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Structures and Enthalpies of Formation in the Gas Phase of the Most Toxic Polychlorinated Dibenzo-*p*-dioxins. A DFT Study

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A theoretical study on the molecular and electronic structures and the enthalpies of formation of several polychlorinated dibenzo-*p*-dioxins, PCDDs, has been carried out using DFT at the B3LYP/6-31G(d) and B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) levels of theory. The calculated molecular structures are planar in all of the studied PCDDs, in agreement with the available X-ray diffraction data. NBO charges, and HOMO and LUMO energies have also been obtained and discussed. The enthalpies of formation have been calculated through isodesmic reactions, and the $\Delta_f H^\circ_m$(g) values obtained have been compared with the few available experimental values and with values estimated by other authors using semiempirical methods or group additivity approaches.

Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) are considered to be among the most acutely toxic compounds in the environment.[1] PCDDs are a series of almost planar aromatic cyclic ethers consisting of two benzene rings connected through oxygen bridges. The general structure is given in Figure 1. The number of chlorine atoms can vary between 1 and 8, so there are 75 possible chlorine-substituted dibenzo-*p*-dioxin isomers.

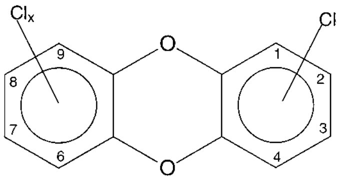

Figure 1. General structure of polychlorinated dibenzo-*p*-dioxins, PCDDs.

PCDDs are a series of compounds with unusual stability; they are solids at room temperature and have a rather low volatility. Understanding the reasons for this stability is of primary importance. These reasons can be of kinetic or thermodynamic origin.[2] Because of their low volatility, dispersion of PCDDs in the atmosphere is likely to occur mainly in particulate aerosols.

The chemical stability and lipophilicity of these compounds and their resistance to degradation result in their persistence in the environment and concentration in the food chain.[3,4] The half-life of PCDDs in soil is about 10 years.[5] Because of their stability, the dioxin toxicants are accumulated in soil, water, plants, and animals, which creates a hazard for humans and other living organisms, because they are many orders of magnitude more toxic than commonly known poisons, such as potassium cyanide.[6]

PCDDs are among the most extensively studied organic chemicals, and there are a large number of publications on the toxicological effects of these compounds.[3,7−9] It is now generally accepted that PCDDs are examples of highly toxic global pollutants.[10,11] This global environmental contamination can be attributed to a series of primary sources, which can be divided[12] into four different categories: chemical, thermal, photochemical, and enzymatic reactions. Of special importance[4,12] are the incineration of various types of wastes, the production of iron and steel, the manufacture of pesticides and other chlorinated chemicals, and the chlorine bleaching of pulp and paper. There is no known technical use for them.

It should be emphasized that not all isomers are toxic. The toxic isomers have halogen atoms in at least three, and for maximal potency four, of the lateral ring positions (positions 2, 3, 7, and 8, see Figure 1), may or may not have halogen atoms in other ring positions, and have at least one hydrogen atom in the molecule.[3]

Toxic equivalency factors (TEFs), that is, relative toxicities of dioxin-like compounds in relation to the most toxic compound, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD), have been introduced for risk assessment and regulation. They are determined from in vitro and in vivo studies. In the TEF scheme, the toxicity of 2,3,7,8-TCDD is set at 1 and the toxicity of the other PCDDs is expressed as fraction of the 2,3,7,8-TCDD toxicity. The toxic equivalency factors for PCDDs recommended by the World Health Organization[13] for human and wildlife are collected in Table 1.

The availability of thermodynamic data for these compounds is of fundamental importance in understanding their formation mechanism in thermal processes. It would assist in the effective control or elimination of the PCDD emissions during the thermal combustion and reduction processes.[14] Because of the large number of PCDDs and the extreme toxicity of certain isomers, the most important thermodynamic data, the standard molar enthalpies of formation in the gas phase ($\Delta_f H^\circ_m$(g)), have only recently been determined from combustion calorimetry

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TABLE 1: Toxic Equivalency Factors (TEFs) for PCDDs Recommended by the World Health Organization[a]

compound	TEF
2,3,7,8-TCDD	1
1,2,3,7,8-PCDD	1
2,3,7,8-substituted-HCDDs	0.1
1,2,3,4,6,7,8-HpCDD	0.01
OCDD	0.0001

[a] Taken from ref 13.

studies[2,15−17] for three of them and with high uncertainties. No experimental data are available for the other PCDDs.

In the absence of experimental data, several studies have been reported predicting the thermodynamic properties of gaseous PCDDs. The results of these predictions differ from one another substantially, and that prohibits one from obtaining reliable data on the stability of PCDDs, conditions of their formation, and relative isomer distributions.[1]

Some studies have estimated the enthalpies of formation of PCDDs using group additivity approaches.[18] The first one was published in 1982 by Shaub,[19,20] who derived a method of prediction of the enthalpy of formation using chlorination of phenol as the basis of its adjustment for successive degrees of chlorination. However, this model is unsatisfactory[1,14] because of strong oxygen−chlorine interaction suggested in it and estimates much lower values than those estimated by other methods. Bozzelli et al.[21] in 1991 developed a method for estimation of thermodynamic properties of multiply substituted aromatics inclusive of chlorinated dioxins based on principles of group additivity and non-next-nearest-neighbor interactions on the aromatic ring.

Thompson[22,23] in 1994 developed a group contribution method based on the experimental data for chlorinated benzenes, quinones, hydroquinones, and phenols. In 1995, the same author[24] revised his results taking into account the recent publication of the available experimental organic thermodynamic data from Pedley.[25] He recommended a value for chlorine substitution with corrections applied for each ortho and meta interaction.

Dorofeeva and Gurvich[26] used the difference method, which is completely consistent with group additivity but can sometimes offer a more accurate estimating scheme, to estimate the $\Delta_f H_m^\circ(g)$ values of PCDDs on the assumption that the difference between the value for any PCDD and dibenzo-*p*-dioxin is the same as the difference between suitable chlorinated benzenes and benzene and considering that the chlorination of each ring has no influence on the other benzene ring. They used an estimated value for the enthalpy of formation of dibenzo-*p*-dioxin, and for benzene and chlorinated benzenes, they took the values from the compilation by Pedley et al.[27] published in 1986.

The recent experimental determinations of the enthalpy of formation of dibenzo-*p*-dioxin and some of its chlorinated derivatives, as well as the experimental and theoretical investigations of vibrational spectra[28,29] led Dorofeeva et al.[1,2] to reexamine in 1999 the thermodynamic data for PCDDs. They have developed the group additivity scheme with nine parameters describing the C−H and C−Cl bonds, the dioxin frame taken as a whole, and six corrections applied for 1,2-, 1,3-, 1,4-, 1,2,3-, 1,2,4-, and 1,2,3,4-interactions of chlorine atoms.

