Editorial Article

Bioconcentration Factor of Polychlorinated Biphenyls and Its Correlation with UV- and IR-Spectroscopic data: A DFT based Study

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Abstract: Polychlorinated biphenyls (PCBs) are important class of persist organic pollutants that were used as a component of paints especially in printings, as plastificator of plastics and insulating materials in transformers and capacitors, heat transfer fluids, additives in hydraulic fluids in vacuum and turbine pumps. There is always a need to establish reliable procedures for predicting the bioconcentration potential of chemicals from the knowledge of their molecular structure, or from readily measurable properties of the substance. Hence, correlation and prediction of biococentration factors (BCFs) based on λ_{max} and vibration frequencies of various bonds viz υ(C-H) and υ(C=C) of biphenyl and its fifty-seven derivatives have been made. For the study, the molecular modeling and geometry optimization of the PCBs have been performed on workspace program of CAChe Pro 5.04 software of Fujitsu using DFT method. UV-visible spectra for each compound were created by electron transition between molecular orbitals as electromagnetic radiation in the visible and ultraviolet (UV-visible) region is absorbed by the molecule. The energies of excited electronic states were computed quantum mechanically. IR spectra of transitions for each compound were created by coordinated motions of the atoms as electromagnetic radiation in the infrared region is absorbed by the molecule. The force necessary to distort the molecule was computed quantum mechanically from its equilibrium geometry and thus frequency of vibrational transitions was predicted. Project Leader Program associated with CAChe has been used for multiple linear regression (MLR) analysis using above spectroscopic data as independent variables and BCFs of PCBs as dependent variables. The reliability of correlation and predicting ability of the MLR equations (models) are judged by R^2, R^2_{adj}, se, q^2_{L10O} and F values. This study reflected clearly that UV and IR spectroscopic data can be used to predict BCFs of a large number of related compounds within limited time without any difficulty.

Keywords: Bioconcentration factor; CAChe; density functional theory; polychlorinated biphenyls; UV and IR spectroscopic data

1. Introduction

In our recent communication, we have employed semiempirical technique to predict the bioconcentration factor (BCF: the ratio of the concentration of a chemical inside an organism to the concentration in the surrounding environment) of organic compounds in fish [1]. In the present work, we present the density functional theory (DFT) [2-4] based prediction of BCF of polychlorinated biphenyls (PCBs: an important class of persist organic pollutants) [5]. PCBs were either washed down into the soil or into the water bodies [6, 7]. From the soil, these are absorbed by the plants along with water and minerals, and from the water bodies these are taken up by aquatic plants and animals [8]. This is one of the ways in which they enter the food chain. As these chemicals are not degradable, these

get accumulated progressively at each tropic level [9-11]. As human beings occupy the top level in any food chains, the maximum concentration of these chemicals gets accumulated in our bodies [12-16]. Fish are the principal target organisms of BCF assessment due to their relevance as food for many species including humans and the availability of standardized testing protocols [17,18]. However, experimental determination of BCFs is expensive and demanding if performed correctly. Hence a number of quantitative structure-activity relationship (QSAR) based study of BCFs of the PCBs were made time to time increase the probability of success and reduce the time and cost in exploring the toxicological and ecological characteristics of molecules [19-35]. Hence, correlation and prediction of bioconcentration factors (BCFs) based on λ_{max} and vibration frequencies of various bonds viz υ(C-H) and υ(C=C) of biphenyl and its fifty-seven derivatives have been made. Our interest in DFT-based prediction of BCFs was stimulated by the fact that DFT methods [2, 36] are capable of generating UV- and IR-spectra quite accurately.

2. Materials and Methods

Table 1. Biphenyl and PCB congeners with their experimental logarithmic BCF [30]

