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A Simple Rule for Classification of Polychlorinated Dibenzo-*p*-dioxin Congeners on the Basis of IR Frequency Patterns

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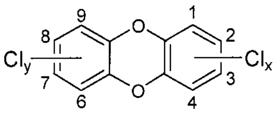
Abstract: The IR spectra of 76 dioxin congeners with zero to eight chlorines have been calculated by the DFT (B3LYP) method. Close inspection of the calculated spectra provides a simple rule for IR spectral analysis in polychlorinated dibenzo-*p*-dioxins (PCDDs). All congeners with a common structural motif of chlorine substitution in either of two benzene rings share the same main IR frequency, and the chlorination of one ring has little influence on the vibrational frequencies of the other ring. As a result, the main ring vibrational frequencies of all dioxin congeners could be classified into 10 groups according to the chlorine substitution pattern. This simplifies the complex IR spectral analysis of PCDDs to identifying two main peaks in essence, each of which corresponds to either of two chlorinated benzene rings. The systematic trend originates from the mass effect of the substituted chlorines. The C−H bending (in plane) character in the ring skeleton vibration mode is affected in quite different ways, depending on whether the chlorine is substituted on longitudinal or lateral positions. In particular, when all the lateral positions (2, 3, 7, 8) are chlorinated in PCDDs, the vibrational frequency of a b_{1u} mode (or its analogues in other symmetry) gives a characteristic IR peak around 1392 cm^{-1}. This peak is unique to all toxic congeners and could be used as an indicator for them.

Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) are among the most intensively studied persistent organic pollutants due to their extreme toxicity and widespread occurrence in the environment.[1] Public concerns centered around this toxic, persistent, and ubiquitous substance are accelerating. The structure of PCDDs shows that there are eight sites for chlorine substitution, allowing the PCDDs to be differentiated by both the substitution pattern and the degree of chlorination. The number of total congeners of PCDDs is 75: i.e., 2, 10, 14, 22, 14, 10, 2, and 1 for mono- to octachlorinated congeners, respectively.



Identification and quantification of 75 PCDD congeners found in environmental samples have been among the major themes in dioxin research since the toxicity of PCDDs is extremely congener-specific.[1,2] IR spectroscopic techniques have been commonly employed for this purpose because the IR spectra of dioxins were sensitively influenced by the chlorine substitution pattern.[3−6] However, IR spectral analyses on dioxins have been focused largely on fingerprint recognition of each congener and have been limited to tetrachlorinated dioxins (TCDDs) in many studies. How the vibrational frequencies of PCDDs are influenced by chlorine substitution patterns, and what the origin of IR frequency shifts among PCDDs is, are not well understood.

Experimental works dealing with dioxins are usually very complicated, laborious, and dangerous, which hinders the progress in this research field. Computational methods are well suited for dioxin research in this respect.[7−9] Furthermore, determination of vibrational spectra by ab initio computational methods has been used to identify unknown structures of experimentally observed molecular species and clusters.[10]

In this study, we employed DFT methods to calculate the IR spectra of 76 dioxin congeners with zero to eight chlorines and attempted a systematic analysis of the PCDDs. We propose here a simple rule for IR spectral analysis of PCDDs: (1) dioxin

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congeners with the same chlorine substitution pattern in either of two benzene rings share the same main IR frequency and (2) the chlorination of one ring has little influence on the vibrational frequencies of the other ring. As a result, a complex IR spectral analysis of PCDDs could be reduced to identifying two main peaks for two chlorinated benzene rings. The presence of a common IR peak that is unique to all toxic congeners is also suggested, and its origin is discussed.

Computational Methods

To investigate normal vibrational modes of PCDDs, we have carried out ab initio calculations at the level of hybrid Becke-3 Lee−Yang−Parr parameters (B3LYP) density functional theory with the 6-31G** basis set using the Gaussian 98 suite of programs.[11] The geometry optimizations were done, and the optimized geometries were characterized as local minima by harmonic vibrational frequency analysis. The equilibrium geometries of all the congeners were calculated to be planar at the above level of theory. The present predicted frequencies should be scaled in order to be directly compared to the experimental frequencies.[9,12] However, we have not carried this out because the experimental frequencies were method-dependent and not available for every congener. To understand the origin of frequency shifts, the normal coordinate calculations were carried out using the Wilson GF matrix method.[13] The internal coordinates were chosen in accordance with Pulay's recommendation.[14] For the approximate characterization of a vibration, we use the conventional potential energy distribution (PED) method obtained from the normal mode analysis.

