complete ab initio MO results were reported. First, the equilibrium geometries were fully optimized on the RHF/6-31G\* potential energy surface with diffuse functions partially included (+O,Cl). This permits direct geometrical and energetic comparison between experimental and theoretical results. On the basis of the optimized geometries, we have calculated harmonic vibrational frequencies of IR- and Raman-active modes at the RHF/6-31G\* level. The latter are compared with Patterson's IR experimental results. Finally, geometry-optimized ab initio MO computations at various folding angles (dihedral angles between the benzene planes) are reported; for which some equilibrium geometry controversies exist.

#### Computational Methods

All computations were performed with an NEC SX-3 supercomputer system and the Gaussian 92 [6] program. The computational resources used in

this study include Kubota, Inc., Vistra workstation and CONVEX C-3J superminicomputer.

Full geometry optimization procedures allowed for variations in bond angles and lengths. The constraints were, however, that the molecule have  $D_{2h}$  symmetry for  $\theta = 180$  and  $C_2$  symmetry at other values of  $\theta$ . Each benzene moiety was not required to be planar. Computations were made at the following levels: RHF/6-31G and RHF/6-31G\*. Calculations including diffuse functions were also performed. This was proposed by Clark et al. [7] for use with the 6-31G\* basis sets. This addition is denoted as 6-31G\*(+O,Cl). It includes a single additional diffuse *sp* shell on oxygen and chlorine atoms only. The total energies (Et) as well as the first ionization potential (IP) are obtained from complete geometry optimization. Estimates for the effect of electron correlation, which require an AO/MO integral transformation process, were not obtained because of the file (Read/Write) size limitation of the Gaussian 92 program package.

Harmonic frequency analysis using analytical second derivatives was carried out at the RHF/6-31G\*(+O, Cl) level at a stationary point to confirm the equilibrium structure and to provide zero-point vibrational energy (ZPE) corrections. The harmonic frequency analysis also provided, with calculated intensities, a prediction of the IR and Raman spectra.

Calculation was done for the dependence of Et of TCDD molecule on angle  $\theta$  (potential energy curve

( $3.6\text{ cm}^{-1}$ ). Fig. 4 also diagrams the animated behavior of this motion in the graph. The  $3.6\text{ cm}^{-1}$  far-infrared frequency implies that the potential is extremely flat and may deform easily by the coupling with other vibrational modes. This finding is consistent with the small energy difference around  $\theta = 180$  on the potential energy curve as a function of the folding angle  $\theta$ .

We also conducted the PEC calculation of the RHF/6-31G\*(+O), as a function of  $\theta$ , against the non-chlorinated dibenzo-p-dioxin (DD). Comparison with TCDD indicates that the PEC in non-chlorinated dioxin is very similar to the corresponding one in TCDD. Both shapes are quadratic. At  $\theta = 170$  the energy difference derived from PES of the former dioxin is 0.008. The corresponding one from the latter dioxin is 0.010. (This passes from 0.008 kcal/mol in TCDD to 0.010 kcal/mol in DD at the folding angle of  $\theta = 170$ ).

The substitution of 4 chlorine atoms at 2,3,7,8-sites of DD molecules has no practical effect on the barrier to puckering motion.

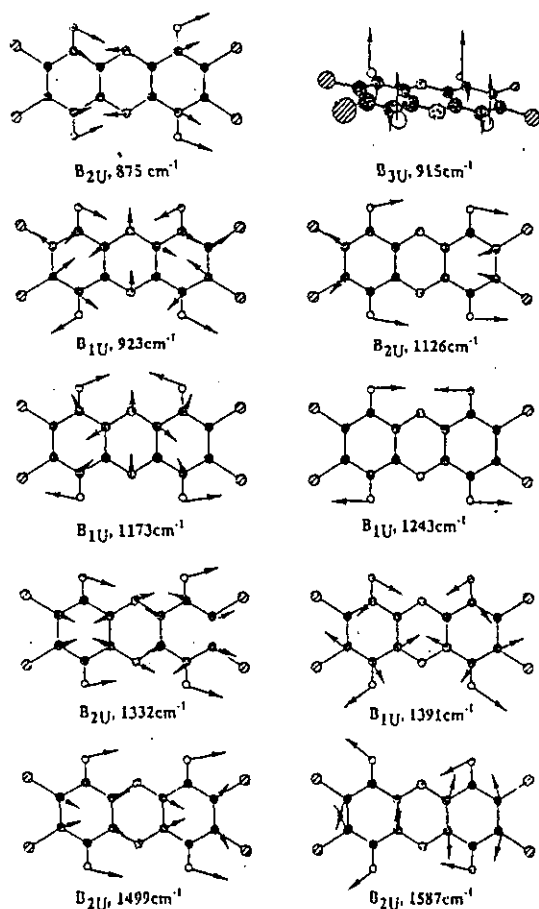


Fig. 2. Normal vibrational modes of 2,3,7,8-TCDD having comparatively strong IR intensities

