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Identification of Isomers from Calculated Vibrational Spectra. A Density Functional Study of Tetrachlorinated Dibenzodioxins

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Abstract: The vibrational spectra of four tetrachlorinated *p*-dibenzodioxins (the 2,3,7,8-, 1,4,6,9-, 1,3,7,8-, and 1,4,7,8-isomers) have been investigated by the scaled quantum mechanical (SQM) method, using quadratic force fields from density functional theory and scale factors transferred from related molecules. This *a priori* (though not fully *ab initio*) method reproduces the experimental infrared spectra, including intensities, very well. It is possible to identify an unknown isomer conclusively by its calculated spectrum, an important point in view of the strong isomer dependence of toxicity. The most toxic 2,3,7,8-isomer shows band doublings for three prominent infrared bands which do not appear in our harmonic calculations, even when the effect of the large-amplitude butterfly vibration ($D_{2h} \rightarrow C_{2v}$) and natural-abundance ^{13}C isotope effects are considered. The extra bands are probably not fundamentals but combination bands in Fermi resonance with strong fundamentals. All fundamentals, including the infrared inactive ones, are predicted and assigned.

Introduction

Experimental investigations of polychlorinated dibenzodioxin isomers and related compounds (e.g. dibenzofurans) are difficult because of the extreme toxicity of these substances (see e.g. ref 1). This is, however, the reason for much interest in these notorious environmental pollutants, in particular the tetrachlorinated dibenzodioxins (TCDDs). Gas chromatographic separation followed by Fourier transform infrared spectroscopy (GC/FT-IR) is an important analytical method for this class of compounds because it can readily distinguish isomers, although its sensitivity is lower than that of mass spectrometry. Isomer differentiation is essential in view of the strong isomer dependence of toxicity.[1,2] The infrared spectra of a number of polychlorinated dibenzodioxins have been measured[3–7] in the gas phase, by diffuse reflectance spectroscopy (DRIFT), and in rare gas matrices. DRIFT spectroscopy, while very sensitive, has a high noise level, and therefore we compare our results with the excellent matrix isolation Fourier transform infrared (MI/FT-IR) spectra of Gurka and co-workers.[5] An empirical assignment[6] of the more important bands has also been attempted by Grainger, although this is difficult for these compounds because of strong kinematic and dynamic couplings between the degrees of freedom.

Recently we have used the Scaled Quantum Mechanical (SQM)[8] force field method applied to harmonic force fields evaluated by density functional theory (DFT) to calculate the spectra of a set of 31 organic molecules.[9] We could reproduce the experimental vibrational frequencies and infrared intensities very well using a nonlocal exchange-correlation functional[10] in the DFT program[11] in combination with the 6-31G(d) basis set[12] and the SQM method. In our previous paper[9] we have established a set of 11 transferable scaling factors for the most important organic structural motifs. These empirical factors minimize the error between the experimental and the calculated harmonic frequencies, correcting for the approximate treatment of electron correlation, for basis set deficiencies, and for anharmonicity. Transferable in this context means that the same set of scaling factors can be used for analogous internal coordinates in different molecules. The scaling factors are established from smaller, well-characterized molecules (the training set) and are transferred to larger molecules. In the present work we have extended this set of scaling factors to chlorinated compounds. It was necessary to introduce a new factor for the C−Cl stretching motion. In the present work we compare the theoretical infrared spectra of four TCDDs [2,3,7,8-TCDD (**1**), 1,4,6,9-TCDD (**2**), 1,3,7,8-TCDD (**3**), and 1,4,7,8-TCDD (**4**)] with experiment and demonstrate that the calculations are sufficiently accurate to distinguish readily different isomers, in spite of the general similarity of the spectra. We are thus in the position to identify isomers, including those not yet characterized experimentally, solely on the basis of the calculated spectra. We also assign all fundamentals and consider the effect of the large-amplitude butterfly vibration on the spectra, as well as the effects of ^{13}C and the deuterium isotope.

Methods

All calculations presented here were obtained using the 6-31G(d) basis set[12] and Becke's nonlocal three-parameter exchange and correlation functional[10] in conjunction with the Lee−Yang−Parr correlation

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[⊗] Abstract published in *Advance ACS Abstracts,* April 1, 1995.