Quantum mechanical calculations have also been devoted to obtain the enthalpies of formation of PCDDs. Because of the size of these molecules, the calculations have been carried out using semiempirical molecular orbital methods. So, in 1988, Koester and Hites[30] applied the MNDO method, and very recently, Saito and Fuwa[31] have obtained the $\Delta_f H_m^\circ(g)$ values for PCDDs using the PM3 method.

In this work, we have obtained the enthalpies of formation of the polychlorinated dibenzo-*p*-dioxins included in Table 1, which compiles the most toxic compounds in the series: 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD), 1,2,3,7,8-pentachlorodibenzo-*p*-dioxin (1,2,3,7,8-PCDD), 1,2,3,4,7,8-hexachlorodibenzo-*p*-dioxin (1,2,3,4,7,8-HCDD), 1,2,3,6,7,8-hexachlorodibenzo-*p*-dioxin (1,2,3,6,7,8-HCDD), 1,2,3,7,8,9-hexachlorodibenzo-*p*-dioxin (1,2,3,7,8,9-HCDD), 1,2,3,4,6,7,8-heptachlorodibenzo-*p*-dioxin (1,2,3,4,6,7,8-HpCDD), and the perchlorinated compound, octachlorodibenzo-*p*-dioxin (OCDD). We have also obtained, for comparison purposes, the enthalpies of formation of the parent compound, dibenzo-*p*-dioxin (DD), and the three PCDDs with experimental $\Delta_f H_m^\circ(g)$ values recently measured: 1-chlorodibenzo-*p*-dioxin (1-CDD), 2-chlorodibenzo-*p*-dioxin (2-CDD), and 2,3-dichlorodibenzo-*p*-dioxin (2,3-DCDD).

The energy and frequency calculations have been carried out using density functional theory, and the enthalpies of formation have been obtained through isodesmic reactions.[32,33] To our knowledge, this is the first time that $\Delta_f H_m^\circ(g)$ values for PCDDs have been obtained using high-level calculations. During the preparation of the manuscript, we have had knowledge of an abstract of a conference by Zhu et al.[34] in which they have determined $\Delta_f H_m^\circ(g)$ values for PCDDs at a DFT level similar to ours and using an isodesmic reaction but only for some mono- and dichloro derivatives. There is also a very recent article in a Chinese publication[35] dedicated to a theoretical study on the structure and thermodynamic properties of 2,3,7,8-TCDD using B3LYP and MP2 methods with different basis sets.

Computational Details

Standard density functional calculations have been performed with the Gaussian 98 series of programs.[36] For all of the species included in this study, full geometry optimizations using the 6-31G(d) basis set[37] and Becke's nonlocal three-parameter hybrid exchange and correlation functional[38] in conjunction with the Lee−Yang−Parr correlation functional[39] (denoted B3LYP)[40] have been carried out. Harmonic vibrational frequencies were evaluated at the same level of theory to confirm that the optimized structures found correspond to minima of the potential energy surface and to evaluate the corresponding zero-point vibrational energies, ZPE, and thermal corrections at 298 K. ZPE values were scaled by the empirical factor 0.9806.[41]

To calculate enthalpy values at 298 K, the difference between the enthalpy at this temperature and 0 K can be evaluated according to standard thermodynamics.[42] The thermal correction is made using B3LYP/6-31G(d)-calculated frequencies for the vibrations in the harmonic approximation for vibrational energy,[43] the classical approximation for translation ($^3/_2RT$) and rotation ($^3/_2RT$ for nonlinear molecules), and an additional RT for converting energy to enthalpy (the pV term).

However, the harmonic oscillator model fails to describe internal rotors adequately when the barrier to rotation is close to or below the thermal energy. In the limit of high temperatures or low frequencies, a harmonic oscillator contributes RT but a free rotor only contributes $^1/_2RT$.[42] Nicolaides et al.[44] recommend to treat the internal rotations with frequencies below 260 cm^{-1} as free rotors rather than as harmonic oscillators in the evaluation of ΔH_T at 298 K.

In this work, the low frequencies, corresponding to ring-bending modes, have been treated as internal rotors in the evaluation of the thermal correction to enthalpies. The list of

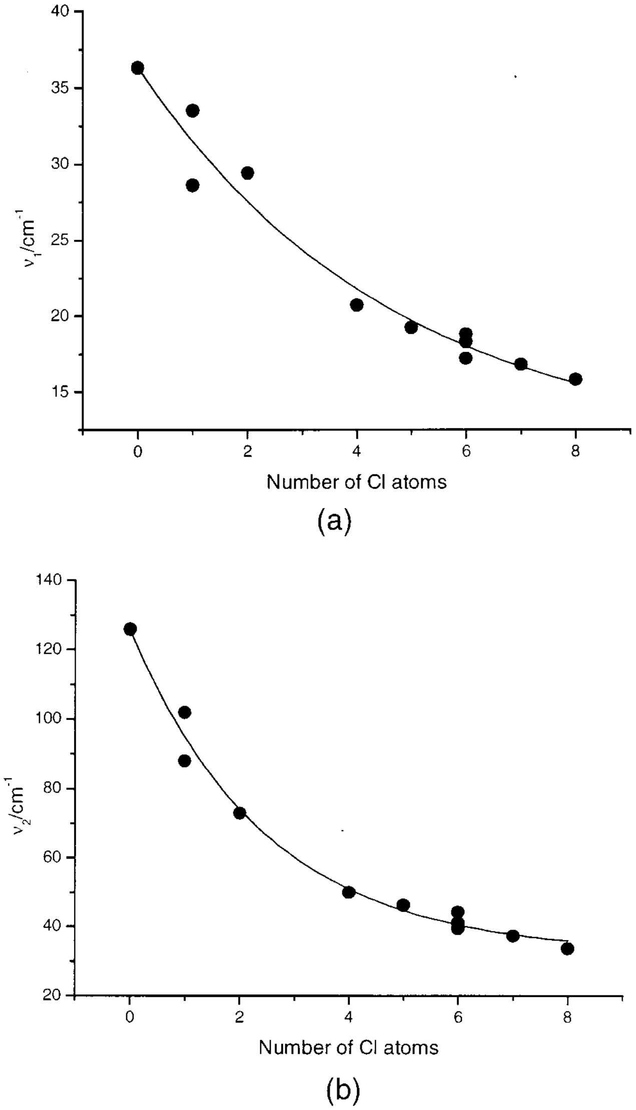


Figure 2. B3LYP/6-31G(d)-calculated harmonic vibrational frequencies corresponding to (a) butterfly-shaped motion and (b) twisting of the central ring vs the number of chlorine atoms in the molecule.

the low frequencies below 260 cm^{-1} calculated for PCDDs, polychlorinated benzenes, and other reference compounds used in this work, as well as the difference between the thermal corrections calculated using both treatments of the low frequencies, are collected in the Supporting Information. Single-point energy calculations at the B3LYP/6-311+G(3df,2p) level[45,46] were carried out to obtain more reliable enthalpies of formation.

