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QSAR Studies of the Dioxins and Interaction of OCDD with Calix[4] Arene Using DFT

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Quantum chemical calculations, based on Density Functional Theory (DFT) method, were performed on Calix[4]arene and Polychlorinated Dibenzo-p-dioxins (PCDDs) in gas and liquid phases for comparison purposes. The simulation results show the 1,2,3,4,6,7,8,9-octachlorodibenzo-p-dioxin (OCDD) is quite a reactive dioxin. This paper attempts to examine the possibility of dioxin adsorption by Calix[n]arene from the environment. The interaction between Calix[4]arene and OCDD is investigated using the B3LYP method and LANL2DZ level of DFT in both gas and liquid phases. The results show that the OCDD acts as an electron acceptor and Calix[4]arene acts as an electron donor. A linear model of Quantitative Structure Activity Relationship (QSAR) has been approximated to calculate the binding affinity (BA) and induction potencies of aryl hydrocarbon hydroxylase (AHH) and 7-ethoxyresorufin O-deethylase (EROD). According to this model, the calculated BA of the dioxins were found to be close to their experimental values.

Keywords: QSAR, PCDD, DFT, OCDD, Calix[4]arene

INTRODUCTION

PCDDs, known as dioxins, are among the most intensively studied environmental pollutants [1]. It has been accepted that almost all these compounds are toxic pollutants. PCDDs have attracted much interest from not only scientists but also the general public because of their extreme toxicities in the global environment through atmospheric transport [2]. PCDDs are resistant to degradation which results in their persistence in the environment [3]. The lifetime of these compounds in soil is about 10 years [3]. These toxic compounds are accumulating in soil, water, air, plants and animals and therefore are harmful for living organisms. Dioxins are transported by lipids in blood serum to liver and fatty tissues in human body [4]. These compounds cause various changes in biological processes and also promote behavioral disorders [5-8]. Researchers are trying to find ways to remove atmospheric contaminants. The absorption of pollutants by absorbing materials is a remarkable method for removal of environmental pollutants.

Calix[n]arenes are macro-cyclic molecules composed of phenol and methylene bridged units. These compounds with their notable properties have many applications in all areas [9]. Since Calix[n]arenes have little to null toxicity [10-12], they can be used for nanomedicine application in drug-delivery systems [13-16]. It has been shown that Calix[n]arenes can be also used to separate and extract different analytes such as the selective removal of aromatic amines [17], heavy metal [18,19], dyes [20-22] and oxyanions [23,24]. In addition to the above mentioned properties, Calix[n]arenes have been utilized to form stable host-guest complexes with many organic molecules and various metal ions [25].

This paper attempts to determine the possibility of dioxin adsorption by Calix[n]arene from the environment using a modeling method. The dibenzodioxins studied in our work are: 1-chlorodibenzo-p-dioxin (1-CDD), 2-

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chlorodibenzop-dioxin (2-CDD), 2,3-dichlorodibenzo-p-dioxin (2,3-DCDD), 2,8-dichlorodibenzo-p-dioxin (2,8-DCDD), 1,2,4-trichlorodibenzo-p-dioxin (1,2,4-TCDD), 2, 3,6-trichlorodibenzo-p-dioxin (2,3,6-TCDD), 2,3,7-tri-chlorodibenzo-p-dioxin (2,3,7-TCDD), 2,3,6,7-tetrachloro-dibenzo-p-dioxin (2,3,6,7-TCDD),1,3,7,8-tetrachlorodi-benzo-p-dioxin (1,3,7,8-TCDD), 1,2,3,4-tetrachlorodibenzo-p-dioxin (1,2,3,4-TCDD), 2,3,7,8-tetrachloro-dibenzo-p-dioxin (2,3,7,8-TCDD), 1,2,4,7,8-pentachloro-dibenzo-p-dioxin (1,2,4,7,8-PCDD), 1,2,3,4,7-pentachloro-dibenzo-p-dioxin (1,2,3,4,7-PCDD), 1,2,3,7,8-pentachloro-dibenzo-p-dioxin (1,2,3,7,8-PCDD), 1,2,3,4,7,8-hexachloro-dibenzo-p-dioxin (1,2,3,4,7,8-HCDD), 1,2,3,6,7,8-hexa-chlorodibenzo-p-dioxin (1,2,3,6,7,8-HCDD), 1,2,3,7,8,9-hexachlorodi-benzo-p-dioxin (1,2,3,7,8,9-HCDD), 1,2,3,4,6, 7,8-hepta-chlorodibenzo-p-dioxin (1,2,3,4,6,7,8-HpCDD) and 1,2,3,4, 6,7,8,9-octachlorodibenzo-p-dioxin (OCDD).

Several research groups have explored Calix[n]arenes and its derivatives [26-30]. Calix[4]arene is one of the best-known members of Calix[n]arene family [31,32]. Calix[4]arene has four stable and relevant conformers: cone, partial-cone, 1,2-alternate, and 1,3-alternate [33].

In this work, structural properties and reactivity of 19 members of PCDDs are theoretically investigated. Global reactivity descriptors of these compounds show that OCDD is the most reactive PCDD. The attachment sites of OCDD to Calix[4]arene may be determined by Fukui indices analysis. The changes in electronic and structural properties of OCDD upon its interaction with Calix[4]arene have been determined in both gas and liquid phases. A linear model of QSAR has been approximated to calculate the BA and induction potencies of AHH and EROD.

COMPUTATIONAL METHODOLOGY

All geometry optimizations and quantum chemical calculations were performed through Gaussian09 [34] package using density functional theory (DFT). The B3LYP (Becke's hybrid 3-parameter functional with Lee-Yang-Parr correlation) functional [35] was selected for the calculations. B3LYP, has been introduced as one of the most accurate methods for energy calculation [36-38]. Calculations were carried out using the LANL2DZ (Los Alamos effective core potential plus DZ) basis set, which this basis set uses effective core potential (ECP) of Hay and Wadt [39] for core electrons. With this choice of basis set, computational time and convergence difficulties are considerably reduced. This basis set uses D95V for first row atoms [40] and Los Alamos ECP plus DZ on Na-La and Hf-Bi [41,42]. The LANL2DZ has been widely used to model the metal atoms [43-45], Nanotubes [46-48] and also other compounds [38,49].

The global molecular descriptors of PCDDs were then compared with those of Calix[4]arene. It is anticipated that the properties of molecules and ions are different in gas and liquid phases. In this work, all calculations for solvent effect were carried out using the integral equation formalism polarized continuum model (IEFPCM [50]). It seems that this method is more suitable for our purpose, because it has been found to be very useful and can describe accurately the charge distribution of solute outside of the PCM cavity [51-53].The IEFPCM method exploits a single common approach for dielectrics of very different nature and it allows reaching a unified analytical solution of the electrostatic interaction for all solute-solvent systems [54,55]. The structures and the optimized configurations of the studied compounds are shown in Fig. 1. These conformers are considered to be minima based on the absence of imaginary frequencies.

The theoretical results can be used to determine compounds which can be studied by QSAR methods [56]. The correlation between the inhibition efficiencies of the compounds indicated that QSAR method could be used to study the BA of these compounds. A linear model has been suggested to calculate the approximate BA efficiencies. According to this model, the regression analyses are well fitted with the experimental data [57] and the calculated BA efficiencies of PCDDs are found to be close to their experimental values.