Results and Discussion

The most intense IR peaks of PCDDs were calculated to be in the range of 1450−1550 cm^{-1}, and they are associated with aromatic ring skeleton vibrations. Figure 1 shows their variation among the selected congeners. It is well known that the chlorine substitutions on the lateral (i.e., 2, 3, 7, 8) vs longitudinal (i.e., 1, 4, 6, 9) positions have different effects on the toxicity. We find that they exhibit different effects on the IR frequencies as well. The thinner solid lines (two parallelograms) in Figure 1 show how the ring vibrational frequencies shift when the chlorines are substituted on the lateral or longitudinal positions: from **0** to **1234** and from **1234** to **12346789** congener. The frequency shift upon the longitudinal substitution is much greater than that upon the corresponding lateral substitution. Table 1 compares how much the ring vibrational frequencies shift upon the lateral vs longitudinal substitution: the frequency shifts accompanying the longitudinal substitution are more than twice those accompanying the lateral substitution in all cases.

The above characteristic IR bands in PCDDs correspond to the ring skeletal vibration mode ν_{19} (1494 cm^{-1}) in benzene, which is the IR-active degenerate e_{1u} mode.[15] Considerable potential energy of this mode is associated with C−H bending (in plane). In dibenzo-*p*-dioxin (**0**), the ether linkage lifts the degeneracy, and two IR-active bands (1512 (b_{1u}) and 1538 (b_{2u}) cm^{-1}) result. Normal-mode analysis for dibenzo-*p*-dioxin shows that the b_{1u} mode has no longitudinal but large lateral C−H bending character, while the b_{2u} mode has the opposite character (32% longitudinal vs 8% lateral C−H bending in the contribution to PED). The b_{1u} and b_{2u} normal vibrational modes of a dibenzo-*p*-dioxin molecule are compared in Figure 2. Due to the difference in C−H bending character, the frequency shift patterns in b_{1u} and b_{2u} modes show totally differently behavior upon longitudinal vs lateral chlorine substitutions. The b_{2u} and its analogous mode frequencies in PCDDs, which are compared in Figure 1 and Table 1, are more shifted upon the longitudinal substitution. On the other hand, b_{1u} frequencies are little affected upon the longitudinal substitutions but drastically lowered when all lateral chlorines are substituted to give a characteristic Group

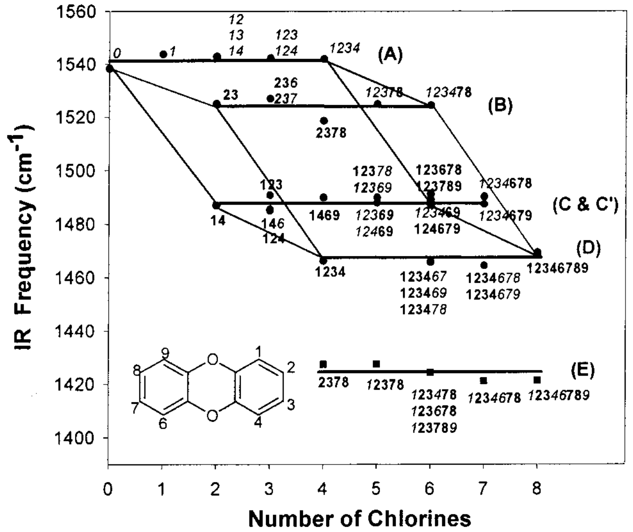

Figure 1. Selected main IR frequency groups (b_{2u} mode analogues, Groups A−D) of PCDDs. Group E (b_{1u} mode analogues) includes minor IR peaks that are unique to all toxic congeners. Each congener is represented by numbers representing the positions of chlorine substitution.