The bonding characteristics of the studied compounds have been investigated using a population partition technique, the natural bond orbital (NBO) analysis of Reed and Weinhold.[47−49] The NBO formalism provides values for the atomic natural total charges at the atoms. The NBO analysis has been performed using the NBO program[50] implemented in the Gaussian 98 package[36] and has been carried out on the B3LYP charge densities to explicitly include electron correlation effects.

Results and Discussion

Molecular Structures. Structural data, measured by X-ray diffraction, for DD[51−53] and for only a small fraction of the 75 PCDDs have been described in the literature.[54−60] In the crystals, the molecules are nearly planar, although some atoms, including Cl atoms, deflect from the plane.[6] Thus, in di-[58] and hexachlorodibenzo-*p*-dioxins,[56] the angle between the C−Cl bond and the plane amounts to 3°−4°, while in mono-,[54] tetra-,[55,58,59] and octachlorodibenzo-*p*-dioxins,[57−60] this angle does not exceed 2°.

TABLE 2: Comparison between Calculated and Experimental COC Bond Angles[a]

compound	DFT[b]	X-ray[c]	FT-IR[d]
DD	116.4	116.3[e]	117.0
1-CDD	116.6−116.8		115.2
2-CDD	116.4	114.3−116.9[f]	116.1
2,3-DCDD	116.3		116.3
2,3,7,8-TCDD	116.2	115.6−115.8[g]	115.1
1,2,3,7,8-PCDD	116.4−116.5		114.7
1,2,3,4,7,8-HCDD	116.7		110.0
1,2,3,6,7,8-HCDD	116.7		111.3
1,2,3,7,8,9-HCDD	116.6−116.8	117−118[h]	112.3
1,2,3,4,6,7,8-HpCDD	116.9		108.5
OCDD	117.2	115.7[i]	

[a] All values in deg. [b] Values calculated at the B3LYP/6-31G(d) level. This work. [c] Experimental values measured by means of X-ray diffraction. [d] Values calculated from FT-IR data in vapor phase. Taken from ref 60. [e] Taken from ref 48. [f] Taken from ref 51. [g] Taken from ref 52. [h] Taken from ref 53. [i] Taken from ref 54.

According to X-ray diffraction data, the central fragment of PCDDs can be considered to be planar.[6] In the 2,3,7,8-TCDD, the oxygen atoms deflect slightly from the plane through the four carbon atoms in different directions, thus forming a “chair” configuration of the central fragment,[59] the angle of deflection being only 0.8°. In the DD molecule,[51] all six atoms of the central fragment lie in a plane but this plane as a whole is 0.5° rotated around axis. It has to be noted[6] that the geometric parameters determined by X-ray diffraction data refer to molecules forming the crystal lattice. No experimental data for these parameters in free PCDDs have been reported in the literature.

The calculated molecular structures, optimized at the B3LYP/6-31G(d) level, are planar in all of the studied PCDDs. Only in some cases, dihedral angles slightly different from 0° or 180° were obtained (0.4° in 1-CDD, and 0.1° in DD, 1,2,3,7,8-PCDD, 1,2,3,4,6,7,8-HpCDD, and OCDD). Previous semiempirical[61] and ab initio[28,62] calculations had obtained planar configurations for DD and 2,3,7,8-TCDD. Nevertheless, the central ring is quite flexible and easily deforms to butterfly-shaped conformations along the O···O line.[28] The B3LYP/6-31G(d)-calculated harmonic vibrational frequencies for these motions are very low, between 15.8 and 36.3 cm^{-1}, for OCDD and DD, respectively. The twisting of the central ring is also a low-energy process, but the normal frequencies are higher, between 33.5 and 125.7 cm^{-1}, for OCDD and DD, respectively. The variation of both frequencies with the number of Cl atoms in the molecule is shown in Figure 2. The low frequency of the intramolecular vibration mode of the “butterfly” type seems to point out that PCDD molecules might occur in different configurations depending on the experimental conditions (temperature, intermolecular interactions).[6]

In Figure 3, the B3LYP/6-31G(d)-calculated bond distances and bond angles for all of the compounds studied in this work are presented and compared with the experimental X-ray diffraction data when they are available. As it can be seen, the calculated geometric parameters agree well with the experimental ones. The calculated C−Cl bond length varies from 1.733 (in 1,2,3,4,6,7,8-HpCDD and OCDD) to 1.758 Å (in 2-CDD) and slightly decreases when the number of Cl atoms in the molecule increases. The C−O bond lengths of the central