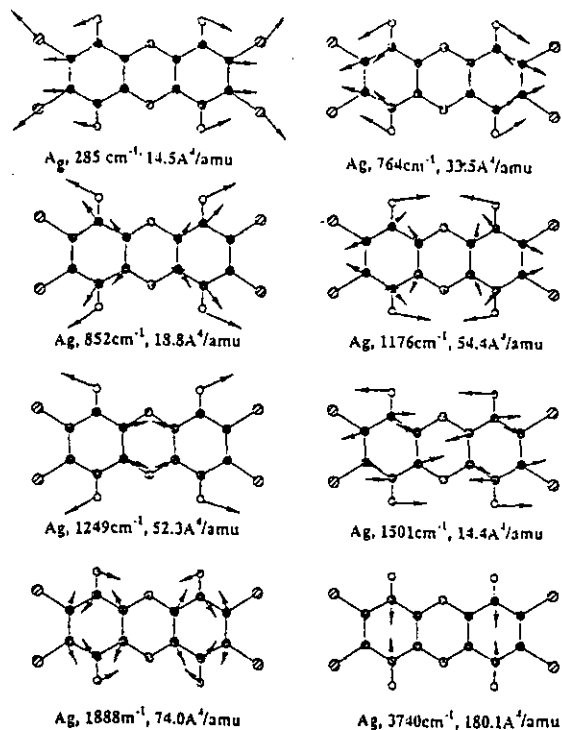


Fig. 3 Raman-active normal vibrational modes of 2,3,7,8-TCDD are illustrated together with symmetry, Raman Scattering Activities ( $\text{A}^4/\text{amu}$ ) and frequency ( $\text{cm}^{-1}$ ).

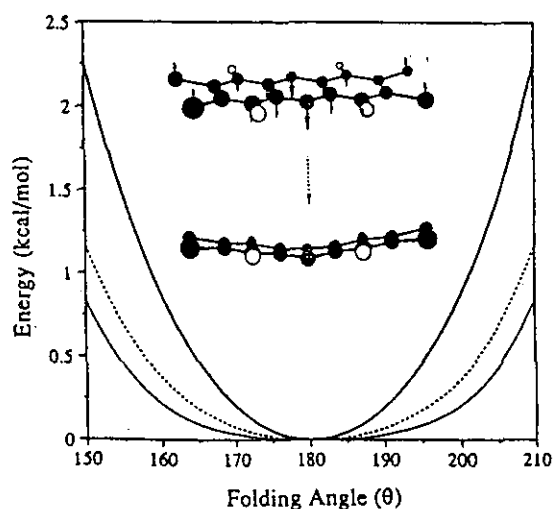


Fig. 4. The ab initio MO potential,  $E(\theta)$ , is displayed against the folding angle  $\theta$  for TCDD at various calculation levels of 6-31G (bold solid line), 6-31G\* (dotted line) and 6-31G\*(+O, Cl) (solid line).  $\theta = 180$  corresponds to a planar molecule, in which the total energy is minimum. In the graph, the normal vibrational mode with a frequency of  $3.6\text{ cm}^{-1}$  is also illustrated.

for the ring puckering). The calculations at the above-mentioned levels were done for every 1 degree increment of  $\theta$  between 150 and 180. Again, no constraint was given with the exception of the  $C_2$  symmetry at values of  $\theta$ .

## Results and Discussion

### 1. Geometry

The geometry and its notation for the TCDD structure are shown in Fig. 1. The optimized structural data for dioxin at different basis set levels of ab initio MO calculations are presented in Table I.

Throughout the calculations, we have noticed the effect of ab initio levels on the bond length. Compared with the experimental result, the RHF/6-31G calculations severely overestimate the C-Cl bond (d, i, n, s) length by as much as 0.065 Å. Calculations with the larger 6-31G\* basis set do much to improve this discrepancy.

The major discrepancy between the calculated (6-31G) and experimentally determined bond angles is observed in the COC angle (ak, fp). The COC bond angle is computed as 118.2 while the experimental value is 115.7. As expected, this difference can be corrected when higher levels are used with polarized basis set and d functions. The other calculated bond angles at the 6-31G level are also considerably different from the measured values with no specific pattern. However, some improvement is realized with the 6-31G\* or 6-31G\*(+O,Cl) calculations. All the dihedral angles are calculated to be 180.0; suggesting no deformations of benzo planes. The agreement between calculated and measured values is not considered because of no precise experimental data.