RESULTS AND DISCUSSION

Reactivity Parameters

Global molecular descriptors [58-71] of the lowest energy structures of PCDDs and Calix[4]arene were calculated. These descriptors are energy of the Highest

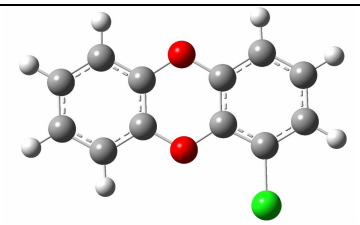
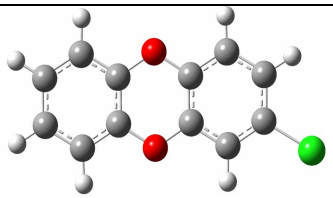
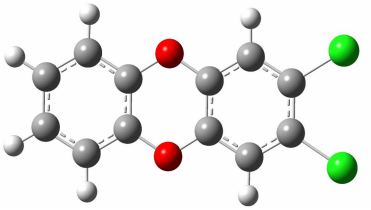
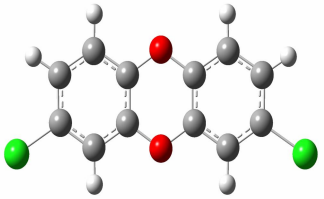
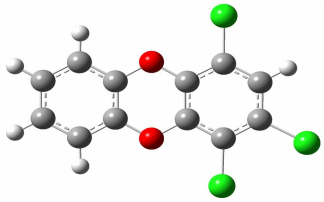
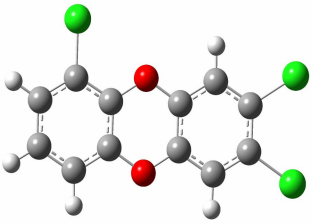
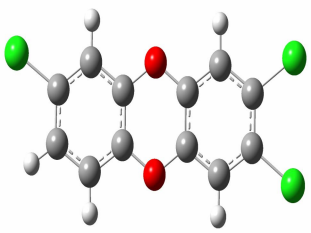
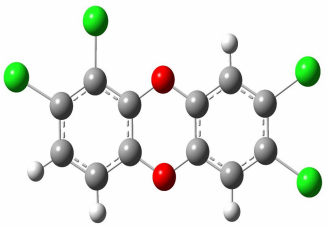
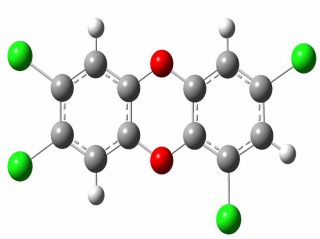
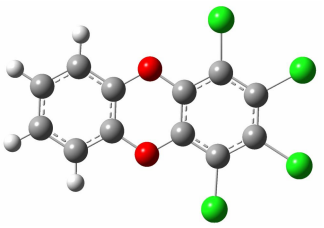
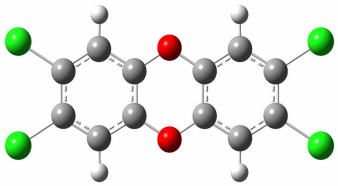
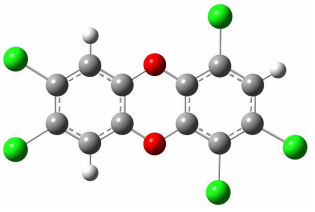
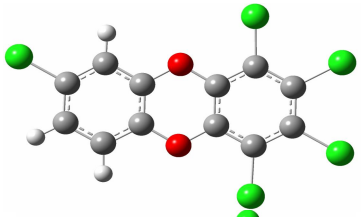
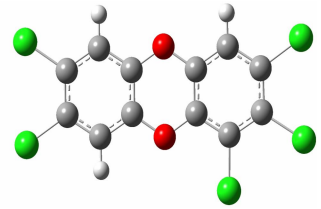
Compounds	Optimized geometries	Compounds	Optimized geometries
1-CDD		2-CDD	
2,3-DCDD		2,8-DCDD	
1,2,4-TCDD		2,3,6-TCDD	
2,3,7-TCDD		2,3,6,7-TCDD	
1,3,7,8-TCDD		1,2,3,4-TCDD	
2,3,7,8-TCDD		1,2,4,7,8-PCDD	

Fig. 1. Chemical structure and Optimized geometries for the studied compounds.

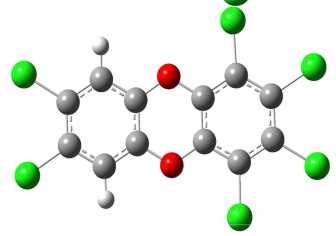
1,2,3,4,7-PCDD



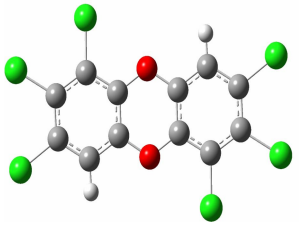
1,2,3,7,8-PCDD



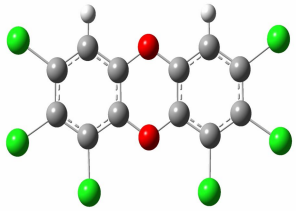
1,2,3,4,7,8-HCDD



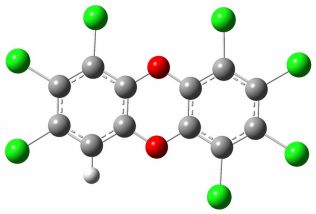
1,2,3,6,7,8-HCDD



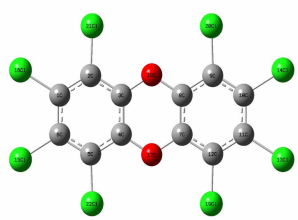
1,2,3,7,8,9-HCDD



1,2,3,4,6,7,8-HpCDD



OCDD



calix[4] arene

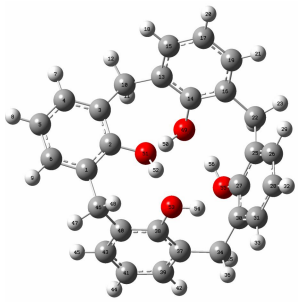


Fig. 1. Continued.

Occupied Molecular Orbital (E_{HOMO}), energy of the Lowest Unoccupied Molecular Orbital (E_{LUMO}), energy gap (ΔE), Ionization Potential (IP), Electron Affinity (EA), global hardness (η), electronegativity (χ), global softness (σ), electrophilicity (ω), electrodonating (ω^-), electroaccepting ($\omega+$), net electrophilicity ($\Delta\omega^{\pm}$), fraction of electron transferred (ΔN), Total Negative Charge (TNC) and dipole moment (μ).

Tables 1-3 show the quantum chemical parameters of PCDDs and Calix[4]arene. The energy of HOMO indicates the ability of a molecule to donate electrons and thus the higher th e value of E_{HOMO}, the more probable the molecule would donate electrons. Table 1 shows that OCDD has a lower E_{HOMO} than other PCDDs and Calix[4]arene has the highest value of E_{HOMO} in comparison to OCDD in both gas and liquid phases. This means that Calix[4]arene is more nucleophilic than OCDD. The energy of LUMO describes the electron accepting ability of a molecule and thus the