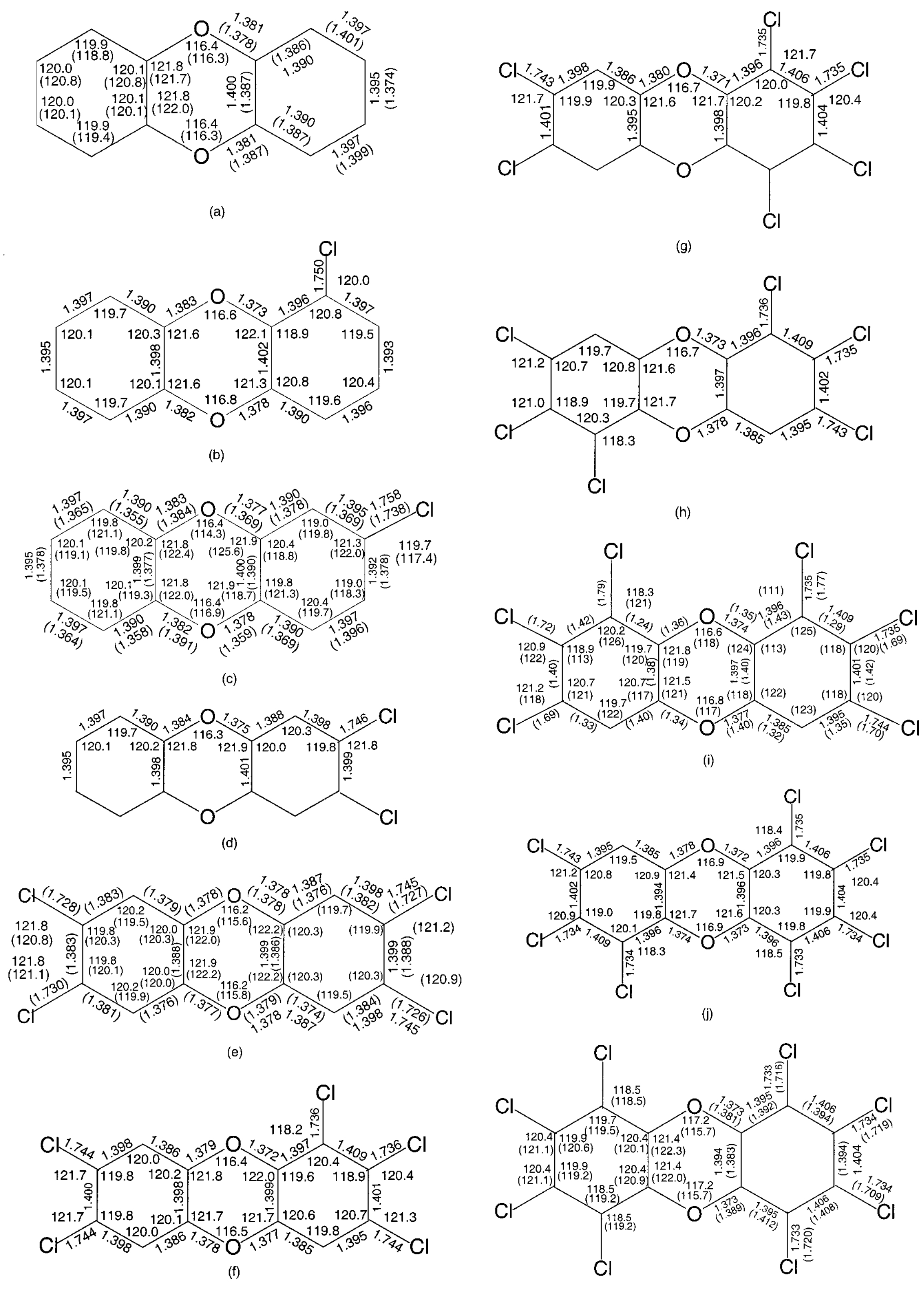

(a) (b) (c) (d) (e) (f) (g) (h) (i) (j) (k)

Figure 3. B3LYP/6-31G(d)-calculated geometric parameters for the studied PCDDs: (a) DD; (b) 1-CDD; (c) 2-CDD; (d) 2,3-DCDD; (e) 2,3,7,8-TCDD; (f) 1,2,3,7,8-PCDD; (g) 1,2,3,4,7,8-HCDD; (h) 1,2,3,6,7,8-HCDD; (i) 1,2,3,7,8,9-HCDD; (j) 1,2,3,4,6,7,8-HpCDD; (k) OCDD. Values in parentheses are experimental X-ray diffraction data taken from ref 48 for DD, ref 51 for 2-CDD, ref 52 for 2,3,7,8-TCDD, ref 53 for 1,2,3,7,8,9-HCDD, and ref 54 for OCDD. Bond distances are given in Å and bond angles in deg.

fragment differ insignificantly, from 1.371 to 1.384 Å. The calculated COC bond angle differs slightly from one compound to another. It normally increases when the number of Cl atoms increases.

In Table 2, these calculated COC angles are compared with the available experimental data measured by X-ray diffraction and with values calculated[62] from a simple triatomic model for the COC asymmetric stretching frequencies measured by FT-

IR in vapor phase. The values calculated in this work compare well with the X-ray diffraction data, all of them being indicative of near planar structures. However, the COC angles calculated from FT-IR data decrease when the number of α-chlorine atoms in the molecule increases and tend to be approximately tetrahedral for PCDDs with longitudinally substituted aromatic rings of low electron-withdrawing capacity.[63] The geometries in vapor phase proposed from these COC angles include near-planar conformations for laterally substituted isomers and folded conformations and twisted conformations that minimize non-bonded interactions in longitudinally substituted isomers.[63] However, this conclusion should be treated critically[6] because the triatomic model is too rough to provide an adequate description of the vibrations of a polyatomic molecule.

According to some authors,[61,64] the DD molecule is nonplanar; the benzene rings are rotated with respect to the axis that passes through the oxygen atoms to form a dihedral angle equal to 167.9°. This molecular configuration is called a "butterfly".

To decide between the planar and nonplanar configurations of the DD and OCDD molecules, Gastilovich et al.[6] have considered the structure of their Raman spectra taking into account the selection rules for the D_{2h} and C_{2v} groups of symmetry and the correlation of their irreducible representations. If the molecule has the "butterfly" configuration (C_{2v}), all of the vibrations should be active in the Raman spectra, including the *u*-type vibrations, which are forbidden in the case of the D_{2h} group. The results of interpretation of the Raman spectra of DD and OCDD[65] demonstrate that all lines in the spectra of these compounds can be assigned to *g*-type vibrations, which implies a planar configuration of the molecule.[6]

In this work, we have also tried to optimize the OCDD molecule in a nonplanar configuration. The calculations were carried out at the B3LYP/6-31G(d) level with several initial geometries with different folding angles, but all of the attempts failed, and the optimized structures were ever the planar configuration. The problem of the structure of PCDDs attracts attention because the toxicity of these compounds is supposed to be correlated with either planar or nonplanar structure of their molecules.[63]

There has been considerable discussion about the molecular geometry of TCDD isomers and its relation to toxicity.[63] The dioxin receptor theory proposed by Poland and Knutson,[3] and improved by Gillner et al.[66] proposes that the dimension of the 2,3,7,8-TCDD molecule allows it to fit exactly into a particular liver cell receptor, called the dioxin receptor, and cause cytochrome-488 induction. This induction is the manifestation of the extreme toxicity of 2,3,7,8-TCDD.

Electronic Structures. We have carried out a population analysis using the natural bond orbital (NBO) analysis[47−49] to obtain the natural charges that characterize the ground electronic state of the PCDDs. The calculated charges located at the heavy atoms for all of the studied PCDDs are collected in Figure 4.

As it can be seen in this figure, the negative charge is located at the oxygen atoms, ranging from −0.47 to −0.49, and at the carbon atoms linked to hydrogen atoms, ranging from −0.23 to −0.26. The carbon atoms linked to chlorine atoms have a very small negative charge, from −0.05 to −0.09. The positive charge is located at the carbon atoms of the central fragment linked to the oxygen atoms, ranging from 0.25 to 0.27, with a very small positive charge at the chlorine atoms, which slightly increases when the number of Cl atoms in the molecule increases (the charge at Cl is 0.00 in 2-CDD, and 0.07 in OCDD).

It has to be noted that the increase in the number of chlorine atoms in the PCDDs does not appreciably change the charge distribution in the central fragment with respect to that in DD. Charge redistribution takes place on the atoms of the C−Cl groups.

TABLE 3: HOMO and LUMO Energies,[a] in hartree, and Ionization Potentials, in eV, for all the studied PCDDs

compound	E_{HOMO}	E_{LUMO}	IP this work[b]	 AM1[c]	 exptl[c]
DD	−0.196 23	−0.014 08	7.55	7.58	7.60
1-CDD	−0.204 59	−0.023 17	7.78		
2-CDD	−0.203 99	−0.024 16	7.76	7.71	7.71
2,3-DCDD	−0.209 83	−0.032 07	7.92		
2,3,7,8-TCDD	−0.221 62	−0.047 17	8.24	7.99	
1,2,3,7,8-PCDD	−0.226 28	−0.052 83	8.37	8.08	
1,2,3,4,7,8-HCDD	−0.230 52	−0.058 47	8.48		
1,2,3,6,7,8-HCDD	−0.230 86	−0.058 09	8.49	8.18	
1,2,3,7,8,9-HCDD	−0.230 53	−0.057 80	8.48		
1,2,3,4,6,7,8-HpCDD	−0.234 77	−0.063 06	8.60	8.28	
OCDD	−0.238 76	−0.067 76	8.71	8.42	

[a] Evaluated at the B3LYP/6-31G(d) level. [b] Values calculated from IP = $-E_{\mathrm{HOMO}}$ + 2.21, in eV. See text. [c] Taken from ref 61.