Table 1. Frequency Shifts ($\Delta\nu/cm^{-1}$) of the Main Ring Vibration Mode (b_{2u} Analogues) upon the Lateral vs Longitudinal Substitution of Chlorines

lateral substitution	$-\Delta\nu$	longitudinal substitution	$-\Delta\nu$
0 → 23	13.3	0 → 14	51.4
0 → 2378	19.8	0 → 1469	48.4
14 → 1234	20.7	23 → 1234	58.8
1469 → 123469	27.1	2378 → 123478	55.9
1234 → 123478	17.4	1234 → 123469	54.6
123469 → 12346789	17.9	123478 → 12346789	55.1
1469 → 12346789	20.6	2378 → 12346789	49.3

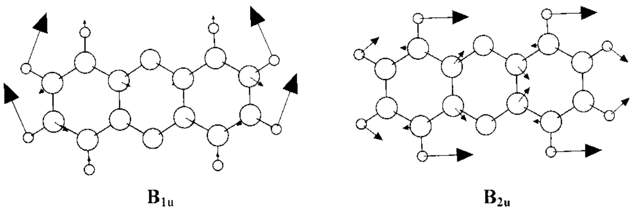
B_{1u} B_{2u}

Figure 2. The b_{1u} and b_{2u} normal vibrational modes of a dibenzo-*p*-dioxin molecule.

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E peak (Figure 1). As for the origin of the frequency shift, we considered both mass and force field effect and found mass effect more clearly explained it. In accordance with the mass effect, we could observe a similar IR frequency shift pattern in deuterated dibenzo-*p*-dioxin. The IR frequency shift patterns in 2378-TDDD and 1469-TDDD (tetradeuterated dibenzo-*p*-dioxin) showed the same behavior as those in 2378-TCDD and 1469-TCDD.

The calculated main IR frequencies and intensities (b_{2u} mode analogues) are summarized in Table 2 for 32 of the 76 congeners. As a result of the chlorine position-dependent frequency shift, the ring vibrational frequencies of all congeners could be classified into 10 groups according to their common motifs of chlorine substitution. Dioxin congeners in the same group have the same geometric chlorine substitution in either of two rings and share a common vibrational frequency. All 76 congeners calculated in this study could be grouped in the same manner without a single exception (see Supporting Information for details). The experimental FT-IR spectra of dioxins that were measured in the vapor phase by Grainger et al.[5] showed the same patterns. The main IR frequency of one ring was little affected by the chlorine substitution pattern of the other ring, which makes the IR analysis much simpler: two main peaks corresponding to two benzene rings, respectively. However, when the chlorine substitution pattern is symmetric against a plane of reflection or a center of inversion (e.g., **27**, **28**, **2378**, **1469**, **123678**, **123789**, **124679**, **12346789**), the ring vibration modes show a strong in-phase coupling of the three-ring systems to give a single intense peak. According to this rule, all 16 dioxin congeners with symmetry (out of 76) show a single main peak. It should also be noted that congeners with lateral chlorines only (e.g., **2**, **23**, **237**, **2378**) tend to have a coupled vibrational frequency: the congener **2** has a strong peak at 1533.6 cm^{-1} (792 km/mol) for the monosubstituted ring component, while its counterpart for the unsubstituted ring component has very weak intensity (39 km/mol). The same tendency is found in **23**, **237**, and **2378** congeners.

Selected IR peak groups of interests are plotted in Figure 1. Group A peaks imply the presence of an unsubstituted ring: all corresponding congeners have four or fewer chlorines and are nontoxic. Group D peaks indicate that either of two rings is fully chlorinated: all corresponding congeners have four or more chlorines. Since dioxin congeners that have chlorines on the 2,3,7,8-positions (7 of the 76 congeners) show significant toxicity, IR peaks indicating their presence are of great importance. The presence of Group B or C peaks is a necessary condition for toxic congeners. However, Group C peaks are hard to differentiate from Group C′ that comprises nontoxic congeners. In this respect, Group E peaks are very informative since they are unique in seven toxic congeners. Although they are not primary peaks of high intensity, experimental vapor-phase FT-IR spectra[5] and matrix isolation FT-IR spectra[6] for all 2,3,7,8-substituted congeners clearly showed their presence at 1392 ± 1 and 1401 ± 2 cm^{-1}, respectively. We propose using this peak as an indicator for the presence of toxic congeners. The development of a sensitive IR monitoring technique could give a rough quantification of the total toxic congeners in a mixed sample by simply measuring the absorbance in this frequency region.