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Table 1. Scaling Factors for the Different Types of Internal Coordinates

no.	mode	scaling factor
1	X−Y[a] stretching	0.922
2	X−Cl stretching	1.017
3	X−H stretching	0.920
4	XYZ bending	0.990
5	XY−H bending	0.950
6	out-of-plane modes	0.976
7	torsions	0.831

[a] X, Y, Z denote C or O atoms.

functional[13] (B3-LYP) as implemented in the latest version of the Gaussian suite of program.[11] An outstanding feature of the latter is the availability of analytical first and second derivatives for density functional wave functions. The Cartesian force constants and dipole moment derivatives obtained from the DFT calculation are transformed to natural internal coordinates[14] and the force constants are scaled with fixed scaling factors transferred from the training set. This method reproduces vibrational frequencies in the fingerprint region within 2%; the average error is usually less. The C−Cl stretchings had to be added as a new scaling factor because they scale differently from stretchings between first-row atoms. This parameter was obtained from fitting the experimental vibrational fundamentals of 1,1-dichloroethene, all four isomers of 1,4-dichloro-*trans*-butadiene, chlorobenzene, and *o*- and *m*-dichlorobenzene and found to be 1.017. The relevant scaling factors, taken from our previous paper,[9] are summarized in Table 1. All calculations were carried out on workstations. The CPU times, while considerable, are still reasonable, e.g. 5 days on an IBM RS6000 Model 390 workstation for the asymmetrical isomers **3** and **4** and significantly less for the symmetrical isomers **1** and **2**. It is clear, however, that the ultimate goal of such calculations should be to parametrize the scaled DFT force field so that the spectra of analogous molecules could be predicted with minimum computational effort.

Results

(a) Geometries. The calculated equilibrium geometries of all these molecules are planar, both at the Hartree−Fock level for the parent dibenzodioxin[15] and also at the DFT level for all chloro derivatives. This agrees with the X-ray[16] structure of **1**, which is essentially planar. Nevertheless, the central ring is quite flexible and easily deforms to butterfly-shaped conformations along the O ··· O line. Our calculated harmonic vibrational frequencies for these motions are very low, between 19 and 29 cm^{-1}. The twisting of the central ring is also a low-energy process, but the normal frequencies are higher, between 39 and 48 cm^{-1}. There has been considerable discussion about the molecular geometry of TCDD isomers and its relation to toxicity.[7]

The most important geometrical parameters for the two symmetrical (D_{2h}) isomers **1** and **2** are given in Table 2 (for the numbering of the atoms see Figure 1). Agreement with the X-ray structure[16] is excellent for the C−O distance, but the other bonds, especially *r*(C−Cl), are slightly too long. The effect of this slight geometry error can be absorbed in the scaling factors, and it is likely to be responsible for the high value of the C−Cl stretching scaling factor. Agreement of the C−O−C bond angle with the values derived by Grainger *et al.*[7] from a simple triatomic model for the vibrational frequencies is poor for isomer **2**, casting doubt on the validity of their model. Without zero-point energy correction the 2,3,7,8 isomer is 2.65 kcal/mol more stable than the 1,4,6,9 isomer.

Table 2. Geometrical Parameters for 2,3,7,8- and 1,4,6,9-TCDD (Bond Lengths in Å, Bond Angles in deg)

no.	geometrical parameter	2,3,7,8-TCDD	X-ray for 2,3,7,8[a]	1,4,6,9-TCDD
1.	*r*(C−O)	1.3783	1.378	1.3737
2.	*r*(C−H)	1.0837	(1.01)	1.0840
3.	*r*(C−Cl)	1.7448	1.728	1.7443
4.	*r*(C_1−C_2)	1.3979	1.382	1.3960
5.	*r*(C_2−C_3)	1.3996	1.388	1.3909
6.	*r*(C_9−C_{10})	1.3869	1.376	1.3952
7.	*r*(C_{10}−C_{11})	1.3990	1.387	1.3995
8.	∠(C−O−C)	116.14	115.56	117.17
9.	∠(X^b−C_1−C_2)	120.57	120.00	120.36
10.	∠(X^b−C_2−C_3)	121.77	121.21	120.58

[a] Taken from ref 16. The average of the two molecules in the unit cell is given, averaged to give D_{2h} symmetry. [b] X can be either H or Cl.