An important characteristic of the ground electronic state of a molecule is the ionization potential, IP. The first IPs for DD and 2-CDD cooled in a supersonic jet of argon have been determined experimentally[64] by the resonance-enhanced two-color two-photon ionization technique.

We have calculated the IP values for the studied compounds, according to Koopmans' theorem.[67,68] The ionization potentials, IP, and electron affinities, EA, correspond approximately to the negatives of the energies of the highest occupied molecular orbital, HOMO, and the lowest unoccupied molecular orbital, LUMO, respectively, with allowance for an adjusting parameter selected empirically for a particular series of molecules.[64]

$$\mathrm{IP} = -E_{\mathrm{HOMO}} \qquad \mathrm{EA} = -E_{\mathrm{LUMO}} \tag{1}$$

The offset correction has been performed as follows.[64] First, the offsets between the measured and the calculated IPs of DD and 2-CDD have been calculated. Then, the average offset is calculated (+2.21 eV) and added to all $-E_{\mathrm{HOMO}}$ values to yield the offset-corrected IPs.

The HOMO and LUMO B3LYP/6-31G(d)-calculated energies and the offset corrected IPs are shown in Table 3. As it can be seen, there is a HOMO stabilization in PCDDs as a function of degree of chlorination. It was found that, as the number of chlorine atoms in the molecule increases, the IP value increases monotonically by approximately 0.1 eV for each additional Cl atom. This is in contrast to the results for chlorinated benzenes. The different behavior is expected to be due to the oxygen atoms present in the dibenzo-*p*-dioxin structure.[64] The knowledge of ionization energies of PCDDs is of particular interest for theoretical investigations of multivariate chemical characterization studies.[69−71]

Enthalpies of Formation. As it has been indicated above, the values of the enthalpy of formation of dibenzo-*p*-dioxin,[72,73] 1-chlorodibenzo-*p*-dioxin,[2,17] 2-chlorodibenzo-*p*-dioxin,[15] and 2,3-dichlorodibenzo-*p*-dioxin,[2,16] were recently determined from combustion calorimetry studies. No experimental data are available for the other 72 PCDDs.

The experimental $\Delta_f H^\circ_m(g)$ value of DD, −59.2 ± 4.4 kJ mol^{-1}, seems well-established. However, this is not the case for the other PCDDs. For 1-CDD, Dorofeeva et al.,[1] in their estimation of the thermodynamic properties of gaseous PCDDs published in 1999, used a value[74] of −85.7 ± 7.0 kJ mol^{-1}, but the same authors[2] in another article published in the same

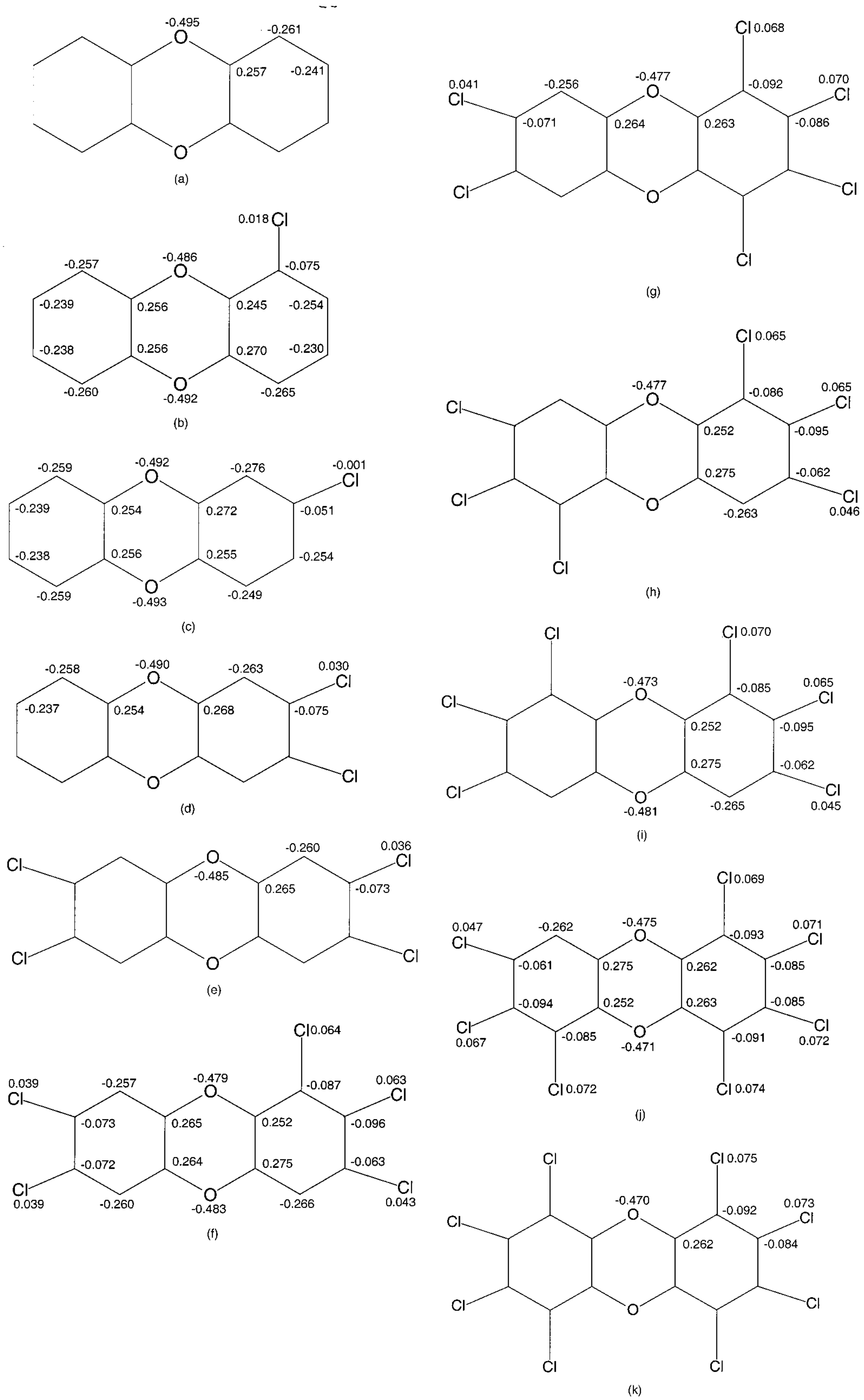


Figure 4. B3LYP/6-31G(d)-calculated NBO charges located at the heavy atoms in the studied PCDDs: (a) DD; (b) 1-CDD; (c) 2-CDD; (d) 2,3-DCDD; (e) 2,3,7,8-TCDD; (f) 1,2,3,7,8-PCDD; (g) 1,2,3,4,7,8-HCDD; (h) 1,2,3,6,7,8-HCDD; (i) 1,2,3,7,8,9-HCDD; (j) 1,2,3,4,6,7,8-HpCDD; (k) OCDD.

year used a redetermined value[17] of −88.2 ± 4.8 kJ mol^{-1}. For 2,3-DCDD, the situation is similar. In ref 1, the authors used a value[74] of −119 ± 20 kJ mol^{-1}, and in ref 2, a new value[16] of −111.9 ± 6.9 kJ mol^{-1} was used. In the case of 2-CDD, there is only one experimental value,[15] −74.1 ± 3.3 kJ mol^{-1}. However, Kolesov et al.[2] have tried a redetermination of this value, but unfortunately they failed to determine accurately the combustion energy although the preliminary experiments suggested that the $\Delta_f H^\circ_m$(g) value would be 12−15 kJ mol^{-1} higher.