S.N.	Chemical Name	LogBCF	S.N.	Chemical Name	LogBCF
1	Biphenyl	2.64	30	2,3,3`,4,4`-pentachloro-	5.00
2	4-chloro-	2.77	31	2,3,3`,4,6-pentachloro-	5.00
3	2,2`-dichloro-	3.38	32	2,3`,4,4`,5-pentachloro-	5.00
4	2,3-dichloro-	4.11	33	3,3`,4,4`,5-pentachloro-	5.81
5	2,3`-dichloro-	3.80	34	2,2`,3,3`,4,4`-hexachloro-	5.77
6	2,4-dichloro-	3.55	35	2,2`3,3`,6,6`-hexachloro-	5.43
7	2,4`-dichloro-	3.57	36	2,2`,3,4,4`,5-hexachloro-	5.88
8	2,5-dichloro-	3.89	37	2,2`3,4,4`,5`-hexachloro-	5.39
9	3,5-dichloro-	3.78	38	2,2`,3,4,5,5`-hexachloro-	5.81
10	4,4`-dichloro-	3.28	39	2,2`,3,4`,5,6-hexachloro-	5.39
11	2,2`,5-trichloro-	4.11	40	2,2`,3,5,5`,6-hexachloro-	5.54
12	2,4,4`-trichloro-	4.20	41	2,2`,4,4`,5,5`-hexachloro-	5.65
13	2,4,5-trichloro-	4.26	42	2,2`,4,4`,6,6`-hexachloro-	4.93
14	2,4`,5-trichloro-	4.23	43	2,3,3`,4,4`,5-hexachloro-	5.39
15	2,2`,3,3`-tetrachloro-	4.23	44	2,3,3`,4,4`,5`-hexachloro-	5.39
16	2,2`,3,5`-tetrachloro-	4.84	45	3,3`,4,4`,5,5`-hexachloro-	5.97
17	2,2`,4,4`-tetrachloro-	4.85	46	2,2`,3,3`,4,5,6`-heptachloro-	5.80
18	2,2`,4,5-tetrachloro-	5.00	47	2,2`,3,4,4`,5,5`-heptachloro-	5.80
19	2,2`,4,5`-tetrachloro-	4.84	48	2,2`,3,4,4`,5,6`-heptachloro-	5.80
20	2,2`,5,5`-tetrachloro-	4.63	49	2,2`,3,4,4`,5`,6-heptachloro-	5.84
21	2,2`,6,6`-tetrachloro-	3.85	50	2,2`,3,4`,5,5`,6-heptachloro-	5.80
22	2,3,4`,6-tetrachloro-	4.60	51	2,3,3`,4,4`,5`,6-heptachloro-	5.84
23	2,3`,4`,5-tetrachloro-	4.77	52	2,2`,3,3`,4,4`5,5`-octachloro-	5.81
24	3,3`,4,4`-tetrachloro-	4.59	53	2,2`,3,3`,4,4`5,6-octachloro-	5.92
25	2,2`,3,4,5`-pentachloro-	5.38	54	2,2`,3,3`,4,4`5,6`-octachloro-	5.92
26	2,2`,3,4`,5-pentachloro-	5.00	55	2,2`,3,3`,4, 5,5`,6-octachloro-	5.88
27	2,2`,3`,4,5`-pentachloro-	5.43	56	2,2`,3,3`,5,5`,6,6`-octachloro-	5.82
28	2,2`,4,4`,5-pentachloro-	5.00	57	2,2`,3,3`,4,5,5`,6,6`-nonachloro-	5.71
29	2,2`,4,5,5`-pentachloro-	5.40	58	Decachloro-	5.44

Biphenyl and fifty-seven PCB congeners (Table 1) are the study materials for the present study. These compounds were taken from the literature with their experimental logarithmic BCF values (LogBCF$_{exp}$) fish species [30]. For the study, the 3D modeling and

geometry optimization of all the fifty-eight compounds were performed on workspace program, active document window of CAChe pro software of Fujitsu(www.CACheSoftware.com), using the B88-PW91 GGA energy function with the DZVP basis set [37-41]. The energies of excited electronic states were computed quantum mechanically. UV-visible spectrum for each compound was created by electron transition between molecular orbitals as electromagnetic radiation in the visible and ultraviolet (UV-visible) region is absorbed by the molecule. After obtaining approximate minimum energy structures, the UV-visible electronic transitions of the each compound were generated by a ZINDO configuration interaction. IR spectrum of transitions for each compound was created by co-ordinated motions of the atoms as electromagnetic radiation in the infrared region is absorbed by the molecule. The force necessary to distort the molecule was computed quantum mechanically from its equilibrium geometry and thus frequency of vibrational transitions was obtained [42].