Table 1. Quantum Chemical Descriptors for the Studied Compound

Compounds	HOMO (eV)		LUMO (eV)		ΔE (eV)		Ionization potential (IP) (eV)				Electron affinity (EA) (eV)				Electron egativity (χ) (eV) (I + A)/2 = χ			
	Gas	Liquid	Gas	Liquid	Gas	Liquid	Energetic IP = [E(+1)-E(0)]		Orbital IP = $-E_{HOMO}$		Energetic EA = [E(0)-E(-1)]		Orbital EA = $-E_{LUMO}$		Energetic		Orbital	
							Gas	Liquid	Gas	Liquid	Gas	Liquid	Gas	Liquid	Gas	Liquid	Gas	Liquid
1-CDD	-5.94	-6.06	-1.07	-1.13	4.88	4.93	7.65[a]	6.00	5.94	6.06	-0.54	1.25	1.07	1.13	3.56	3.63	3.51	3.60
2-CDD	-5.94	-6.01	-1.08	-1.12	4.86	4.90	7.64[b]	5.95	5.94	6.01	-0.52	1.24	1.08	1.12	3.56	3.59	3.51	3.57
2,3-DCDD	-6.13	-6.12	-1.30	-1.28	4.84	4.84	7.78[c]	6.06	6.13	6.12	0.47	1.32	1.30	1.28	4.13	3.69	3.71	3.70
2,8-DCDD	-6.17	-6.14	-1.35	-1.28	4.83	4.86	7.81	6.07	6.17	6.14	0.22	-1.39	1.35	1.28	4.02	2.34	3.76	3.71
1,2,4-TCDD	-6.33	-6.31	-1.55	-1.50	4.78	4.81	7.97	6.24	6.33	6.31	0.00	-1.24	1.55	1.50	3.99	2.50	3.94	3.90
2,3,6-TCDD	-6.36	-6.30	-1.53	-1.44	4.84	4.86	7.98	6.23	6.36	6.30	0.01	-1.56	1.53	1.44	3.99	2.34	3.95	3.87
2,3,7-TCDD	-6.36	-6.25	-1.55	-1.42	4.81	4.83	7.95	6.18	6.36	6.25	-0.01	-1.54	1.55	1.42	3.97	2.32	3.95	3.84
2,3,6,7- TCDD	-6.52	-6.39	-1.73	-1.57	4.78	4.81	8.08	6.32	6.52	6.39	-0.23	-1.69	1.73	1.57	3.93	2.31	4.12	3.98
1,3,7,8-TCDD	-6.56	-6.41	-1.77	-1.59	4.79	4.82	8.12	6.34	6.56	6.41	-0.27	-1.71	1.77	1.59	3.93	2.32	4.17	4.00
1,2,3,4-TCDD	-6.45	-6.38	-1.79	-1.91	4.66	4.47	8.04	6.31	6.45	6.38	-0.12	-1.93	1.79	1.91	3.96	2.19	4.12	4.14
2,3,7,8-TCDD	-6.52	-6.36	-1.73	-1.56	4.80	4.80	8.07[d]	6.29	6.52	6.36	0.03	1.45	1.73	1.56	4.05	3.87	4.13	3.96
1,2,4,7,8-TCDD	-6.71	-6.53	-1.96	-1.75	4.75	4.79	8.25	6.46	6.71	6.53	-0.48	-1.56	1.96	1.75	3.89	2.45	4.33	4.14
1,2,3,4,7-PCDD	-6.65	-6.50	-1.93	-1.94	4.72	4.56	8.20	6.43	6.65	6.50	-0.45	-1.96	1.93	1.94	3.87	2.23	4.29	4.22
1,2,3,7,8-PCDD	-6.67	-6.48	-1.92	-1.71	4.76	4.77	8.19[e]	6.41	6.67	6.48	-0.16	-1.59	1.92	1.71	4.01	2.41	4.29	4.10
1,2,3,4,7,8-HCDD	-6.81	-6.60	-2.09	-1.97	4.72	4.63	8.30[f]	6.52	6.81	6.60	-0.49	-1.99	2.09	1.97	3.91	2.27	4.45	4.28
1,2,3,6,7,8-HCDD	-6.82	-6.61	-2.08	-1.85	4.74	4.76	8.32[g]	6.53	6.82	6.61	-0.36	-1.68	2.08	1.85	3.98	2.42	4.45	4.23
1,2,3,7,8,9-HCDD	-6.81	-6.62	-2.07	-1.85	4.74	4.76	8.31[h]	6.54	6.81	6.62	-0.62	-1.69	2.07	1.85	3.84	2.42	4.44	4.23
1,2,3,4,6,7,8-HpCDD	-6.95	-6.73	-2.24	-2.03	4.71	4.70	8.42[i]	6.65	6.95	6.73	-0.67	-2.07	2.24	-2.03	3.87	2.29	4.59	4.38
OCDD	-7.07	-6.85	-2.38	-2.16	4.69	4.69	8.52k	6.77	7.07	6.85	0.98	2.26	2.38	2.16	4.75	4.51	4.73	4.51
Calix[4]arene	-6.07	-6.23	-0.66	-0.80	5.41	5.43	7.36	6.12	6.07	6.23	-0.66	0.96	0.66	0.80	3.35	3.54	3.37	3.52

[a]7.78 eV from Ref. [3]. [b]7.76 and 7.71 eV from Refs. [3,35]. [c]7.92 eV from Ref. [3]. [d]8.24 and 7.99 eV from Refs. [3,35]. [e]8.37 and 8.08 eV from Refs. [3,35]. [f]8.48 from Ref. [3]. [g]8.49 and 8.18 eV from Refs. [3,35]. [h]8.48 eV from Ref. [3]. [i]8.60 and 8.8 eV from Refs. [3, 35]. [k]8.71 and 8.42 eV from Refs. [3,35].

Table 2. Quantum Chemical Descriptors for the Studied Compound

Compounds	Global hardness (η) (eV) η=(I-A)/2				Chemical potential (μ) (eV) μ = - χ				Global softness (σ) (eV^{-1}) $=1/^{\eta\sigma}$				Electrophilicity (ω) (eV) $\omega = \chi^2/2\eta$			
	Energetic		Orbital		Energetic		Orbital		Energetic		Orbital		Energetic		Orbital	
	Gas	Liquid	Gas	Liquid	Gas	Liquid	Gas	Liquid	Gas	Liquid	Gas	Liquid	Gas	Liquid	Gas	Liquid
1-CDD	4.10	2.38	2.44	2.47	-3.56	-3.63	-3.51	-3.60	0.24	0.42	0.41	0.41	1.54	2.77	2.52	2.62
2-CDD	4.08	2.36	2.43	2.45	-3.56	-3.59	-3.51	-3.57	0.25	0.42	0.41	0.41	1.55	2.74	2.54	2.60
2,3-DCDD	3.65	2.37	2.42	2.42	-4.13	-3.69	-3.71	-3.70	0.27	0.42	0.41	0.41	2.33	2.87	2.85	2.83
2,8-DCDD	3.80	3.73	2.41	2.43	-4.02	-2.34	-3.76	-3.71	0.26	0.27	0.41	0.41	2.13	0.73	2.93	2.83
1,2,4-TCDD	3.98	3.74	2.39	2.40	-3.99	-2.50	-3.94	-3.90	0.25	0.27	0.42	0.42	1.99	0.84	3.25	3.17
2,3,6-TCDD	3.98	3.90	2.42	2.43	-3.99	-2.34	-3.95	-3.87	0.25	0.26	0.41	0.41	2.00	0.70	3.22	3.08
2,3,7-TCDD	3.98	3.86	2.41	2.41	-3.97	-2.32	-3.95	-3.84	0.25	0.26	0.42	0.41	1.98	0.70	3.25	3.05
2,3,6,7-TCDD	4.15	4.00	2.39	2.41	-3.93	-2.31	4.12	-3.98	0.24	0.25	0.42	0.42	1.86	0.67	3.56	3.29
1,3,7,8-TCDD	4.20	4.03	2.40	2.41	-3.93	-2.32	-4.17	-4.00	0.24	0.25	0.42	0.42	1.84	0.67	3.62	3.33
1,2,3,4-TCDD	4.08	4.12	2.33	2.24	-3.96	-2.19	-4.12	-4.14	0.25	0.24	0.43	0.45	1.92	0.58	3.64	3.84
2,3,7,8-TCDD	4.02	2.42	2.40	2.40	-4.05	-3.87	-4.13	-3.96	0.25	0.41	0.42	0.42	2.04	3.09	3.55	3.26
1,2,4,7,8-TCDD	4.36	4.01	2.38	2.39	-3.89	-2.45	-4.33	-4.14	0.23	0.25	0.42	0.42	1.73	0.75	3.95	3.58
1,2,3,4,7-PCDD	4.32	4.20	2.36	2.28	-3.87	-2.23	-4.29	-4.22	0.23	0.24	0.42	0.44	1.74	0.59	3.90	3.91
1,2,3,7,8-PCDD	4.18	4.00	2.38	2.39	-4.01	-2.41	-4.29	-4.10	0.24	0.25	0.42	0.42	1.93	0.73	3.88	3.52
1,2,3,4,7,8-HCDD	4.40	4.26	2.36	2.32	-3.91	-2.27	-4.45	-4.28	0.23	0.23	0.42	0.43	1.73	0.60	4.19	3.96
1,2,3,6,7,8-HCDD	4.34	4.11	2.37	2.38	-3.98	-2.42	-4.45	-4.23	0.23	0.24	0.42	0.42	1.82	0.72	4.18	3.76
1,2,3,7,8,9-HCDD	4.46	4.11	2.37	2.38	-3.84	-2.42	-4.44	-4.23	0.22	0.24	0.42	0.42	1.65	0.71	4.16	3.76
1,2,3,4,6,7,8-HpCDD	4.55	4.36	2.35	2.35	-3.87	-2.29	-4.59	-4.38	0.22	0.23	0.43	0.43	1.65	0.60	4.48	4.08
OCDD	3.77	2.26	2.35	2.35	-4.75	-4.51	-4.73	-4.51	0.27	0.44	0.43	0.43	2.99	4.51	4.76	4.32
Calix[4]arene	4.01	2.58	2.71	2.72	-3.35	-3.54	-3.37	-3.52	0.25	0.39	0.37	0.37	1.40	2.43	2.09	2.28