TABLE 4: Experimental and Calculated (taken from the literature) Enthalpies of Formation (kJ mol^{-1}) of Polychlorinated Dibenzo-*p*-dioxins

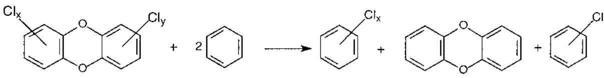
		semiempirical		group additivity		
compound	exptl	Saito−Fuwa[a] (2000)	Koester−Hites[b] (1988)	Dorofeeva et al.[c] (1999)	Thompson[d] (1995)	Shaub[e] (1983)
DD	−59.2 ± 4.4[f]	−40.2		−59.2	−55	−62.8
1-CDD	−88.2 ± 4.8[g]	−61.0		−89.8	−84.5	−95.0
2-CDD	(−74.1 ± 3.3)[h]	−67.1		−89.8	−84.5	−137.7
2,3-DCDD	−111.9 ± 6.9[i]	−89.1		−112	−106.5	−204.0
2,3,7,8-TCDD		−137.2	−186.8	−164	−158	−345.2
1,2,3,7,8-PCDD		−153.2	−192.5	−190	−177	
1,2,3,4,7,8-HCDD		−169.1	−196.6	−220	−197	−382.2
1,2,3,6,7,8-HCDD		−169.1	−198.1	−217	−197	
1,2,3,7,8,9-HCDD		−166.9	−196.1	−217	−197	
1,2,3,4,6,7,8-HpCDD		−184.8	−200.8	−246	−216.5	−401.5
OCDD		−200.5	−203.5	−275	−236	−419.2

[a] Taken from ref 31. [b] Taken from ref 30. [c] Taken from refs 1 and 2. [d] Taken from ref 24. [e] Taken from refs 19 and 20. [f] Taken from refs 72 and 73. [g] Taken from ref 17. [h] Taken from ref 15. This value has been questioned. See text. [i] Taken from ref 16.

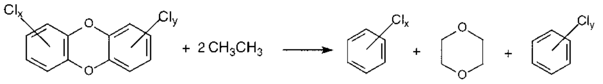
Experimental enthalpies of formation for chlorinated organic compounds are often subjected to considerable uncertainties.[24] This arises because the chlorine is not completely converted to hydrogen chloride in basic bomb calorimetry, and the preferred modification to procedure is use of a rotating bomb with arsenious acid added to reduce the chlorine. So, Thompson has pointed out[24] that some caution must be exercised in accepting the data of any particular group.

In Table 4, we have collected the experimental enthalpies of formation of the studied PCDDs and the values calculated previously by other authors from semiempirical and group additivity approaches. In this work, we have obtained the enthalpies of formation of PCDDs from theoretical DFT calculations through the use of isodesmic reactions.

Electronic energies, obtained at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) level of theory, and zero-point vibrational energies and thermal corrections to enthalpies, obtained at the B3LYP/6-31G(d) level, for all of the PCDDs studied in this work and also for chlorobenzenes and other compounds used as references are collected in Table 5. The first isodesmic reactions proposed by us are the reactions 2 and 3, taking polychlorinated benzenes and dibenzo-*p*-dioxin or 1,4-dioxane as reference compounds, respectively. To check the validity of our method, we have first calculated the enthalpy of formation of DD. Obviously, in this case only one isodesmic reaction 4 can be applied with 1,4-dioxane as reference, because in the other reaction DD is itself the reference. With the use of the values taken from Pedley's compilation for $\Delta_f H^\circ_m$(g) of 1,4-dioxane and benzene,[25] −315.3 ± 0.8 and 82.6 ± 0.7 kJ mol^{-1}, respectively, and for ethane the value recommended by Manion in a very recent evaluation[75] of the enthalpies of formation of C1 and C2 hydrocarbons, −84.0 ± 0.4 kJ mol^{-1}, the $\Delta_f H^\circ_m$(g) value for DD, evaluated at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) level, is −61.3 ± 1.4 kJ mol^{-1}, in good agreement with the experimental value.



(2)



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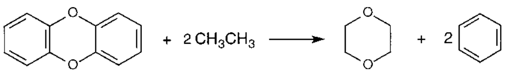


(4)

TABLE 5: Electronic Energies, Evaluated at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) Level, Zero-Point Vibrational Energies, ZPE, and Thermal Corrections to Enthalpies, TCH, in hartree, for PCDDs, Polychlorinated Benzenes, and Other Reference Compounds Used in This Work

compound	B3LYP/6-311+G(3df,2p)// B3LYP/6-31G(d)	ZPE[a]	TCH[a,b]
DD	−612.731 549	0.168 257	0.178 106
1-CDD	−1072.355 432	0.158 616	0.169 435
2-CDD	−1072.358 055	0.158 497	0.169 319
2,3-DCDD	−1531.980 181	0.148 833	0.160 626
2,3,7,8-TCDD	−2451.227 956	0.129 334	0.143 030
1,2,3,7,8-PCDD	−2910.846 026	0.119 608	0.134 268
1,2,3,4,7,8-HCDD	−3370.463 471	0.109 873	0.125 504
1,2,3,6,7,8-HCDD	−3370.464 015	0.109 850	0.125 484
1,2,3,7,8,9-HCDD	−3370.463 730	0.109 873	0.125 502
1,2,3,4,6,7,8-HpCDD	−3830.081 098	0.100 123	0.116 710
OCDD	−4289.698 214	0.090 378	0.107 924
chlorobenzene	−691.955 656	0.091 225	0.097 548
1,2-dichlorobenzene	−1151.578 953	0.081 629	0.088 872
1,3-dichlorobenzene	−1151.582 514	0.081 574	0.088 843
1,4-dichlorobenzene	−1151.582 444	0.081 574	0.088 875
1,2,3-trichlorobenzene	−1611.200 977	0.071 940	0.080 144
1,2,4-trichlorobenzene	−1611.204 793	0.071 911	0.080 126
1,3,5-trichlorobenzene	−1611.207 998	0.071 837	0.080 068
1,2,3,4-tetrachlorobenzene	−2070.822 296	0.062 201	0.071 379
1,2,3,5-tetrachlorobenzene	−2070.825 913	0.062 161	0.071 335
1,2,4,5-tetrachlorobenzene	−2070.826 449	0.062 193	0.071 362
pentachlorobenzene	−2530.442 912	0.052 439	0.062 291
hexacholorobenzene	−2990.058 584	0.042 673	0.053 382
benzene	−232.327 448	0.100 772	0.106 105
1,4-dioxane	−307.773 369	0.123 257	0.129 351
ethane	−79.861 426	0.075 240	0.079 653

[a] Evaluated at the B3LYP/6-31G(d) level. [b] Thermal corrections calculated treating frequencies below 260 cm^{-1} as free rotors. See text.