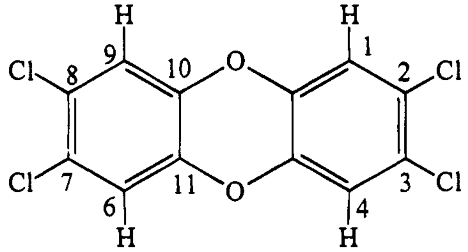

Figure 1. The numbering of the *p*-dibenzodioxin skeleton shown for 2,3,7,8-TCDD.

(b) Frequencies of Planar Structures. The harmonic frequencies and calculated infrared intensities of the two D_{2h} isomers **1** and **2** are given in Table 3 and those of the less symmetrical (C_s) isomers **3** and **4** are given in Table 4. The infrared spectra of these compounds are dominated by an extremely strong band (or a cluster of strong bands in the less symmetrical isomers) near 1500 cm^{-1}. The intensity of this band is remarkable, over 1200 km/mol in **1**. The approximate form of this normal vibration in 2,3,7,8-TCDD is shown in Figure 2. The unusual high intensity of this band can be explained by a strong in-phase coupling of the three-ring systems. Figures 3−6 compare the simulated spectra of **1** to **4** with the experimental matrix isolation FT-IR spectra.[5] Spectra recorded in the gas phase[6,7] and by diffuse reflectance,[5] while similar, are in general of lower quality. The general level of agreement between the theoretical and experimental spectra is striking in view of the *a priori* character of our calculations (i.e. no experimental data on benzodioxines were used) and the fact that the bandwidth used in our simulated spectra are crude estimates only. Small systematic deviations in the frequencies are readily discernible and could be eliminated by slight tuning of the scaling factors. We have not chosen to do so in the present work. We plan, however, to establish a transferable *parametrized* force field for these molecules. In this project we plan to rescale the force field slightly to improve agreement with experiment.

The obvious correlation of the theoretical and experimental spectra allows the assignment of a number of experimental bands to theoretical fundamentals and the indirect establishment of the symmetry and the approximate vibrational character of the latter. As mentioned in the Introduction, many of the skeletal vibrations are extremely mixed, and thus the identification of normal vibrations with specific internal modes is difficult in the more symmetric isomers **1** and **2** and is virtually impossible in the less symmetric isomers **3** and **4**. We have based our assignment on the Total Energy Distribution (M matrix) technique.[17] We were able to identify weaker bands which were not listed in the tables of ref 5 but which are evident in the

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Table 3. Vibrational Frequencies (cm^{-1}) and IR Intensities (km/mol) for the Planar D_{2h} Structures of 2,3,7,8- and 1,4,6,9-TCDD (Orientation in Space According to IUPAC Conventions)[a]