Table 3. Quantum Chemical Descriptors for the Studied Compound

Compounds	Electrodonating (ω^-) (eV) $\omega^- = (3I+A)^2/16(I-A)$				Electro accepting (ω^+) (eV) $\omega^+ = (I+3A)^2/16(I-A)$				Net electrophilicity ($\Delta\omega^\pm$) (eV) $\Delta\omega^\pm = (\omega^+ + \omega^-)$				Total negative charge (TNC)		Dipole moment (μ) (D)	
	Energetic		Orbital		Energetic		Orbital		Energetic		Orbital					
	Gas	Liquid	Gas	Liquid	Gas	Liquid	Gas	Liquid	Gas	Liquid	Gas	Liquid	Gas	Liquid	Gas	Liquid
1-CDD	3.84	4.88	4.58	4.73	0.28	1.25	1.07	1.13	4.11	6.12	5.65	5.86	2.69	2.75	2.05	2.71
2-CDD	3.84	4.83	4.60	4.69	0.28	1.24	1.09	1.12	4.12	6.07	5.68	5.81	2.74	2.80	2.62	3.23
2,3-DCDD	4.85	5.02	5.01	4.98	0.72	1.32	1.30	1.28	5.58	6.34	6.31	4.84	2.53	2.59	4.06	5.07
2,8-DCDD	4.61	2.37	5.11	4.98	0.59	0.03	1.35	1.28	5.20	2.40	6.46	6.26	2.57	2.63	2.21	2.86
1,2,4-TCDD	4.49	2.55	5.52	5.42	0.50	0.05	1.58	1.52	4.98	2.61	7.09	6.94	2.28	2.32	3.00	3.64
2,3,6-TCDD	4.50	2.36	5.50	5.32	0.50	0.02	1.55	1.45	5.00	2.38	7.05	6.77	2.31	2.15	3.93	5.12
2,3,7-TCDD	4.46	2.34	5.52	5.27	0.49	0.02	1.57	1.43	4.95	2.36	7.09	6.70	2.37	2.43	2.01	2.60
2,3,6,7-TCDD	4.34	2.32	5.92	1.60	0.41	0.01	1.79	1.60	4.75	2.34	7.71	7.18	2.12	2.17	2.92	3.97
1,3,7,8-TCDD	4.33	2.33	6.01	5.63	0.40	0.01	1.84	1.63	4.73	2.34	7.85	7.25	2.15	2.21	1.42	1.99
1,2,3,4-TCDD	4.41	2.20	5.99	6.19	0.45	0.00	1.87	2.05	4.86	2.20	7.86	8.24	2.09	2.08	4.22	5.28
2,3,7,8-TCDD	4.57	5.33	5.92	5.54	0.52	1.46	1.79	1.58	5.09	6.79	7.70	7.13	2.15	1.67	0.00	0.00
1,2,4,7,8-TCDD	4.22	2.47	6.41	5.95	0.33	0.02	2.08	1.81	4.55	2.50	8.50	7.76	1.90	1.94	1.25	1.76
1,2,3,4,7-PCDD	4.21	2.23	6.34	6.31	0.34	0.00	2.05	2.09	4.55	2.23	8.39	8.39	2.09	1.70	2.17	2.44
1,2,3,7,8-PCDD	4.46	2.43	6.32	5.87	0.44	0.02	2.03	1.77	4.90	2.45	8.35	7.64	1.93	1.95	1.39	2.00
1,2,3,4,7,8-HCDD	4.24	2.27	6.71	6.40	0.33	0.00	2.26	2.11	4.57	2.27	8.97	8.51	1.72	1.72	0.24	0.29
1,2,3,6,7,8-HCDD	4.35	2.44	6.70	6.17	0.38	0.02	2.25	1.94	4.73	2.46	8.95	8.11	1.71	1.70	0.00	0.00
1,2,3,7,8,9-HCDD	4.13	2.44	6.67	6.18	0.29	0.02	2.23	1.95	4.42	2.46	8.91	8.12	1.71	1.70	2.64	2.44
1,2,3,4,6,7,8-HpCDD	4.15	2.29	7.07	6.57	0.28	0.00	2.48	2.19	4.43	2.29	9.55	8.75	1.70	1.71	1.26	1.93
OCDD	5.84	7.05	7.42	6.87	1.09	2.54	2.69	2.37	6.93	9.59	10.12	9.24	1.36	1.27	0.00	0.00
Calix[4]arene	3.57	4.52	4.11	4.37	0.22	0.98	0.75	0.86	3.80	5.50	4.86	5.23	7.99	8.15	2.30	2.41

lower the value of E_{LUMO}, the more probable the molecule would accept electrons. Table 1 indicates that OCDD and Calix[4]arene have the lowest and the highest values of E_{HOMO} in both gas and liquid phases, respectively. This implies that dioxins are more electrophilic than Calix[4]arene and OCDD is more electrophilic than other PCDDs. The energy gap between the HOMO and LUMO energy levels of a molecule is an important parameter, because it is a function of the molecule reactivity. Our calculations indicate that the dioxins have lower energy gaps than Calix[4]arene in both gas and liquid phases. Therefore, moving an electron from a HOMO to a LUMO is more easily achieved in the OCDD than in other dioxins.

Ionization potential (IP) is a basic description of the chemical reactivity of atoms and molecules. High IP pertains to towering stability. Table 1 shows that both orbital and energy parameter methods calculate towering IP values for OCDD compared with other PCDDs in gas and liquid phases. Calix[4]arene is more nucleophilic than OCDD because both orbital and energy parameter methods calculate a lower IP for this compound than that for OCDD in both phases. León *et al*. [3] used the Koopman theorem [72] ($IP = -E_{HOMO}$) to calculate IP values and reported the IP values for 10 of PCDDs. They calculated an offset correction value for E_{HOMO} (+2.21 eV) and added this to $-E_{HOMO}$ values to yield the offset-corrected IPs. As seen in Table 1, the theoretical data obtained by the energy method are close to the data obtained by using AM1 [73] and DFT [3] calculations.

As shown in Table 1, calculations of both orbital and energy parameter methods indicate that OCDD has more electron affinity and electronegativity than other dioxins and Calix[4]arene has lower values of electron affinity and electronegativity than OCDD in two phases. Electronegativity indicates electron flow from a lower to a higher state of electronegativity. Calix[4]arene is more nucleophilic than OCDD. The absolute hardness and softness are important properties to measure the molecular stability and reactivity. As shown in Table 2, calculations of both orbital and energy parameter methods indicate that OCDD and 1,2,3,4-TCDD have a lower absolute hardness than other PCDDs in two phases. The orbital parameter method indicates that Calix[4]arene is a hard molecule in comparison to other PCDDs in both gas and liquid phases, and, therefore, has a large energy gap in comparison to other PCDDs. The orbital parameter method indicates that OCDD is a soft molecule in comparison to Calix[4]arene and other PCDDs except 1,2,3,4-TCDD in two phases. A hard molecule has a large energy gap and a soft molecule has a small energy gap. Soft molecules are more reactive than hard ones because they could easily offer electrons to an acceptor.

The ability of the molecules to accept electrons may be described by the electrophilicity index. In our study, both orbital and energy parameter methods calculated high values of electrophilicity for OCDD in two phases and showed that OCDD is a stronger electronphile than other PCDDs. Based on orbital and energy parameter calculations, Calix[4]arene has a lower value of electrophilicity than OCDD in two phases. In other words, OCDD is an electronphile and Calix[4]arene is a nucleophile. The calculated electrodonating, electroaccepting and net electrophilicity values of PCDDs and Calix[4]arene are listed in Table 3. A large electroaccepting value corresponds to a better capability of accepting charge, whereas a small value of the electrodonating value of a system makes it a better electron donor. Calculations of the energy and orbital parameter methods indicate that OCDD molecule has a good capability of accepting charge in gas and liquid phases. The energy and orbital parameters methods indicate Calix[4]arene is a better electron donor than OCDD in two phases. The total electrophilicity indicates that OCDD is the strongest electrophile and Calix[4]arene is the strongest nucleophile. These are similar to the results obtained from the electrophilicity index data.