However, an important problem arises from the use of polychlorinated benzenes as references, and it is the controversy about the experimental enthalpies of formation of these compounds. Platonov and Simulin have measured the $\Delta_f H^\circ_m$(g) values for all of them.[76−79] Pedley, in his recent compilation,[25] takes the values of Platonov and Simulin, except for chlorobenzene, the three dichlorobenzenes, and hexachlorobenzene. There are also experimental values for the three trichlorobenzenes, measured by Yan et al.[80] All of these values are collected in Table 6.

As it can be seen in that table, there are slight discrepancies between the values of Platonov and Simulin[77,78] and the compiled ones by Pedley[25] for chlorobenzene and dichlorobenzenes. However, Thompson[24] did not use the Platonov and Simulin's values because insufficient details of their work were given to justify reliance on their values for accurate information. The discrepancies between the $\Delta_f H^\circ_m$(g) values for trichlo-

TABLE 6: Experimental and Calculated Enthalpies of Formation (kJ mol^{-1}) of Polychlorinated Benzenes

	experimental			calculated[a]
compound	Platonov−Simulin	Pedley[b]	Yan et al.[c]	this work
chlorobenzene	54.4[d]	52.0 ± 1.3		
1,2-dichlorobenzene	33.0[e]	30.2 ± 2.1		34.0 ± 2.0
1,3-dichlorobenzene	28.1[e]	25.7 ± 2.1		24.6 ± 2.0
1,4-dichlorobenzene	24.6[e]	22.5 ± 1.5		24.8 ± 2.0
1,2,3-trichlorobenzene	3.8[f]		8.2 ± 1.8	19.2 ± 2.5
1,2,4-trichlorobenzene	−8.1[d]		4.9 ± 1.6	9.1 ± 2.5
1,3,5-trichlorobenzene	−13.4[d]		−2.6 ± 1.4	0.6 ± 2.5
1,2,3,4-tetrachlorobenzene	−25.4[d]			6.2 ± 2.9
1,2,3,5-tetrachlorobenzene	−34.9[d]			−3.4 ± 2.9
1,2,4,5-tetrachlorobenzene	−32.6[f]			−4.8 ± 2.9
pentachlorobenzene	−40.0[g]			−5.9 ± 3.2
hexachlorobenzene	−44.7[f]	−35.5 ± 9.3		−4.5 ± 3.5

[a] At the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) level, using isodesmic reaction 5. [b] Values taken from ref 24. [c] Values taken from ref 80. [d] Value taken from ref 78. [e] Value taken from ref 77. [f] Value taken from ref 76. [g] Value taken from ref 79.

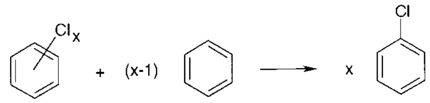
TABLE 7: Calculated (in this Work) Enthalpies of Formation (kJ mol^{-1}) of Polychlorinated Dibenzo-*p*-Dioxins

	calculated[a]				
compound	isodesmic 2[b]	isodesmic 3[c]	isodesmic 7[d]	isodesmic 8[e]	mean value[f]
DD		−61.3 ± 1.4		−61.3 ± 1.4	−61.3 ± 1.4
1-CDD	−78.7 ± 4.6	−80.8 ± 1.8	−78.7 ± 4.6	−80.8 ± 1.8	−79.8 ± 4.9
2-CDD	−85.9 ± 4.6	−88.0 ± 1.8	−85.9 ± 4.6	−88.0 ± 1.8	−87.0 ± 4.9
2,3-DCDD	−104.7 ± 4.9	−106.8 ± 2.4	−100.9 ± 4.9	−103.0 ± 2.1	−102.0 ± 5.3
2,3,7,8-TCDD	−148.2 ± 5.4	−150.3 ± 3.1	−140.6 ± 5.3	−142.7 ± 2.9	−141.7 ± 6.0
1,2,3,7,8-PCDD	−159.9 ± 5.3 [−148.9][g]	−162.0 ± 2.9 [−151.0][g]	−145.1 ± 5.5	−147.2 ± 3.3	−146.2 ± 6.4
1,2,3,4,7,8-HCDD	−183.3 ± 5.1 [−151.7][h]	−185.4 ± 2.5 [−153.8][h]	−148.0 ± 5.7	−150.1 ± 3.6	−149.1 ± 6.7
1,2,3,6,7,8-HCDD	−171.5 ± 5.2 [−149.5][g]	−173.6 ± 2.7 [−151.6][g]	−149.5 ± 5.7	−151.6 ± 3.6	−150.6 ± 6.7
1,2,3,7,8,9-HCDD	−170.7 ± 5.2 [−148.7][g]	−172.8 ± 2.7 [−150.8][g]	−148.6 ± 5.7	−150.7 ± 3.6	−149.7 ± 6.7
1,2,3,4,6,7,8-HpCDD	−194.0 ± 5.0 [−151.4][g,h]	−196.1 ± 2.3 [−153.5][g,h]	−151.4 ± 5.9	−153.5 ± 3.9	−152.5 ± 7.1
OCDD	−216.6 ± 4.7 [−153.4][h]	−218.7 ± 1.7 [−155.5][h]	−153.4 ± 6.1	−155.5 ± 4.2	−154.5 ± 7.4

[a] At the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) level. [b] Values calculated using isodesmic reaction 2. [c] Values calculated using isodesmic reaction 3. [d] Values calculated using isodesmic reaction 7. [e] Values calculated using isodesmic reaction 8. [f] From values obtained using isodesmic reactions 7 and 8. [g] Value calculated taking for 1,2,3-trichlorobenzene the value of the enthalpy of formation calculated in this work. See Table 6. [h] Value calculated taking for 1,2,3,4-tetrachlorobenzene the value of the enthalpy of formation calculated in this work. See Table 6.

robenzenes measured by Platonov and Simulin[76,78] and by Yan et al.[80] are very large, up to 13 kJ mol^{-1}. Also, there are severe discrepancies between the $\Delta_{sub}H°$ values measured by Platonov and Simulin and by Sabbah and An[81] for some of the higher polychlorinated benzenes.

These discrepancies have prompted us to carry out a theoretical study on the enthalpies of formation of polychlorinated benzenes, at the DFT level used in this work, using the isodesmic reaction 5:



(5)

For chlorobenzene, we have used as the $\Delta_f H^\circ_m$(g) value that recommended by Pedley,[25] 52.0 ± 1.3 kJ mol^{-1}. A recent theoretical determination of this value by Curtiss et al.[82] at the G3 level, 51.0 kJ mol^{-1}, seems to confirm the reliability of the experimental value.