3. Results and Discussion

The general chemical structure of PCBs [5] is based upon the skeleton of biphenyl, which containing one to ten atoms of chlorine and has 12 sites viz. 1,2,3,4,5,6,1',2',3',4',5' and 6'(Figure 1). The biphenyl and its fifty seven chloro-derivatives i.e. mono-, di-, tri, tetra-, penta-, hexa-, hepta-, nona- and decachlorobiphenyl are one, eight, four, ten, nine, twelve, six, five and one in number, respectively. Benzene shows three absorption bands at 184 nm (intense band, due to an allowed transition), 203.5 nm (weaker K-band, due to forbidden transition) and 254 nm (weaker B-band, also due to forbidden transition). When one of the hydrogen atoms of benzene (C_6H_5-H or Ph-H) is replaced by phenyl group, then we get biphenyl molecule (C_6H_5-C_6H_5 or Ph-Ph). Although biphenyl is symmetrical molecule (dipole moment, μ =0 and dihedral angle between both ring planes through the interring bond = 0°), therefore, conjugation between the ring is not affected. Biphenyl thus shows a very intense absorption bands at 252 nm (K-band). Biphenyl derivative with chloro substitutions in ortho positions are more stable in twisted conformations (compound no. 11, 15-22, 25-29, 31, 32, 34-53, 46-58) than in planar conformation (compound no. 1-10, 12-14, 23, 24, 30, 33, 45 and 45). These suffer serious non-bonded compressions from the juxtaposed substitutions. The compounds with twisted