	2,3,7,8-TCDD					1,4,6,9-TCDD				
no.	mode	IR	V_{calc}, cm^{-1}	int	ν_{exp}, cm^{-1}	mode	IR	δ_{calc}, cm^{-1}	int	ν_{exp}, cm^{-1}
1.	butterfly	B_{3u}	19.2	0.1		butterfly	B_{3u}	28.8	1.5	
2.	twist	A_u	48.0	0.0		twist	A_u	38.5	0.0	
3.	RT	B_{2g}	110.1	0.0		RT, CCl bop	B_{1g}	95.1	0.0	
4.	SV(CO), CCl bop	B_{1u}	110.8	0.1		RT, CCl bop	B_{3u}	98.6	1.3	
5.	CCl bop, RT	B_{1g}	134.3	0.0		RDef, CCl bip	B_{1u}	99.1	0.3	
6.	CCl bop, RT	B_{3u}	168.3	1.9		CCl bip	A_g	152.7	0.0	
7.	CCl bip	A_g	182.9	0.0		CCl bip, RDef	B_{3g}	174.4	0.0	
8.	CCl bip	B_{2u}	198.2	0.2		RT	B_{2g}	182.1	0.0	
9.	RT	A_u	216.4	0.0		CCl bip	B_{2u}	219.4	0.8	
10.	CCl bip, RDef	B_{3g}	227.5	0.0		iRT	B_{1g}	267.0	0.0	
11.	SV(CO), CCl st	A_g	253.8	0.0		iRT	B_{3u}	293.6	0.0	
12.	RT	B_{2g}	277.2	0.0		CCl bop	A_u	299.3	0.0	
13.	RDef, CCl bip	B_{1u}	326.3	0.1		CCl bop, RT	B_{2g}	308.9	0.0	
14.	iRT, CCl bop	B_{1g}	372.4	0.0		RDef, CCl st	A_g	330.5	0.0	
15.	iRT, CCl bop	B_{3u}	383.2	4.2		RDef, CCl st	B_{2u}	332.3	0.2	
16.	RDef, CCl str	B_{3g}	391.1	0.0		CCl bip, SV(CO)	B_{1u}	412.4	0.2	
17.	RT, iRT	B_{1g}	437.2	0.0		RDef, SV(CO)	A_g	431.5	0.0	
18.	RT, iRT	B_{3u}	444.5	3.1		RDef, CCl st bip	B_{3g}	443.6	0.0	
19.	CCl st, RDef	B_{2u}	445.1	16.6		RT	A_u	518.0	0.0	
20.	CCl st, RDef	B_{1u}	497.3	10.8		CCl st, RDef	B_{1u}	520.8	25.7	
21.	CCl bip, RDef	B_{3g}	538.1	0.0		RT	B_{2g}	521.8	0.0	
22.	RDef	A_g	555.5	0.0		CCl bop, iRT	B_{1g}	563.9	0.0	
23.	CCl bop, RT	B_{2g}	610.1	0.0		CCl bop, iRT	B_{3u}	565.8	16.9	
24.	CCl bop, RT	A_u	610.3	0.0		RDef	B_{3g}	579.6	0.0	
25.	RT	A_u	624.9	0.0		RDef, SV	A_g	609.0	0.0	
26.	RT	B_{3g}	642.1	0.0		CCl st, RDef	B_{3g}	646.5	0.0	
27.	RDef, CCl st	B_{2g}	648.1	0.0		RT	A_u	659.4	0.0	
28.	CCl st	A_g	661.2	0.0		RT	B_{2g}	669.1	0.0	
29.	RDef, CCl st	B_{2u}	686.3	16.5	864 (vw)	RDef, SV	B_{1u}	684.6	6.5	
30.	SV	A_g	740.8	0.0		SV, RDef	B_{2u}	706.1	0.1	