The calculations show that OCDD has the lowest TNC and Calix[4]arene has the highest TNC in both gas and liquid phases. The TNC value of the OCDD molecule is higher in gas phase than in liquid phase. In contrast, the TNC value of the Calix[4]arene molecule is higher in liquid phase than in gas phase. The TNC property expresses the electron donating capability of a molecule. The polarity of a molecule describes its dipole moment. 1,2,3,6,7,8-HCDD and OCDD have low dipole moments in gas and liquid phases. Tables 1-3 show that OCDD molecule has a better

capability of accepting charge than other PCDDs. In reactions between OCDD and Calix[4]arene, OCDD can act as an electrophile and Calix[4]arene can act as a nucleophile.

The fractional number of electrons (ΔN) [74] and electrophilic charge transfer (ECT) [75] methods may be used to study charge transfer between OCDD and Calix[4]arene. ΔN and ECT may be obtained from Eqs. (1) and (2).

$$\Delta N = \frac{\mu_b - \mu_a}{2(\eta_a + \eta_b)} \quad (1)$$

$$ECT = (\Delta N_{\max})_a - (\Delta N_{\max})_b = 2[\omega_a/\chi_a - \omega_b/\chi_b] \quad (2)$$

If "a" and "b" are reactants and ΔN and ECT are greater than zero, then charge transfers occur from "b" to "a" ("a" acts as an electron acceptor and "b" acts as an electron donor) and if ΔN and ECT are less than zero, then charge transfers occur from "a" to "b"("b" acts as an electron acceptor and "a" acts as an electron donor) [74,75]. In this work, "a" is OCDD and "b" is Calix[4]arene. Table 4 shows that both the energy and orbital parameter methods calculate ΔN and ECT to be greater than zero in two phases, and, therefore, charge flows from Calix[4]arene to OCDD. It means that Calix[4]arene acts as an electron donor (nucleophilic) and OCDD toxins acts as electron acceptors (electrophile). These are similar to the results obtained by quantum chemical calculations (Tables 1-3).

QSAR CONSIDERATION

Several research groups have explored QSAR models to determine the BA and induction potencies of AHH and EROD of PCDDs using quantum chemical descriptors [76], DFT-calculated tensors [1] and other methods [77-82]. In this work, the QSAR method was used to correlate the BA values (log1/EC50) of PCDDs with their molecular structures in gas and liquid phases using two quantum chemical parameters. Attempts were made to establish a relationship between the experimental toxicity values and the calculated quantum chemical parameters. To obtain equations that are useful in predicting the BA, AHH and EROD induction potencies and their quantum chemical parameters, Eqs. (3) and (4) have been proposed to calculate the log1/EC50 values of PCDDs in gas and liquid phases, respectively.

$$\log 1/EC_{50} = A + B_1X_1 + B_2X_2^2 + B_3X_3^3 + ... + B_nX_n^n \quad (3)$$

$$\log 1/EC_{50} = A + B_1X_1 + B_2X_2 + B_3X_3 + ... + B_nX_n \quad (4)$$

Where A and B_n are constants obtained by regression analysis and X_n parameters are the independent variables consisting of quantum chemical values. To simplify the Eqs. (3) and (4), only the first eight terms were used and we obtained Eqs. (5) and (6).

$$\log 1/EC_{50} = A + B_1X_1 + B_2X_2^2 + B_3X_3^3 + B_4X_4^4 + B_5X_5^5 + B_6X_6^6 + B_7X_7^7 + B_8X_8^8 \quad (5)$$

$$\log 1/EC_{50} = A + B_1X_1 + B_2X_2 + B_3X_3 + B_4X_4 + B_5X_5 + B_6X_6 + B_7X_7 + B_8X_8 \quad (6)$$

Equations (5) and (6) were utilized to correlate the composite index of the quantum chemical parameters with the experimental BA, AHH and EROD induction potencies of the studied PCDDs. The QSAR for the BA, AHH and EROD induction potencies is obtained by Eqs. (7-9) in gas phase and Eqs. (10-12) in liquid phase.

Table 4. Calculated ECT and ΔN Using B3LYP/LANL2DZ

Molecular descriptors		Parameter	Calix[4]arene -1-OCDD	
			Gas	Solvent
	ECT	Energetic	1.51	1.46
		Orbital	1.62	1.48
ΔN		Energetic	0.09	0.10
		Orbital	0.13	0.09

$$\log 1/EC_{50}(BA) = -5.275\times10^{2} + 9.791\times10^{1}\Delta E - 5.412\times10^{1}\eta^{2} - 4.511\times10^{-1}HOMO^{3} - 2.047\times10^{-2}IP^{4}_{Energy} - 1.039\times10^{-1}LUMO^{5} - 3.570\times10^{-3}\mu^{6}_{Orbital} - 4.058\times10\sigma^{7}_{Energy} + 5.948\times10^{4}\sigma^{8}_{Orbital} \quad (7)$$

$$\log 1/EC_{50}(AHH) = -2.714\times10^{1} - 6.934\Delta E + 1.466\times10^{1}\eta^{2} + 1.908\times10^{-1}\omega^{3}_{Energy} - 7.947\times10^{-2}IP^{4}_{Energy} + 5.342LUMO^{5} + 2.947\times10^{-3}\omega^{(-)6}_{Orbital} - 8.184\times10^{6}\sigma^{7}_{Energy} + 2.2\times10^{4}\sigma^{8}_{Orbital} \quad (8)$$

$$\log 1/EC_{50}(EROD) = 4.612\times10^{1} - 1.217\times10^{1}\Delta E + 2.0859\times10^{1}\eta^{2} + 2.627\times10^{1}\omega^{3}_{Energy} - 1.128\times10^{-1}IP^{4}_{Energy} + 7.232LUMO^{5} + 4.032\times10^{-3}\omega^{(-)6}_{Orbital} - 1.0696\times10^{6}\sigma^{7}_{Energy} + 3.022\times10^{-4}\omega^{(-)6}_{Energy} \quad (9)$$

$$\log 1/EC_{50}(BA) = 1.228\times10^{3} + 4.528\times10^{3}\Delta E - 2.512\times10^{2}\eta^{2} - 2.782\times10^{1}\omega^{3}_{Orbital} - 2.532\times10^{2}\chi^{4}_{Energy} - 9.109\times10^{3}LUMO^{5} + 8.820\times10^{3}\chi^{6}_{Orbital} + 2.221\times10^{1}\sigma^{7}_{Energy} - 1.372\times10^{3}\sigma^{8}_{Energy} \quad (10)$$

$$\log 1/EC_{50}(AHH) = 2.693\times10^{3} + 3.345\times10^{3}\Delta E - 3.335\times10^{1}\eta^{2} - 6.707\times10^{1}\omega^{3}_{Orbital} - 5.178\times10^{1}\chi^{4}_{Energy} - 7.334\times10^{3}LUMO^{5} + 7.716\times10^{3}\chi^{6}_{Orbital} + 1.861\times10^{2}\sigma^{7}_{Energy} - 3.231\times10^{3}\sigma^{8}_{Energy} \quad (11)$$

$$\log 1/EC_{50}(EROD) = 2.674\times10^{3} + 2.542\times10^{3}\Delta E - 2.114\times10^{2}\eta^{2} - 5.989\times10^{1}\omega^{3}_{Orbital} - 2.324\times10^{2}\chi^{4}_{Energy} - 5.538\times10^{3}LUMO^{5} + 5.217\times10^{3}\chi^{6}_{Orbital} + 2.121\times10^{2}\sigma^{7}_{Energy} - 3.189\times10^{3}\sigma^{8}_{Energy} \quad (12)$$

The biological activity data of PCDDs are presented in Table 5 and they may be compared with their experimental values [57] and [76]. The R^2 coefficient values, obtained by different QSAR approaches, are shown in Table 6. The calculated and observed results for the BA, AHH and EROD induction potencies are shown in Fig. 2.