conformations have HOMO-LUMO gap greater than 3.590 eV and their dihedral angle is also greater than 53.3°. While those having planar structures have HOMO-LUMO gap lower than 3.590 eV and their dihedral angle is either zero or equal to 1. To correlate the effect of number and position of chlorine atoms on UV-visible spectra, we have presented UV-visible spectra of all the compounds in Scheme 1. A close look at the scheme 1 also sports the loss of conjugation in the twisted conformations of compounds.
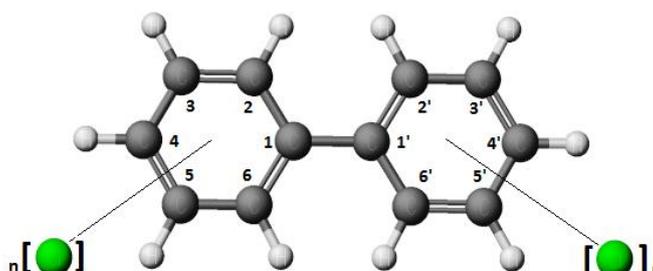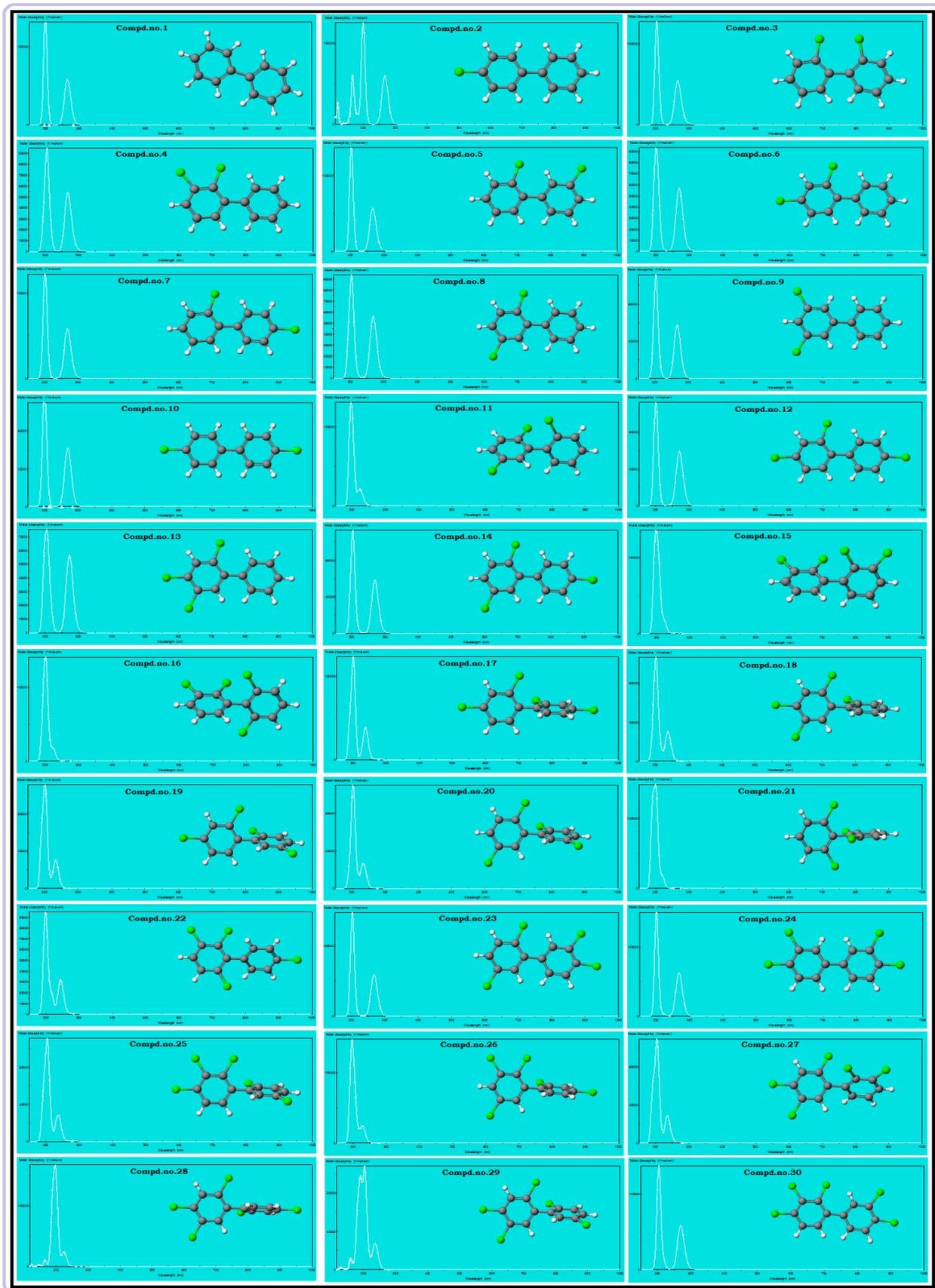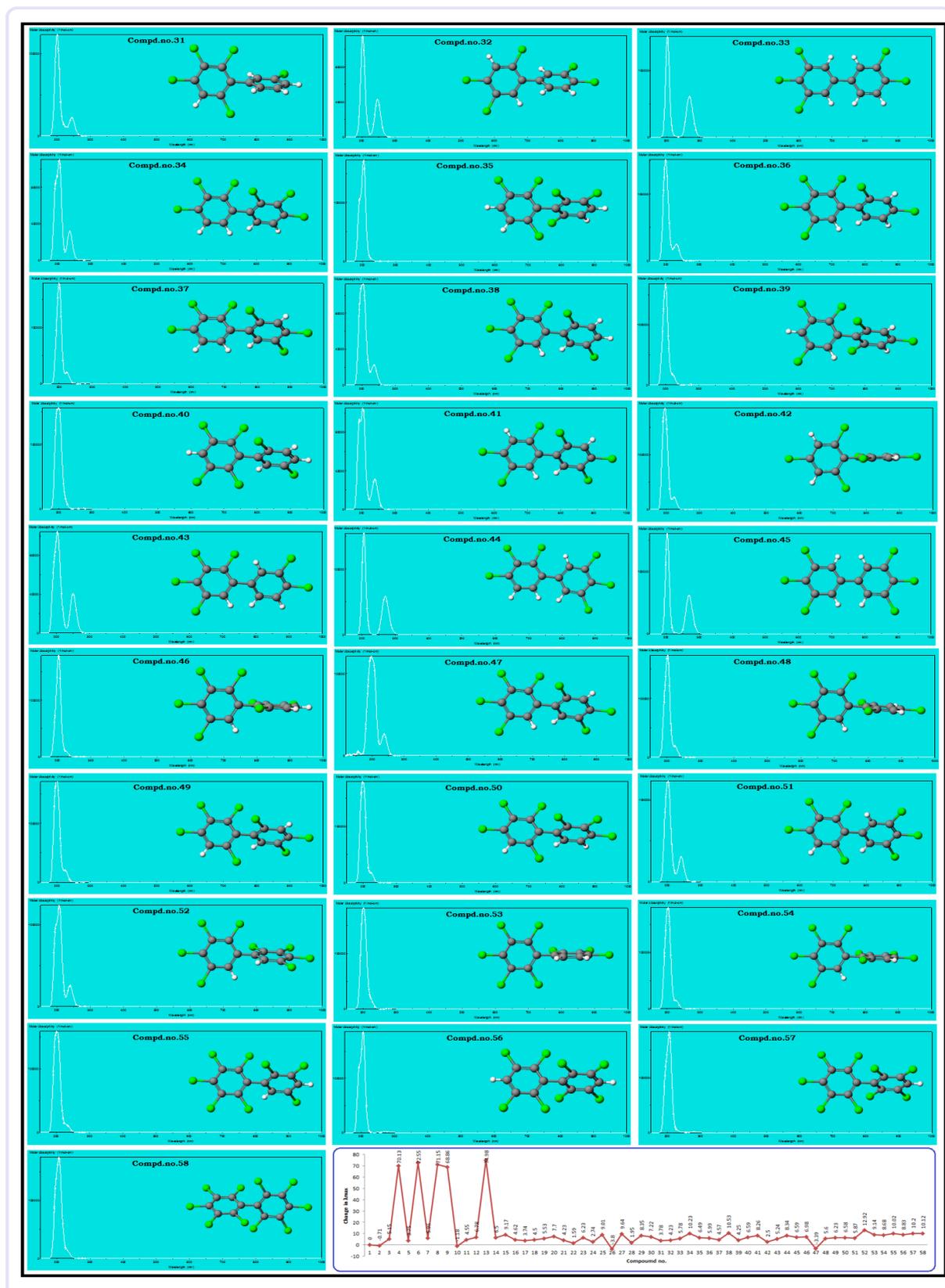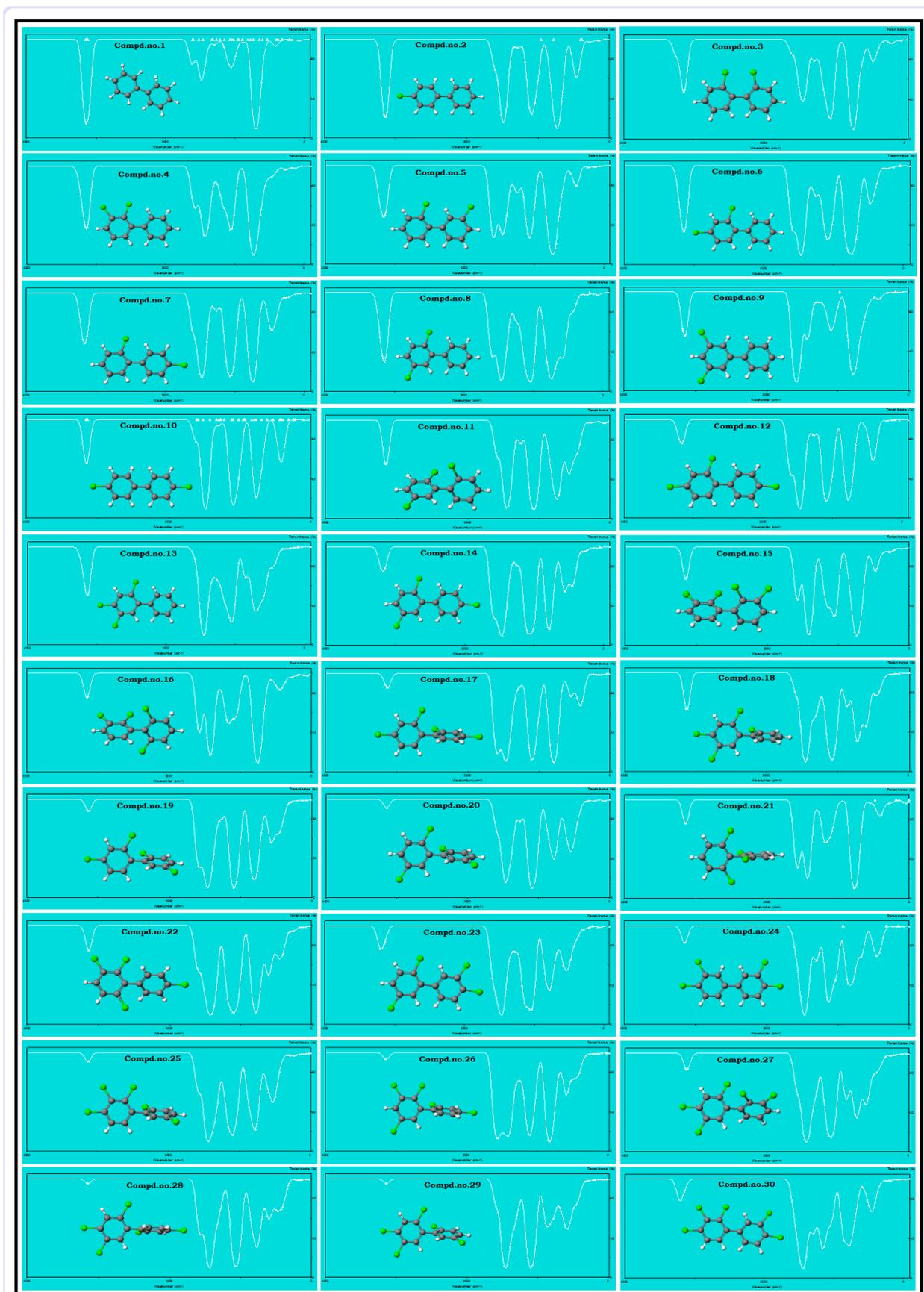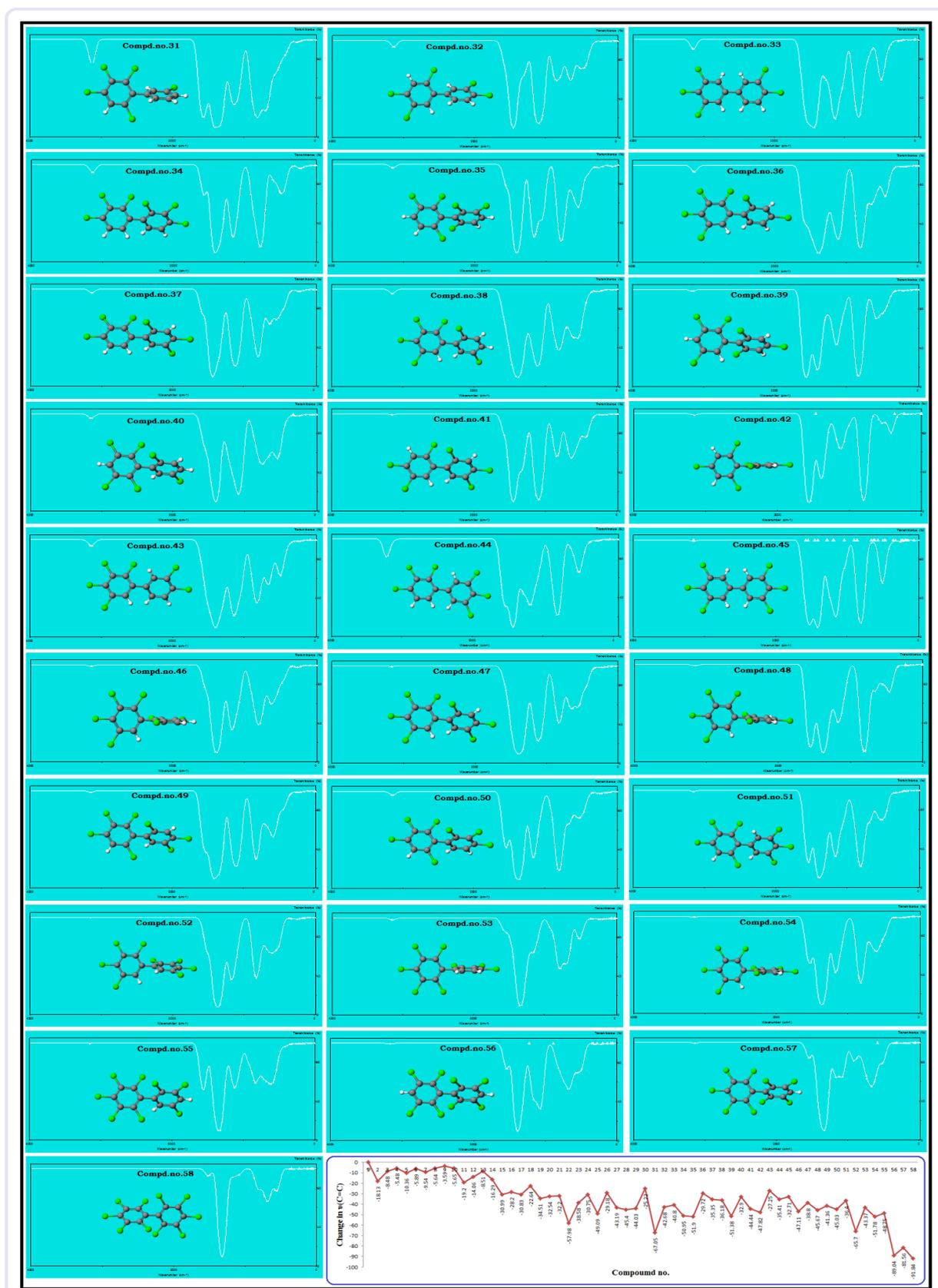