31.	RDef	B_{1u}	785.6	28.8	791 (w)	CH bop	B_{3u}	793.0	55.1	796 (w)
32.	CH bop	A_u	844.8	0.0		CH bop	B_{1g}	793.1	0.0	
33.	CH bop	B_{2g}	846.3	0.0		CCl st, SV(CO)	A_g	897.5	0.0	
34.	SV	B_{2u}	870.3	197.7	878 (s)	RDef, SV(CO)	B_{3g}	916.2	0.0	
35.	CH bop	B_{1g}	874.3	0.0		CH bop	B_{2g}	926.8	0.0	
36.	CH bop	B_{3u}	875.1	79.3	890 (vw)	CH bop	A_u	927.0	0.0	
37.	CCl st, RDef	B_{1u}	929.9	29.7	938 (w)	RDef, SV(CO)	B_{1u}	946.8	224.0	955 (m)
38.	RDef, Cl st	B_{3g}	985.7	0.0		SV, CCl st	B_{2u}	963.7	197.2	965 (m)
39.	CH bip, SV	B_{2u}	1107.5	246.5	1107 (m)	SV, CH bop	A_g	1127.0	0.0	
40.	CH bip, SV	A_g	1110.8	0.0	1117 (m)	SV, CH bop	B_{2u}	1128.6	0.9	
41.	SV(CO), RDef	B_{3g}	1153.4	0.0		RDef, SV	B_{3g}	1151.5	0.0	
42.	SV(CO), RDef	B_{1u}	1170.2	72.1	1176 (m)	RDef, SV	B_{1u}	1186.9	62.9	1196 (w)
43.	CH bip	B_{3g}	1218.5	0.0		SV, CH bip	A_g	1206.9	0.0	
44.	SV(CO)	A_g	1226.0	0.0		CH bip, SV	B_{1u}	1207.6	7.4	
45.	CH bip	B_{1u}	1233.9	17.3		SV(CO), RDef	B_{3g}	1224.1	0.0	
46.	SV	B_{2u}	1268.8	64.8	1270 (w)	SV	B_{2u}	1257.1	130.4	1262 (w)
47.	SV	A_g	1296.2	0.0		SV, CH bop	B_{2u}	1281.3	39.7	1287 (m)
48.	SV(CO)	B_{2u}	1303.6	454.0	1306 (s)	SV	A_g	1309.1	0.0	
49.	SV, RDef	B_{3g}	1358.3	0.0	1330 (m)	SV	A_g	1431.9	0.0	
50.	SV, RDef	B_{1u}	1387.1	31.6		SV	B_{2u}	1435.5	1009.2	1456 (vs)
51.	SV, CH bip	B_{2u}	1470.6	1220.8	1470 (vs)	SV, CH bip	B_{3g}	1448.8	0.0	
52.	SV, CH bip	A_g	1482.6	0.0	1488 (s)	SV, CH bip	B_{1u}	1472.0	129.8	1477 (m)
53.	SV	B_{2u}	1557.1	85.9	1576 (m)	SV	B_{3g}	1552.9	0.0	
54.	SV	B_{3g}	1574.3	0.0		SV, CH bop	B_{2u}	1566.5	35.7	1579 (w)
55.	SV	A_g	1595.0	0.0		SV, CH bop	A_g	1600.0	0.0	
56.	SV	B_{1u}	1629.4	3.6		SV, RDef	B_{1u}	1602.6	6.1	*1612 (vw)*
57.	CH st	B_{3g}	3106.7	0.0		CH st	B_{3g}	3094.4	0.0	
58.	CH st	B_{lu}	3106.9	2.6		CH st	B_{1u}	3094.5	0.4	
59.	CH st	B_{2u}	3108.0	1.2		CH st	A_g	3106.5	0.0	
60.	CH st	A_g	3108.2	0.0		CH st	B_{2u}	3106.5	0.7	