Figure 2, Tables 5 and 6 data clearly indicate that the results of our study are in good agreement with the experimental data [57].

LOCAL MOLECULAR REACTIVITY

Fukui functions can be used to predict reactivity sites of a molecule. Fukui indices (f^+ and f^-) permit the distinction between the reactive regions and the nucleophilic and electrophilic behavior of a molecule, as well as the molecule chemical reactivity [83]. The maximum value of f^+ corresponds to nucleophilic attack sites and the maximum value of f^- indicates the preferred site for adsorption of electrophilic agents [84]. Calix[4]arene is a nucleophile, and, therefore, its maximum value of f^- is suitable for the electrophilic attack. In contrast, the OCDD is electrophile and its maximum value of f^+ indicates suitable sites for adsorption of nucleophile agents. The calculated values of the f^+ and f^- for OCDD and Calix[4]arene atoms are reported in Tables 7 and 8. For OCDD, the highest f^+ is associated with O17 and O18 while the highest f^- is at C3, C4 and C8 in the two phases. For Calix[4]arene, the sites for nucleophilic attack are the oxygen atoms in gas and liquid phases. However, Calix[4]arene sites for electrophilic attack are H50, H54, H56 and H52 in both gas and liquid phases. From Tables 1-3 data, one can infer the significance of electrophilic attack associated with nucleophilic Calix[4]arene and also the significance of nucleophilic attack associated with electrophilic OCDD. Tables 1-3 also show that high negative charges exist on the oxygen atoms in our studied compounds because these oxygen atoms have a lone pair of electrons.

The interaction energy (E), the enthalpy (H), the entropy (S) and the Gibbs free energy (G) of interaction between Calix[4]arene and OCDD can be obtained from Eq. (13).

$$\Delta X = X_{Complex} - (X_{Calix[4]arene} + nX_{OCDD}) \quad (13)$$

Where $X_{complex}$ is Calix[4]arene-n-OCDD and n is 1 or 2. The E values and quantum chemical descriptors of Calix[4]arene-1-OCDD and Calix[4]arene-2-TCDD complex systems are listed in Table 9 for both gas and liquid phases. The E, the H and the G of interaction increase with increasing OCDD in both gas and liquid phases. Positive values of the G for a complex system suggest that this interaction is spontaneous and solubility of the complex system in aqueous media increases with the increase of OCDD. The H value is negative in gas phase but is positive in liquid phase. Therefore, this interaction is exothermic in its gas phase and endothermic in its liquid phase. Table 9 shows that the global hardness and the energy gap of the complex system will increase as OCDD increases. This is in contrast to the decrease of the global hardness and energy gap of the pristine Calix[4]arene. The increase in the global hardness and the energy gap of the complex system will

Table 5. Calculated Toxicity Values of PCDDs with other Works

Compounds	BA[a]		AHH[a]		EROD[a]		BA[b]	AHH[b]	EROD[b]	BA[c]
	Gas	Liquid	Gas	Liquid	Gas	Liquid				
1-CDD	4.03	4.21	3.99	3.97	3.94	3.96	4.00	4.00	4.00	4.10
2-CDD	4.58	5.89	4.34	5.74	4.61	6.54	-	-	-	-
2,3-DCDD	5.14	6.51	5.45	8.01	6.68	8.54	-	-	-	-
2,8-DCDD	5.65	5.26	4.19	3.95	3.99	3.63	5.50	4.00	4.00	6.79
1,2,4-TCDD	4.60	5.08	5.27	5.81	4.42	4.56	4.89	5.66	4.32	5.23
2,3,6-TCDD	6.55	6.42	6.18	6.14	5.40	5.59	6.66	-	-	6.41
2,3,7-TCDD	7.01	7.15	6.87	6.68	6.63	6.74	7.15	6.85	6.44	7.32
2,3,6,7-TCDD	6.79	6.67	7.37	7.82	6.95	7.42	6.80	7.96	7.22	6.69
1,3,7,8-TCDD	6.66	6.08	7.18	7.40	6.52	7.06	6.10	6.50	6.23	7.01
1,2,3,4-TCDD	5.85	5.73	5.50	5.50	5.18	5.30	5.89	5.62	5.43	5.23
2,3,7,8-TCDD	7.79	7.81	9.62	9.51	10.02	9.79	8.00	9.72	10.14	7.87
1,2,4,7,8-TCDD	5.70	5.86	7.22	6.97	6.95	6.57	5.96	7.96	7.68	6.17
1,2,3,4,7-PCDD	5.81	5.58	7.05	6.51	6.97	6.72	5.19	6.09	6.18	5.70
1,2,3,7,8-PCDD	7.17	7.73	8.13	8.32	7.98	8.23	7.10	7.77	7.96	-
1,2,3,4,7,8-HCDD	6.10	6.20	8.13	7.87	8.74	7.99	6.55	8.39	8.68	6.21
1,2,3,6,7,8-HCDD	6.43	7.14	7.80	8.07	7.88	7.97	-	-	-	-
1,2,3,7,8,9-HCDD	6.16	6.98	10.35	8.11	11.80	7.89	-	-	-	-
1,2,3,4,6,7,8-HpCDD	5.20	5.44	12.09	7.28	15.00	7.72	-	-	-	-
OCDD	5.07	4.97	6.15	6.35	6.51	6.82	5.00	6.16	6.51	4.63

[a]This work. [b]Ref. [1].

Table 6. Calculated Determination Coefficient (R^2) with other Works

	R^2	Ref.
1	0.92	[57]
2	0.84	[58]
3	0.78	[59]
4	0.75	[60]
5	0.84	[61]
6	0.88	[62]
7	0.92	(BA) [1]
8	0.77	(BA) [1]
9	0.927	This work (BA)
10	0.94	This work (BA)
11	0.84	(AHH) [1]
12	0.92	This work (AHH)
13	0.92	This work (AHH)
14	0.83	(EROD) [1]
15	0.97	This work (EROD)
16	0.92	This work (EROD)