Figure 1. Structure of PCB

(a)

(b)

Scheme 1. (a) UV-visible spectra of compound no. 1-30; (b) UV-visible spectra of compound no. 31-58

(a)

(b)

Scheme 2. (a) IR spectra of compound no. 1-30; (b) IR spectra of compound no. 31-58

The calculated vibrational spectrum has proved to be a powerful tool to investigate changes in molecular aggregation, orientation, and structure at the level of functional groups [42]. Biphenyl and PCBs in the ground state have 60 fundamentals with various symmetries. Since almost all the vibrational modes are delocalized over whole molecule, they cannot be ascribed to several local vibrational motions. These are (IR tors), (IR str + R ip def), (R oop def), (R ip def + IR str + CC str), (CH oop bend), (R ip def), (CC str), (CH ip bend), (IR str + CH ip bend), (CC str + R ip def) and (CH str). This is the characteristic feature of aromatic compounds. For comparative study the IR spectra of all the compounds are placed in scheme 2. Among the above modes, we have extracted CC str + R ip def i.e. υ(C=C) and CH str i.e. υ(C-H) for correlation with BCF and are tabulated in Table 2.

Table 2. Calculated HOMO-LUMO gap, λ_{max} from UV-visible spectra and frequencies from IR spectra, experimental BCF and predicted BCF of PCBs

S.N.	[a]μ	Dihedral Angle (°)	HOMO-LUMO gap	λ_{max} (nm)	υ(C=C)	υ(C-H)	LogBCF$_{exp}$	LogBCF$_{pre}$
1	0	00.0	3.575	197.10	1624.70	3140.04	2.64	3.68
2	2.005	00.1	3.434	196.39	1606.57	3145.50	2.77	4.26
3	3.141	01.0	3.382	202.25	1616.22	3140.76	3.38	3.96
4	2.667	00.0	3.502	267.23	1619.22	3130.48	4.11	3.96
5	3.442	00.0	3.498	200.85	1614.34	3140.96	3.80	4.02
6	2.076	00.1	3.430	269.65	1618.81	3140.01	3.55	3.98
7	2.713	00.1	3.407	203.06	1615.16	3149.25	3.57	3.99
8	0.789	00.1	3.485	268.25	1619.06	3131.92	3.89	3.97
9	2.414	00.1	3.523	265.96	1621.11	3147.59	3.78	3.90
10	0	00.1	3.308	195.92	1619.05	3145.20	3.28	3.86
11	1.770	79.5	4.141	201.65	1605.50	3146.56	4.11	4.30
12	1.295	00.1	3.291	203.88	1610.64	3149.07	4.20	4.14
13	2.200	00.2	3.385	272.08	1616.19	3128.25	4.26	4.06
14	1.168	00.2	3.346	203.60	1608.41	3148.91	4.23	4.21
15	3.668	79.6	4.235	206.27	1593.71	3147.98	4.23	4.68
16	2.875	82.2	4.214	201.72	1596.50	3144.20	4.84	4.59
17	2.024	66.5	3.935	200.84	1593.87	3140.01	4.85	4.67
18	2.845	67.6	3.929	201.60	1602.06	3135.16	5.00	4.41
19	1.376	69.9	3.931	202.63	1590.19	3148.04	4.84	4.79
20	0.409	66.6	3.857	204.80	1592.16	3149.73	4.63	4.73
21	0.011	88.7	4.382	201.33	1592.50	3136.28	3.85	4.71
22	2.050	61.5	3.777	198.69	1566.72	3140.25	4.60	5.54
23	2.204	01.3	3.312	203.33	1586.12	3138.84	4.77	4.92
24	2.542	00.3	3.250	199.84	1593.95	3141.00	4.59	4.67
25	2.311	66.9	3.801	206.11	1575.61	3137.76	5.38	5.26
26	1.611	76.7	4.000	193.30	1595.52	3147.36	5.00	4.61
27	2.648	68.5	3.882	206.74	1581.51	3144.25	5.43	5.07
28	1.309	82.9	3.844	199.05	1579.30	3136.62	5.00	5.13
29	1.437	68.6	3.844	205.45	1580.67	3147.31	5.40	5.10
30	3.152	00.1	3.224	204.32	1599.48	3140.77	5.00	4.50
31	1.993	66.5	3.827	200.88	1557.65	3139.70	5.00	5.83
32	1.282	54.2	3.644	201.33	1582.02	3142.06	5.00	5.05
33	1.412	00.3	3.236	202.88	1583.90	3145.88	5.81	4.99