[a] Experimental frequencies are taken from Gurka *et al.*[5] or estimated from the figures given therein (values in italics). Experimental intensities are estimated from the spectra of the same authors (v = very, w = weak, m = medium, s = strong). The following abbreviations are used: bop = bending out of plane, bip = bending in plane; R = ring; T = torsion; i = inter; st = stretching; Def = Deformation; SV = Skeleton Vibration (SV(CO) is for instance a skeleton vibration with a main contribution in the CO bonds, SV only means an aromatic ring skeleton vibration or ring breathing).

matrix isolation spectra and obviously correspond to calculated fundamentals.

The most significant deviation between the theoretical and experimental results occurs for isomer **1**. Three prominent bands in the experimental infrared spectrum of **1**, near 1480, 1310, and 1110 cm^{-1}, are split in two components with a separation of 10–20 cm^{-1}. This splitting, in particular that of the extremely strong cluster near 1480 cm^{-1}, appears in all

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Table 4. Vibrational Frequencies (cm^{-1}) and IR Intensities (km/mol) for Planar 1,3,7,8- and 1,4,7,8-TCDD[a]

	1,3,7,8-TCDD				1,4,7,8-TCDD			
no.	IR	ν_{calc}, cm^{-1}	int	ν_{exp}, cm^{-1}	IR	ν_{calc}, cm^{-1}	int	ν_{exp}, cm^{-1}
1.	A″	19.8	0.0		A″	24.0	0.2	
2.	A″	46.1	0.0		A″	44.5	0.0	
3.	A′	105.1	0.0		A″	96.1	0.9	
4.	A″	119.4	0.1		A′	100.8	0.0	
5.	A″	120.6	0.1		A″	137.4	0.0	
6.	A′	140.8	0.0		A″	149.8	1.3	
7.	A″	158.4	1.7		A′	165.7	0.1	
8.	A′	192.3	0.3		A′	199.8	0.0	
9.	A″	198.3	0.1		A′	207.3	0.3	
10.	A′	213.6	0.2		A″	253.4	0.0	
11.	A″	220.0	0.2		A″	282.6	0.0	
12.	A′	262.6	0.0		A″	305.2	0.0	
13.	A′	333.2	0.2		A′	322.4	1.1	
14.	A″	343.4	0.1		A′	332.9	1.3	
15.	A″	378.1	2.0		A′	343.5	0.0	
16.	A′	396.1	5.6		A″	377.1	1.7	
17.	A′	418.9	0.5		A″	439.0	2.0	
18.	A″	439.7	1.8		A′	449.2	0.0	
19.	A′	469.1	8.8		A′	487.4	13.3	
20.	A″	523.3	0.3		A″	520.4	0.0	
21.	A′	535.9	0.2		A′	533.8	5.3	
22.	A′	559.8	2.9		A″	565.2	8.2	
23.	A″	560.2	1.4		A′	592.4	3.1	
24.	A′	571.4	4.1		A′	607.2	3.6	
25.	A″	610.0	0.0		A″	609.9	0.0	
26.	A″	630.5	0.1		A′	617.1	7.6	
27.	A″	656.3	0.8		A″	631.4	0.0	
28.	A′	663.6	1.2		A″	665.4	0.0	
29.	A′	666.1	4.3		A′	692.9	6.1	
30.	A′	745.3	3.9		A′	747.9	14.9	
31.	A′	818.1	127.5	840 (m)	A″	792.3	28.3	
32.	A″	843.5	32.4		A′	806.7	22.3	
33.	A″	846.6	3.0		A″	847.1	0.0	
34.	A′	853.0	34.0	849 (w)	A″	876.1	39.4	876 (w)
35.	A″	856.7	3.4		A′	924.1	65.9	932 (w)
36.	A″	875.6	39.9	870 (m)	A″	926.0	0.0	
37.	A′	933.1	84.9	953 (m)	A′	940.2	178.0	949 (m)
38.	A′	965.9	114.1	986 (m)	A′	966.8	61.3	*970 (w)*
39.	A′	1076.9	45.0	*1088 (vw)*	A′	1108.0	106.0	1113 (m)
40.	A′	1119.4	100.5	1114 (m)	A′	1127.4	3.2	
41.	A′	1152.9	35.2	*1164 (vw)*	A′	1150.6	84.1	1164 (m)
42.	A′	1182.3	25.9	1199 (w)	A′	1177.3	1.4	
43.	A′	1219.1	2.3		A′	1212.6	7.1	
44.	A′	1229.5	5.6		A′	1215.8	0.2	
45.	A′	1234.0	1.7		A′	1228.0	1.5	
46.	A′	1307.3	74.3		A′	1269.5	78.2	*1271 (w)*
47.	A′	1318.6	155.6	1309 (s)	A′	1289.4	210.5	1300 (s)
48.	A′	1330.1	7.7		A′	1302.6	3.1	
49.	A′	1366.4	8.0		A′	1369.8	8.7	
50.	A′	1407.4	118.0	1421 (s)	A′	1431.3	675.9	1451 (vs)
51.	A′	1477.2	877.7	1473 (vs)	A′	1461.2	78.2	1476 (s)
52.	A′	1494.1	436.6	1488 (s)	A′	1477.5	483.4	1493 (vs)
53.	A′	1589.6	99.5	1576 (m)	A′	1560.8	2.2	
54.	A′	1596.4	3.8		A′	1562.0	54.5	1577 (m)
55.	A′	1620.4	26.5	*1612 (vw)*	A′	1597.3	0.7	
56.	A′	1644.2	9.7		A′	1618.7	0.0	
57.	A′	3078.6	0.1		A′	3094.5	0.2	
58.	A′	3146.0	1.7		A′	3106.6	0.3	
59.	A′	3147.4	1.8		A′	3106.9	1.9	
60.	A′	3159.8	0.5		A′	3108.4	0.6	

[a] Experimental frequencies are taken from Gurka *et al.*[5] or estimated from the figures given therein (italicized values). Experimental intensities are estimated from the spectra of the same authors (v = very, w = weak, m = medium, s = strong).

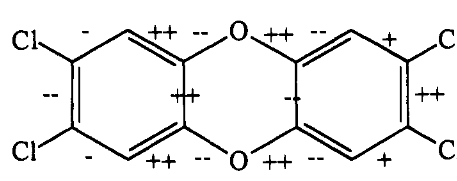

Figure 2. The approximate form of the intense normal vibration of 2,3,7,8-TCDD at 1470 cm^{-1} (calculated).