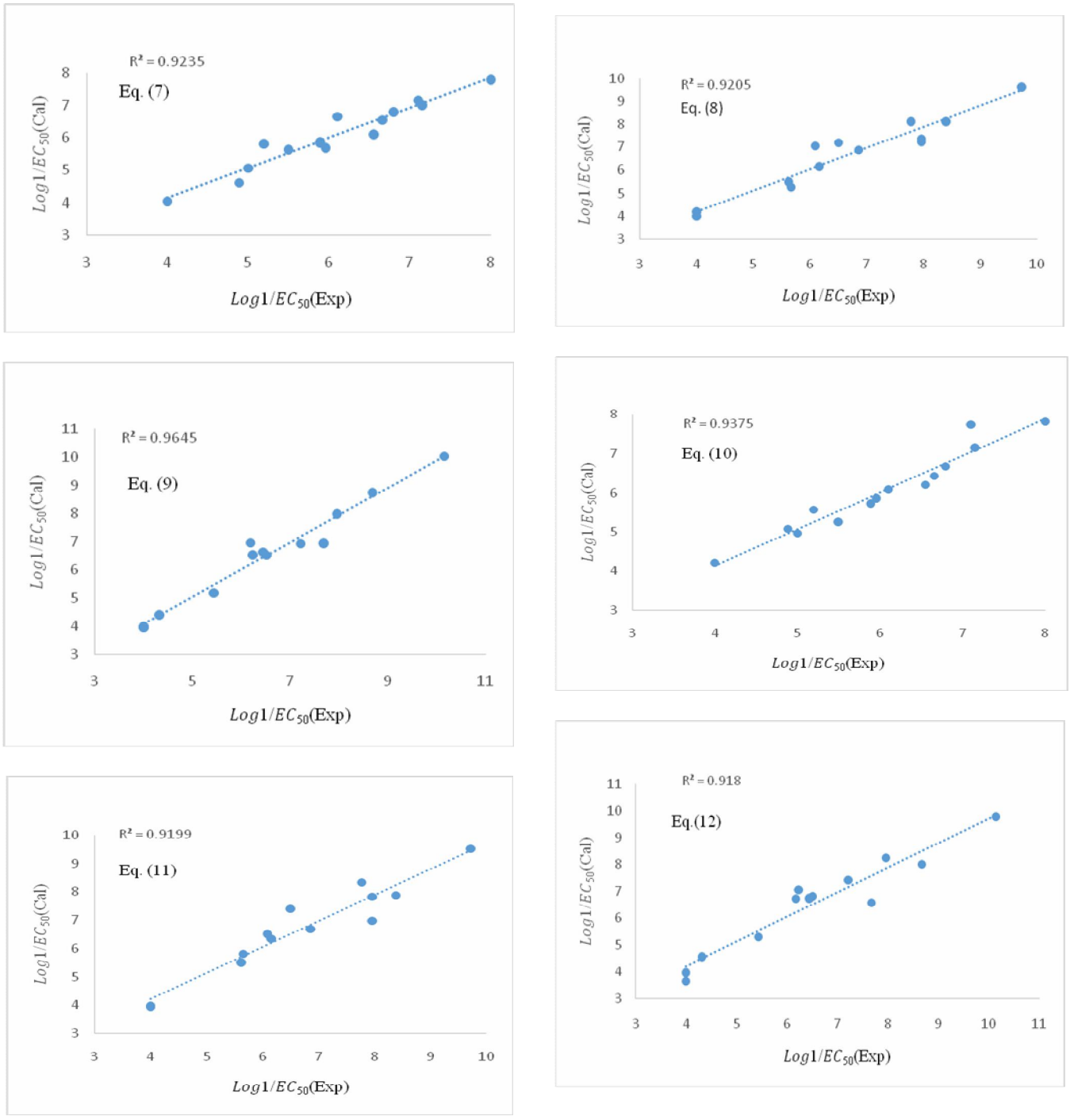


Fig. 2. The plots of experimental BA, AHH and EROD induction potencies of PCCDs vs calculated at different using [7-9] in gas phase and Eqs. (10-12) in liquid phase. The R^2 values are also reported.

Table 7. Calculated Fukui Functions for OCDD Using B3LYP/LANL2DZ

Atom	Gas					Liquid				
	Q_N	Q_{N+1}	Q_{N-1}	f^+	f^-	Q_N	Q_{N+1}	Q_{N-1}	f^+	f^-
C1	-0.04	0.03	0.02	0.06	-0.07	-0.03	0.04	0.02	0.05	-0.07
C2	-0.04	-0.03	-0.04	0.00	0.00	-0.03	-0.02	-0.04	-0.01	-0.01
C3	0.27	0.19	0.18	-0.09	0.08	0.28	0.21	0.18	-0.10	0.07
C4	0.27	0.19	0.18	-0.09	0.08	0.28	0.21	0.18	-0.10	0.07
C5	-0.04	-0.03	-0.04	0.00	0.00	-0.03	-0.02	-0.04	-0.01	-0.01
C6	-0.04	0.03	0.02	0.06	-0.07	-0.03	0.04	0.02	0.05	-0.07
C7	-0.04	0.19	0.18	0.22	-0.23	0.28	0.21	0.18	-0.10	0.07
C8	0.27	0.19	0.18	-0.09	0.08	0.28	0.21	0.18	-0.10	0.07
C9	-0.04	-0.03	-0.04	0.00	0.00	-0.03	-0.02	-0.04	-0.01	-0.01
C10	-0.04	0.03	0.02	0.06	-0.07	-0.03	0.04	0.02	0.05	-0.07
C11	-0.04	0.03	0.02	0.06	-0.07	-0.03	0.04	0.02	0.05	-0.07
C12	-0.04	-0.03	-0.04	0.00	0.00	-0.03	-0.02	-0.04	-0.01	-0.01
Cl13	0.03	0.08	-0.02	-0.05	-0.05	0.01	0.05	-0.02	-0.03	-0.04
Cl14	0.03	0.08	-0.02	-0.05	-0.05	0.01	0.05	-0.02	-0.03	-0.04
Cl15	0.03	0.08	-0.02	-0.05	-0.05	0.01	0.05	-0.02	-0.03	-0.04
Cl16	0.03	0.08	-0.02	-0.05	-0.05	0.01	0.05	-0.02	-0.03	-0.04
O17	-0.52	-0.12	-0.27	0.25	-0.40	-0.52	-0.11	-0.28	0.25	-0.41
O18	-0.52	-0.12	-0.27	0.25	-0.40	-0.52	-0.11	-0.28	0.25	-0.41
Cl19	0.03	0.04	-0.01	-0.04	-0.01	0.02	0.03	-0.01	-0.03	-0.01
Cl20	0.03	0.04	-0.01	-0.04	-0.01	0.02	0.03	-0.01	-0.03	-0.01
Cl21	0.03	0.04	-0.01	-0.04	-0.01	0.02	0.03	-0.01	-0.03	-0.01
Cl22	0.03	0.04	-0.01	-0.04	-0.01	0.02	0.03	-0.01	-0.03	-0.01

Table 8. Calculated Fukui Functions for Calix[4]arene Using B3LYP/LANL2DZ

Atom	Gas					Liquid				
	Q_N	Q_{N+1}	Q_{N-1}	f^+	f^-	Q_N	Q_{N+1}	Q_{N-1}	f^+	f^-
C1	-0.05	0.00	-0.02	0.04	-0.02	-0.10	-0.03	-0.03	0.06	-0.06
C2	0.33	0.20	0.17	-0.16	0.12	0.33	0.21	0.16	-0.17	0.12
C3	-0.04	0.01	-0.02	0.02	-0.06	-0.06	0.02	-0.01	0.05	-0.08
C4	-0.21	-0.11	-0.10	0.11	-0.10	-0.21	-0.11	-0.09	0.12	-0.10
C5	-0.22	-0.03	-0.11	0.11	-0.18	-0.23	-0.04	-0.13	0.10	-0.19
C6	-0.21	-0.10	-0.11	0.10	-0.11	-0.23	-0.10	-0.10	0.13	-0.14
H7	0.22	0.12	0.10	-0.11	0.10	0.23	0.12	0.11	-0.12	0.11
H8	0.22	0.12	0.10	-0.12	0.10	0.23	0.12	0.11	-0.12	0.11
H9	0.22	0.12	0.10	-0.11	0.09	0.23	0.12	0.11	-0.12	0.11
C10	-0.46	-0.23	-0.23	0.23	-0.22	-0.46	-0.23	-0.23	0.23	-0.22
H11	0.25	0.13	0.12	-0.13	0.12	0.24	0.13	0.12	-0.12	0.11