### 2. Energy

In case of RHF/6-31G\*(+O, Cl), comparing the total energies of the positive ion and neutral ( $\Delta$ SCF's IP) leads to IP = 7.4 eV. Whereas the orbital energy of the neutral (Koopmans theorem) leads to IP = 8.6 eV. This is typical. The  $\Delta$ SCF procedure leads to too small an IP. Koopmans theorem assumes that the orbitals do not relax upon ionization, leading to too large a value. The average value of 8.0 eV may be a good prediction [8] as a TCDD IP. No comparison with experimental results can be made because of non-availability.

### 3. Vibrational Frequency Analysis

Harmonic vibrational frequencies are calculated for TCDD at the RHF/6-31G, RHF/6-31G\* and RHF/6-31G\*(+O, Cl) levels of theory on the basis of optimized geometries. However, they are barely affected by the calculation levels, although there is some improvement. For example, the frequency for the skeletal vibration mode at the RHF/6-31G\*(+O, Cl) level is smaller, in closer agreement with the experimental value of 1566  $\text{cm}^{-1}$ . Only the results at RHF/6-31G\*(+O, Cl) levels, together with computed IR intensities at more than

25 KM/mole and animated vibrational modes are shown in Fig. 2, because the description, based on animation of the normal modes for the equilibrium geometries, is approximate. The most intense bands are due to the skeletal vibrations at 1499  $\text{cm}^{-1}$ .

Fig 3 gives the animated normal vibrational modes of 2, 3, 7, 8-TCDD having comparatively strong Raman scattering activities with the intensity of more than 10  $\text{Å}^4/\text{amu}$ . These modes should be prominent in the Raman spectrum of TCDD. We hope these results will help coming experimental investigations of Raman spectrum on this interesting molecule.

### 4. PEC & Puckering

Fig. 4 shows a plot of the relative energy difference, located on the potential energy surface, [calculated with full geometry optimization subject to the constraints of  $D_{2h}$  for the planar ring and  $C_{2s}$  symmetry for bended conformations at the RHF/6-31G, RHF/6-31G\* and RHF/6-31G\*(+O, Cl) levels] as a single structural parameter of the folding angle,  $\theta$ , which is the dihedral angle specifying the puckering of two benzo-planes. Computations were made with  $\theta$  of one by one degree increments.

All the basis sets imply the planar form of TCDD as most stable. They do not indicate two shallow potentials (a double minimum potential). The barrier to ring puckering motion is, as expected, lower when higher ab initio levels are used with extended basis sets and diffuse functions. A difference could arise from a less than adequate description of oxygen and chlorine atoms. Since the RHF/6-31G model pictures oxygen and chlorine lone pairs as being too tightly bound, this has an overestimated effect on the calculated potential curve.

Compared to thermal energies, the potential has low curvature near 180; especially, at RHF/6-31G\*(+O,Cl). The six energies at RHF/6-31G\*(+O,Cl) are given as follows: At 180 the total energy is -2444.23729 au and the relative energies at other angles are, in kcal/mol (degrees); 0.006 (175), 0.030 (170), 0.089 (165), 0.210 (160), 0.438 (155) and 0.834 (150). At ambient temperatures, nonplanar conformations will be significantly populated for this potential. This prediction accounts for the experimental results that the electric dipole moment of the DD molecules is reported to be 0.64D [9].

The structural changes due to the bending conformers show some interesting features. The bond length changes during the ring puckering are very small ( $< \pm 0.003$  Å). All the angles change by less than  $\pm 0.2$  in passing from the planar to the equilibrium conformer at  $\theta = 150$ . These results provide some justification for the very flat potential curve.

It was predicted from vibrational analyses that the puckering motion of two benzo-planes is a motion having a very low fundamental frequency

### 5. Concluding Remarks

The ab initio MO approach to TCDD, utilizing the Gaussian 92, has proved to be very useful for fundamental studies of the structure and energy, as well as dynamic behaviors.

It may be concluded that agreement in structural information, obtained by the X-ray diffraction study and the ab initio MO calculations, is really satisfactory in bond distances and bond angles. It should be noted that some differences may occur between the structures optimized at the HF and the correlated MP level. The value of 8.0 eV is given for the first IP of the TCDD molecule, which also, must be recognized as being approximate. Future work at higher electron correlated calculations will extend and modify the present results.

The IR spectroscopic data are in excellent agreement with the results of ab initio MO calculations. This leads to the assumption that the predicted Raman data will help the interpretation of other experimental data.

It was shown that TCDD is a very flexible molecule. It bends easily along the folding angle  $\theta$ . The information about this dynamic behavior may be essential; especially, when the important role of the largely amplified butterfly motion [10] has been considered.

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