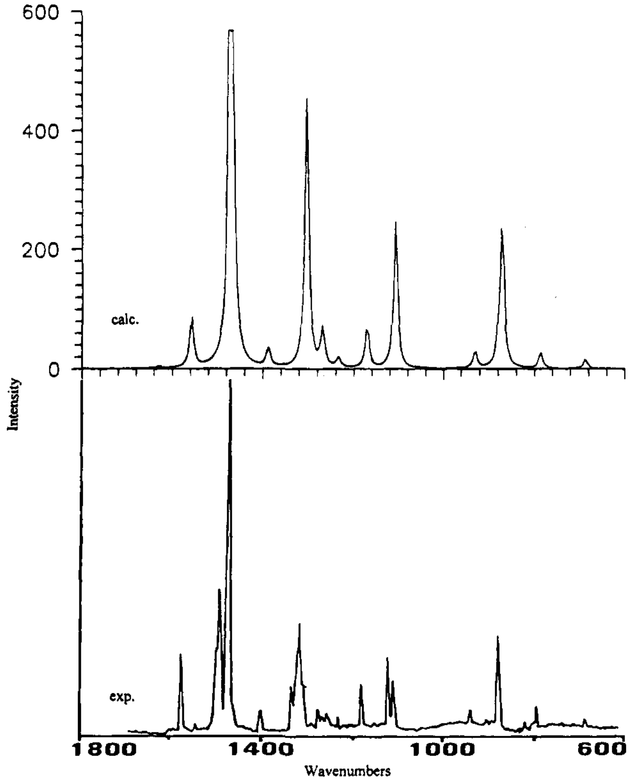

Figure 3. Comparison of the calculated and experimental (taken from ref 5) vibrational spectra of 2,3,7,8-TCDD. The calculations used a planar (D_{2h}) equilibrium geometry. Spectra are plotted as absorbances, scaled to correspond roughly with the experimental spectra. The absorbance scale in the calculated spectra corresponds to the band intensity in km/mol at the band maximum.

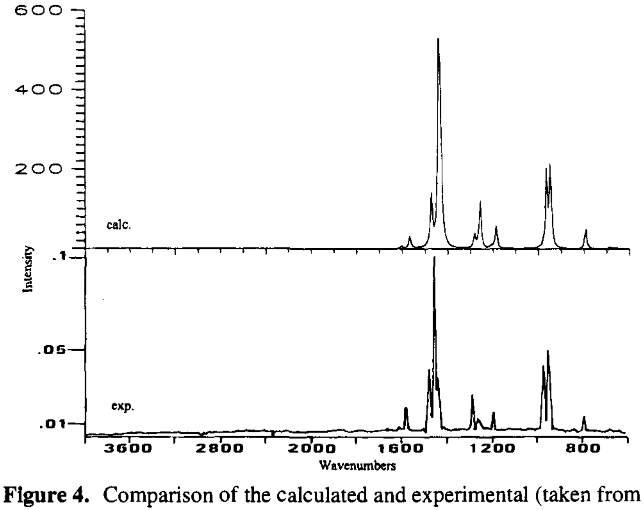

Figure 4. Comparison of the calculated and experimental (taken from ref 5) vibrational spectra of 1,4,6,9-TCDD. The calculations used a planar (D_{2h}) equilibrium geometry. See the caption for Figure 3.

spectra including gas-phase ones,[6,7] eliminating the possibility that it is caused by impurities, crystal field splitting, or other artifacts. According to Grainger *et al.*,[6] this splitting is characteristic of TCCD isomers of two or more β-chlorine atoms, with the exception of isomers containing two β-chlorines and two α-chlorines on different rings. For this reason we have calculated the spectra of 1,3,7,8- (**3**) and 1,4,7,8-TCDD (**4**), which indeed show the splitting of this dominant band. Due to the high symmetry of **1**, no other IR active bands are expected

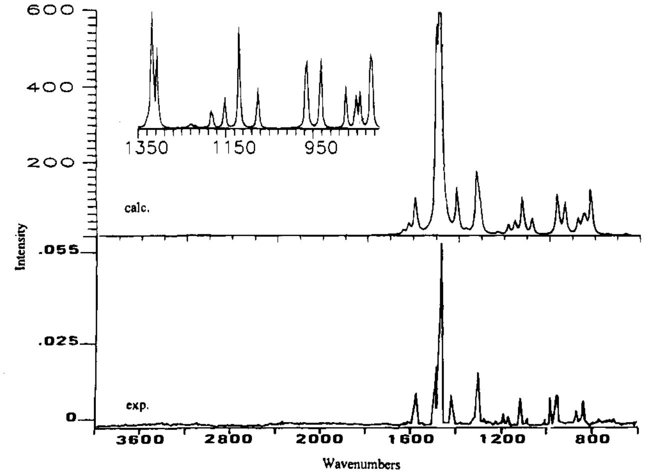

Figure 5. Comparison of the calculated and experimental (taken from ref 5) vibrational spectra of 1,3,7,8-TCDD. The calculations used a planar (C_s) equilibrium geometry. See the caption for Figure 3.