34	3.269	68.7	3.880	207.33	1573.75	3145.81	5.77	5.32
35	1.453	89.5	4.092	203.59	1572.80	3138.16	5.43	5.35
36*	1.928	77.5	3.971	203.09	1594.98	3149.85	5.88	4.64
37*	1.997	89.4	4.065	201.67	1589.35	3145.27	5.39	4.82
38*	2.049	70.7	3.801	207.63	1588.52	3144.43	5.81	4.85
39*	1.073	86.7	4.041	201.35	1573.32	3151.80	5.39	5.33
40*	0.472	89.7	3.919	203.69	1591.80	3150.06	5.54	4.74
41*	0.156	67.1	3.764	205.36	1580.26	3147.60	5.65	5.11
42*	0.004	88.6	4.382	199.60	1576.88	3154.16	4.93	5.21
43*	1.712	53.3	3.592	202.34	1597.45	3156.12	5.39	4.56
44*	2.096	01.1	3.218	205.44	1589.29	3141.73	5.39	4.82
45*	0.002	00.1	3.218	203.69	1591.99	3148.28	5.97	4.73
46	2.751	88.7	4.060	204.08	1577.59	3147.04	5.80	5.20
47	0.839	71.0	3.782	193.71	1585.90	3156.23	5.80	4.91
48	1.823	88.5	4.057	202.70	1579.03	3146.02	5.80	5.15
49	0.933	86.3	3.941	203.33	1583.34	3140.42	5.84	5.01
50	2.193	89.0	4.114	203.68	1579.67	3158.18	5.80	5.13
51	1.833	66.1	3.753	202.97	1588.30	3145.37	5.84	4.85
52	1.101	69.4	3.744	210.02	1559.00	3145.42	5.81	5.80
53	1.956	88.7	3.995	206.24	1581.33	3142.83	5.92	5.08
54	1.529	85.5	3.961	205.78	1572.92	3144.99	5.92	5.35
55	0.875	79.2	3.782	207.12	1575.95	3149.12	5.88	5.25
56	0.002	89.8	3.937	205.93	1535.66	3167.46	5.82	6.54
57	0.915	87.1	3.866	207.30	1543.14	3146.68	5.71	6.30
58	0.006	82.2	3.791	207.22	1532.86	0.00	5.44	6.63

[a]Dipole moment of the compound, *compounds involved in test set

To correlate BCFs of the compounds with UV- and IR spectral data, we have performed multiple linear regression (MLR) analysis. For this electronic spectral data and vibration frequencies were used as independent variables and the experimental BCFs of the compounds as dependent variables. To test the predictive ability of the model, we have performed external cross validation model with leave-ten-out (L_{10O}) technique, where ten compounds are removed at a time and a number of models were generated and among them following model was found reliable.

$$\log BCF_{pre} = -0.0319944 \times \upsilon(C=C) + 0.00151573 \times \lambda_{max} + 55.3602$$

$R^2_{L10O} = 0.650$, $R^2_{adj} = 0.642$, se = 0.60, F = 111.86, $q^2_{L10O} = 0.535$

where $\upsilon(C=C)$ is the first descriptor and λ_{max} is the second descriptors. $\upsilon(C=C)$ has negative descriptor coefficient magnitudes that shows indirect relationship with BCF, while λ_{max} has positive descriptor coefficient magnitudes that shows direct relationship with BCF. The predicted BCF values as obtained from this model are also given in Table 2, while the trend of experimental and predicted BCF is shown in Figure 2.