The calculated enthalpies of formation of polychlorinated benzenes are shown in Table 6 and compared with the available experimental values. As it can be seen, the calculated $\Delta_f H^\circ_m$(g) values for dichlorobenzenes agree well with the experimental ones, within the error limits. However, for higher polychlorinated benzenes, the discrepancies between experimental and calculated values increase when the number of chlorine atoms in the molecule increases too. For trichlorobenzenes, the calculated values are closer to the values measured by Yan et al.[80] than to those measured by Platonov and Simulin.[76,78] As it can be seen in that table, the $\Delta_f H^\circ_m$(g) values calculated for chlorinated benzenes do not monotonically increase with the number of Cl atoms in the ring but they also depend of the interactions between Cl atoms. It is possible to carry out a regression analysis of the results as function of the number of Cl atoms in the ring, n_{Cl}, and the number of ortho, meta, and para interactions, n_o, n_m, and n_p, respectively. The equation obtained, in kJ mol^{-1}, is

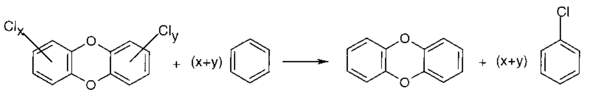
$$\Delta_f H^\circ_m(\text{g})\ [\text{chlorinated benzenes}] = \Delta_f H^\circ_m(\text{g})\ [C_6H_6] - (30.0 \pm 0.2)n_{Cl} + (12.1 \pm 0.3)n_o + (2.5 \pm 0.3)n_m + (2.0 \pm 0.4)n_p \quad (6)$$

In the isodesmic reactions proposed by us to calculate the enthalpies of formation of the studied PCDDs, reactions 2 and 3, chlorobenzene, 1,2-dichlorobenzene, 1,2,3-trichlorobenzene, and 1,2,3,4-tetrachlorobenzene have to be used as references. For the two first compounds, the values recommended by Pedley[25] have been used. For 1,2,3-trichlorobenzene, we have used the value measured by Yan et al.,[80] and for 1,2,3,4-tetrachlorobenzene, the only experimental value measured by Platonov and Simulin[78] has been used.

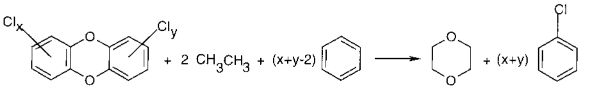
For all of the PCDDs studied in this work, we have obtained the corresponding enthalpies of formation applying isodesmic reactions 2 and 3 and using the energies evaluated at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) level of theory. The $\Delta_f H^\circ_m$(g) values obtained, with the corresponding error limits, are collected in Table 7.

It is worthwhile to point out that reaction 4 is equal to reaction 3 minus reaction 2, so the difference between the two $\Delta_f H^\circ_m$(g) values calculated for PCDDs using reactions 2 and 3 is equal to the difference between the experimental $\Delta_f H_m^\circ$(g) value for DD and that calculated from reaction 4, that is, 2.1 kJ mol^{-1}.

To avoid the problems derived by the use of polychlorinated benzenes as references another two isodesmic reactions 7 and 8 have been proposed in which only monochlorobenzene is used



(7)



(8)

as reference. The enthalpies of formation for the studied PCDDs obtained using isodesmic reactions 7 and 8 are also collected in Table 7, with the corresponding error limit ranges. As in the case of the other isodesmic reactions previously used, the difference between the values obtained from isodesmis reactions 7 and 8 is 2.1 kJ mol^{-1}. If we calculate the enthalpies of formation of PCDDs using isodesmic reactions 2 and 3 but for 1,2,3-trichlorobenzene and 1,2,3,4-tetrachlorobenzene the $\Delta_f H_m^\circ$(g) values obtained in this work (see Table 6) are used instead of the experimental values, the enthalpies of formation of the studied PCDDs agree with those obtained from the other isodesmic reactions 7 and 8.

In Table 7, we have also shown the average $\Delta_f H_m^\circ$(g) values obtained from the last two isodesmic reactions, which we consider the more reliable values of the enthalpies of formation of the studied PCDDs, evaluated at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) level of theory. The error limit ranges are large because of the number of molecules that enter in the isodesmic reactions.

The mean $\Delta_f H_m^\circ$(g) values seem to suggest that when there are more than two Cl atoms in one or the two of the rings the interactions between them destabilize the molecule and the $\Delta_f H_m^\circ$(g) value calculated is much less negative than the expected value. This behavior is observed in the MNDO results of Koester and Hites,[30] (see Table 4). As it can be seen, comparing the data in Tables 4 and 7, group additivity methods predict much more negative $\Delta_f H_m^\circ$(g) values than do computational molecular modeling methods.

We think that to have reliable enthalpies of formation of PCDDs a careful redetermination of the enthalpies of formation of polychlorinated benzenes is necessary. Nonetheless, the enthalpies of formation of PCDDs obtained in this work in addition to knowledge of their mechanism of formation[14,82] could be of significant value to assist in design of strategies to effectively control or eliminate emissions of these compounds.

Conclusions

The calculated molecular structures, optimized at the B3LYP/6-31G(d) level, are planar in all of the studied PCDDs, in agreement with the experimental X-ray diffraction data. Several attempts to optimize the OCDD molecule in a nonplanar configuration failed, and the optimized structures were ever in the planar configuration.

An NBO analysis has been carried out to obtain the natural charges that characterize the ground electronic state of the PCDDs. The increase in the number of chlorine atoms does not appreciably change the charge distribution in the central fragment with respect to that in DD.

Ionization potentials of PCDDs have been calculated according to Koopmans' theorem. There is a HOMO stabilization in PCDDs as a function of degree of chlorination. It was found that, as the number of chlorine atoms in the molecule increases, the IP value increases monotonically by approximately 0.1 eV for each additional Cl atom.

The enthalpies of formation of the studied PCDDs have been obtained at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) level through the use of isodesmic reactions taking chlorinated benzenes and dibenzo-*p*-dioxin or 1,4-dioxane as reference compounds. Because of the discrepancies in the experimental enthalpies of formation of chlorinated benzenes, a theoretical study on them have also been carried out. The calculated $\Delta_f H_m^\circ$(g) values of PCDDs are much less negative than those predicted by group additivity methods. The enthalpies of formation of PCDDs obtained in this work in addition to knowledge of their mechanism of formation could be of significant value to assist in design of strategies to effectively control or eliminate emissions of these compounds.

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Supporting Information Available: A table with the B3LYP/6-31G(d)-calculated frequencies below 260 cm^{-1} for PCDDs, polychlorinated benzenes, and other reference compounds used in this work, and the difference between the thermal corrections calculated using the two treatments of the low frequencies (2 pages). This material is available free of charge via the Internet at http://pubs.acs.org.

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