Table 8. Continued

H12	0.23	0.12	0.11	-0.12	0.10	0.24	0.13	0.12	-0.13	0.11
C13	-0.05	-0.01	-0.01	0.04	-0.07	-0.05	0.03	-0.01	0.04	-0.08
C14	0.33	0.22	0.16	-0.17	0.08	0.33	0.25	0.15	-0.17	0.08
C15	-0.21	-0.09	-0.10	0.11	-0.09	-0.22	-0.12	-0.10	0.12	-0.10
C16	-0.05	0.02	0.00	0.04	-0.05	-0.06	0.00	-0.01	0.05	-0.06
C17	-0.22	-0.02	-0.12	0.10	-0.21	-0.23	0.00	-0.13	0.10	-0.22
H18	0.22	0.12	0.10	-0.12	0.10	0.23	0.12	0.11	-0.12	0.11
C19	-0.22	-0.12	-0.09	0.12	-0.12	-0.22	-0.10	-0.10	0.12	-0.12
H20	0.22	0.12	0.10	-0.12	0.10	0.23	0.12	0.11	-0.12	0.11
H21	0.21	0.12	0.10	-0.11	0.09	0.23	0.12	0.11	-0.12	0.11
C22	-0.45	-0.23	-0.23	0.23	-0.22	-0.46	-0.23	-0.23	0.23	-0.23
H23	0.23	0.13	0.11	-0.12	0.10	0.25	0.13	0.12	-0.13	0.12
H24	0.24	0.13	0.11	-0.13	0.11	0.24	0.13	0.12	-0.13	0.12
C25	-0.06	0.01	0.01	0.06	-0.05	-0.05	-0.01	-0.01	0.04	-0.04
C26	-0.20	-0.11	-0.08	0.12	-0.09	-0.21	-0.11	-0.09	0.12	-0.11
C27	0.34	0.20	0.16	-0.18	0.17	0.31	0.18	0.15	-0.17	0.14
C28	-0.22	-0.05	-0.13	0.09	-0.14	-0.22	-0.08	-0.13	0.09	-0.14
H29	0.22	0.12	0.10	-0.12	0.10	0.23	0.12	0.11	-0.12	0.11
C30	-0.10	-0.03	-0.02	0.08	-0.08	-0.05	-0.02	-0.01	0.04	-0.03
C31	-0.25	-0.11	-0.09	0.15	-0.15	-0.21	-0.09	-0.09	0.12	-0.12
H32	0.22	0.12	0.10	-0.12	0.10	0.23	0.12	0.11	-0.12	0.11
H33	0.22	0.12	0.10	-0.12	0.11	0.23	0.12	0.11	-0.12	0.11
C34	-0.45	-0.23	-0.23	0.23	-0.22	-0.46	-0.23	-0.23	0.23	-0.23
H35	0.25	0.13	0.12	-0.13	0.13	0.25	0.13	0.12	-0.13	0.12
H36	0.23	0.13	0.11	-0.12	0.10	0.25	0.13	0.12	-0.13	0.12
C37	-0.05	-0.01	0.00	0.05	-0.01	-0.11	-0.04	-0.04	0.07	-0.06
C38	0.31	0.18	0.15	-0.16	0.11	0.34	0.20	0.16	-0.18	0.14
C39	-0.20	-0.10	-0.09	0.11	-0.09	-0.23	-0.11	-0.11	0.13	-0.12
C40	-0.05	-0.02	-0.01	0.04	-0.05	-0.05	0.00	-0.01	0.04	-0.05
C41	-0.21	-0.05	-0.12	0.09	-0.14	-0.23	-0.07	-0.13	0.10	-0.16
H42	0.22	0.12	0.10	-0.12	0.10	0.23	0.12	0.11	-0.12	0.11
C43	-0.20	-0.10	-0.09	0.11	-0.10	-0.20	-0.10	-0.09	0.11	-0.10
H44	0.22	0.12	0.10	-0.12	0.10	0.23	0.12	0.11	-0.12	0.11
H45	0.22	0.12	0.10	-0.12	0.10	0.23	0.12	0.11	-0.12	0.11
C46	-0.46	-0.23	-0.23	0.23	-0.23	-0.46	-0.23	-0.23	0.23	-0.23
H47	0.23	0.13	0.11	-0.12	0.10	0.25	0.13	0.12	-0.13	0.12
H48	0.25	0.13	0.12	-0.13	0.12	0.24	0.13	0.12	-0.13	0.11
O49	-0.82	-0.37	-0.41	0.41	-0.49	-0.81	-0.33	-0.41	0.40	-0.48
H50	0.53	0.27	0.27	-0.27	0.26	0.54	0.27	0.27	-0.27	0.27
O51	-0.80	-0.34	-0.40	0.41	-0.50	-0.80	-0.30	-0.40	0.39	-0.50
H52	0.54	0.27	0.27	-0.27	0.27	0.53	0.27	0.26	-0.26	0.26
O53	-0.78	-0.36	-0.40	0.39	-0.45	-0.76	-0.33	-0.39	0.38	-0.43
H54	0.53	0.27	0.27	-0.26	0.27	0.52	0.26	0.26	-0.26	0.26
O55	-0.77	-0.30	-0.39	0.38	-0.40	-0.78	-0.37	-0.39	0.39	-0.41
H56	0.53	0.26	0.26	-0.27	0.25	0.54	0.27	0.27	-0.27	0.27

Table 9. Thermodynamic Parameters and Quantum Molecular Descriptors for Calix[4]arene-1-OCDD and Calix[4]arene-2-OCDD Calculated

Molecular descriptors	Calix[4]arene-1-OCDD		Calix[4]arene-2-OCDD	
	Gas	Solvent	Gas	Solvent
ΔH_{int} (Kcal mol^{-1})	-1.18	2.93	-3.30	3.86
ΔG_{int} (Kcal mol^{-1})	8.54	16.38	14.62	23.72
ΔS_{int} (cal mol^{-1} k^{-1})	-32.58	-45.11	-60.09	-66.59
HOMO (eV)	-6.23	-6.30	-6.23	-6.31
LUMO (eV)	-2.05	-2.15	-2.46	-2.17
ΔE (eV)	4.18	4.15	3.77	4.14
IP = $-E_{HOMO}$ (eV)	6.23	6.30	6.23	6.31
EA = $-E_{LUMO}$ (eV)	2.05	2.15	2.46	2.17
(I-A)/2 (eV) = η	2.09	2.07	1.89	2.07
(I+A)/2 (eV) = χ	4.14	4.23	4.35	4.24
$\mu = \chi$ (eV)	-4.14	-4.23	-4.35	-4.24
$\sigma = 1/\eta$ (eV^{-1})	0.48	0.48	0.53	0.48
$\omega = \chi^2/2\eta$ (eV)	4.10	4.31	5.01	4.34
Dipole moment (μ) (D)	3.31	3.97	3.68	4.03

increase the complex system reactivity in both gas and liquid phases. It is also observed that in the presence of solvents, the energy gap and the S value of the complex system are lower in the gas phase which validates an increase in the complex system solubility. Electron affinity and electronegativity of the complex system will increase as the OCDD increases, implying that Calix[4]arene can withdraw electrons more readily from the complex system in both gas and liquid phases.

CONCLUSIONS

The quantum chemical parameters provide information about the chemical reactivity of our studied molecules in gas and solution. From these parameters, calculated for the 18 members of PCDD molecules, it can be inferred that OCDD is the most reactive dioxin. When two molecules interact, one will act as a nucleophile and the other one acts as an electrophile. OCDD has high values of electrophilicity index, electronegativity, electroaccepting, electron affinity and a low value of E_{LUMO} in comparison to Calix[4]arene, while Calix[4]arene has low values of electrophilicity index, electronegativity, electroaccepting, electron affinity and a high value of E_{HOMO} in comparison to OCDD. Therefore, OCDD acts as an electron acceptor and Calix[4]arene acts as an electron donor.

The following conclusions may be drawn using the molecular properties of PCDDs and Calix[4]arene:

(1) The quantum chemical descriptors of PCDDs and Calix[4]arene obtained using energetic mode are similar with those obtained using orbital mode in gas and liquid phases.

(2) The E_{HOMO} and E_{LUMO} values indicate that dioxins are more electrophilic than Calix[4]arene and OCDD is more electrophilic than other PCDDs.

(3) The ΔE values suggest that OCDD is more reactive than other dioxins in both phases.

(4) Low ionization potential indicates low stability, OCDD has lower ionization energy than other dioxins.

(5) The electron affinity, electronegativity, electrophilicity

and total electrophilicity indicate that OCDD is the strongest electrophile and Calix[4]arene is the strongest nucleophile.

(6) Both methods appear to give a higher sum of the negative charges for Calix[4]arene in two phases. This property expresses the capability of a molecule's donating electrons.

The Fukui indices have been used to explain the intramolecular reactivity of the studied compounds. Behavior of molecules as electrophiles or nucleophiles during reaction depends on how the atomic sites of the molecule react towards the approaching reagent. The results show that for OCDD (electrophile) the highest f^+ is associated with oxygen atoms and for calix [4]arene the sites for electrophilic attack are the hydrogen atoms (H50, H54, H56 and H52) which connect to oxygen atoms in the gas and liquid phases. This means that the hydrogen bonding between oxygen atoms of the OCDD and OH of Calix[4]arene has been assigned as the dominant interaction. Increasing the number of OCDD molecules loaded onto Calix[4]arene leads to a decrease in global hardness, energy gap and entropy energy, indicating that the reactivity of the system increases in both gas and liquid phases. A linear model of QSAR has been approximated to calculate the BA and induction potencies of AHH and EROD. According to this model, the calculated BA efficiencies of the dioxins were found to be close to their experimental values.

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