Previously, we have also predicted the BCF of these compounds using DFT-method and the descriptors used were atomic in nature viz., partial atomic charges and HOMO densities [43]. The values of above descriptors were calculated at twelve sites of PCBs. And the study reflected that partial atomic charges have more reliable predicting power than the HOMO densities. The ability of these models was r^2 between 0.645 and 0.916 for atomic charges and r^2 between 0.638 and 0.840 for HOMO densities. And the r^2_{CV} for these

models was 0.639 to 0.916 (atomic charge) and 0.614 to 0.693 (HOMO density). The s values for these models were 0.482 to 0.288 for atomic charges and 0.532 to 0.397 for HOMO densities. The reliable model with respect to atomic charge was:

$$logBCF_{pre}=1.65 \times Q_6 +3.82 \times Q_5 +3.56 \times Q_4 +4.68 \times Q_3 +4.326 \times Q_2 +0.425 \times Q_1 +1.25 \times Q_{5'} +7.78$$

$r^2 = 0.917$, $r^2_{CV} = 0.879$, $s = 0.270$, $n = 56$, $k = 7$

While, the reliable model with respect to HOMO density was:

$$logBCF_{pre}= -5.76 \times \varrho6H - 15.398 \times \varrho5H - 1.764 \times \varrho4H - 17.15 \times \varrho3H - 11.205 \times \varrho2H - 11.828 \times \varrho1'H - 21.27 \times \varrho2'H - 11.26 \times \varrho3'H - 12.95 \times \varrho6'H + 12.318$$

$r^2 = 0.902$, $r^2_{CV} = 0.837$, $s = 0.307$, $n = 52$, $k = 10$

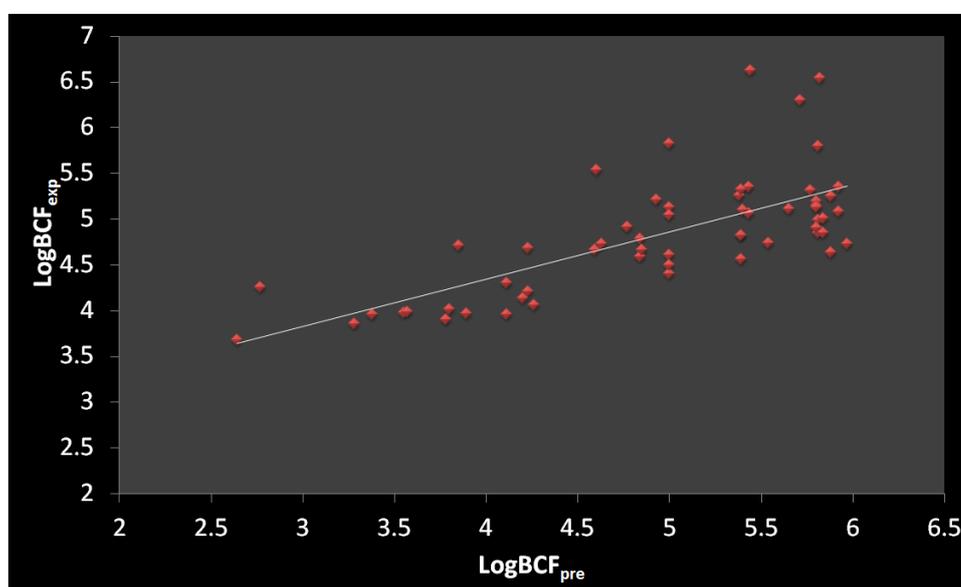**Figure 2.** Trends of experimental ($logBCF_{exp}$) and predected bioconcentration factors ($logBCF_{pre}$)

Further, we have also made DFT based prediction of BCF these compounds using molecular descriptors. The descriptors used were dipole moment (μ), ionization energy (IE), electron affinity (EA), electronegativity (χ), hardness (η), softness (S) and electrophilicity index (ω) [44]. Here, the study reflected that μ and IP are reliable descriptors for correlation of BCF of PCBs with their electronic structures. The resulted model as shown below has $r^2 = 0.914$, $r^2_{CV} = 0.898$, $s = 0.267$, $n = 52$, $k = 2$

$$logBCF_{pre}= 0.0319265 \times \mu +3.68314 \times IP -17.7294$$

A comparative study of these results shows that atomic and molecular properties are reliable descritors to predict the BCF of PCBs and can also made valuable contribution to descovered the methodology that help to degradate these persistants pollutants. While the spectroscopic data based descriptors help to find out the route and the mechanism that help to reduce the wealth and time for descovering the new pathway of the degradation of these persistant organic pollutants.

4. Conclusion:

On the basis of present study it has been concluded that DFT-based υ(C=C) and λ_{max} have sufficient reliability to relate the bioconcentration factors of polychlorinated biphenyls with their structures. Thus UV-visible and IR-spectroscopic properties can be used to predict BCFs of a large number of related compounds within limited time without any difficulty and help to find out the route and the mechanism that help to reduce the wealth and time for descovering the new pathway of the degradation of these persistant organic pollutants.

Acknowledgement

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