Table 2. B3LYP/6-31G** Predicted Harmonic Vibrational Frequencies (cm^{-1}) and Their IR Intensities (km/mol) for Dioxin Congeners Grouped by a Common Motif of Chlorine Substitution

Congener Group		Congener	Calculated (mode) Freq./Int.	Exp.[a] Freq.
0		0	(b_{2u}) 1538.3/668	1489
		1	(a') 1543.6/244	
(unsubstituted ring)		2	(a') 1545.4/39	
		12	(a') 1542.8/255	
		13	(a') 1542.3/262	
		14	(a_1) 1542.7/293	
Group **A**		23	(a_1) 1543.1/142	1489
		123	(a') 1542.3/314	1493
		124	(a') 1542.2/299	1496
		1234	(a_1) 1541.8/351	
2		**2**	(a') 1533.7/792	1489
		1**7**	(a') 1536.5/317	
		27	(b_u) 1530.0/1008	1484
		28	(b_2) 1529.5/996	1485
		137	(a') 1535.2/335	
		237	(a') 1536.9/95	1486
23		**23**	(a_1) 1525.0/816	1478
		236	(a') 1526.9/335	
		237	(a') 1523.0/1053	1470
Group **B**		**2378**	(b_{2u}) 1518.6/1299	1465
		123**78**	(a') 1524.8/493	1471
		1234**78**	(a_1) 1524.4/586	1472
1		**1**	(a') 1517.4/348	
		17	(a') 1514.8/555	
		14**6**	(a') 1516.5/319	
		23**6**	(a') 1513.1/650	
13		**13**	(a') 1513.9/487	
		137	(a') 1510.7/712	
		12**79**	(a') 1512.1/197	
12		**12**	(a') 1505.8/348	
		1279	(a') 1503.2/893	
		1234**67**	(a') 1504.3/585	
123		**123**	(a') 1490.7/615	1446
		12378	(a') 1489.8/868	1447
		12369	(a') 1490.1/849	
Group **C**		**123678**	(b_u) 1491.2/1364	1445
		123789	(b_2) 1487.0/1399	1445
		1234**678**	(a') 1490.2/753	1451
14	Group **C′**	**14**	(a_1) 1486.9/597	
		146	(a') 1485.0/390	
		1469	(b_{2u}) 1489.9/1032	
		123**69**	(a') 1484.7/268	
		12**469**	(a') 1487.9/1105	
		123**469**	(a_1) 1487.2/848	
124		**124**	(a') 1485.4/635	1446
		124679	(b_u) 1489.0/1136	
		1234**679**	(a') 1487.3/783	
1234		**1234**	(a_1) 1466.2/825	
		123467	(a') 1465.8/764	
(fully chlorinated ring)		**1234**69	(a_1) 1462.7/449	
		123478	(a_1) 1462.8/950	1423
Group **D**		**1234**678	(a') 1462.8/764	1422
		1234679	(a') 1464.5/740	
		12346789	(b_{2u}) 1469.3/1577	1424
2378-substituted		**2378**	(b_{1u}) 1427.4/32	1391
		1**2378**	(a') 1423.7/91	1394
(all toxic congeners)		1**23**4**78**	(b_2) 1424.3/101	*b*
		1**23**6**78**	(b_u) 1421.1/210	1392
		1**2378**9	(a_1) 1422.4/94	1391
Group **E**[c]		1**23**46**78**	(a') 1421.2/169	1392
		1**23**46**78**9	(b_{1u}) 1421.4/207	*b*

[a] The experimental IR frequencies were taken from ref 5, which provided vapor-phase FT-IR spectra of 15 dioxin congeners. [b] Not resolved as a peak but present as a shoulder around 1392 cm^{-1}. [c] Group E corresponds to a ring vibration normal mode that is different from the above 10 groups.

Much interest has been directed to the development of efficient and simple methods for dioxin congener differentiation. In this study, we show that the main IR peaks of all dioxin congeners could be classified into 10 groups according to their common structural motifs of chlorine substitution and propose an indicator IR peak for toxic dioxin congeners. The present results could be a useful basis for dioxin congener classification using IR spectral analysis. Further experimental FT-IR studies confirming this rule are called for.

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Supporting Information Available: Tables of IR frequencies and intensities for 76 dioxin congeners (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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