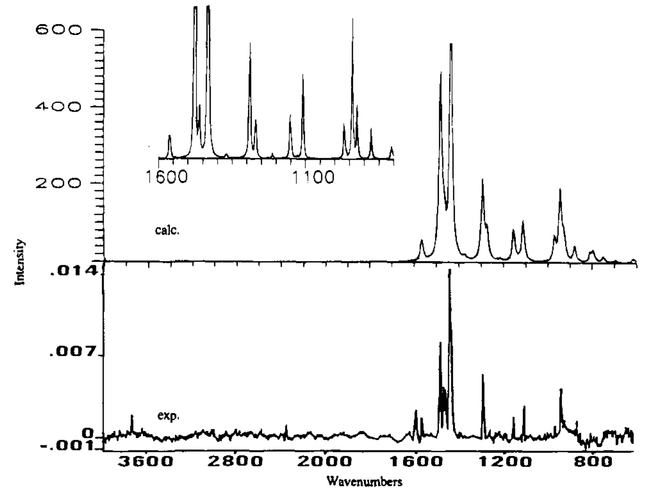

Figure 6. Comparison of the calculated and experimental (taken from ref 5) vibrational spectra of 1,4,7,8-TCDD. The calculations used a planar (C_s) equilibrium geometry. See the caption for Figure 3.

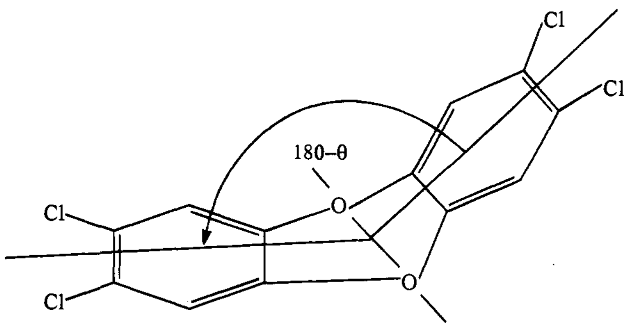

Figure 7. The definition of the butterfly angle in *p*-dibenzodioxins.

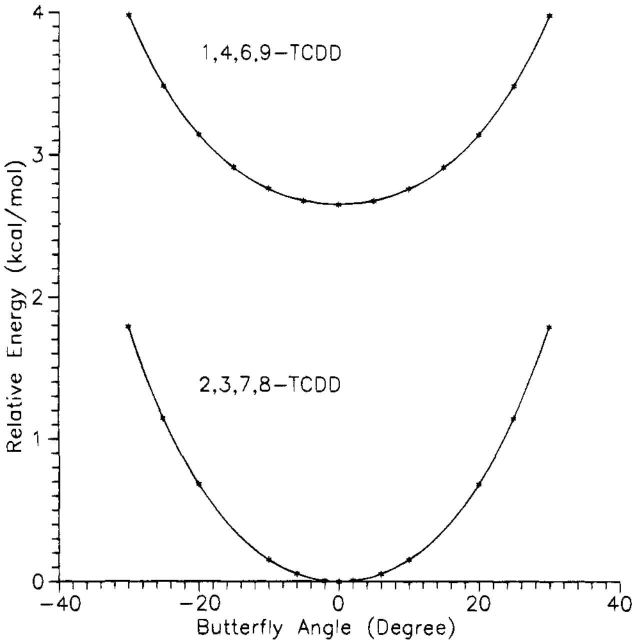

Figure 8. Energies of optimized geometries as a function of the fixed butterfly angle in 2,3,7,8- and 1,4,6,9-TCDD.

in the neighborhood of these bands. As is evident from Figures 3−6, the reproduction of the spectra, aside from the splitting, is very good.

We have considered several hypotheses to explain the band splittings in **1**: effect of the large-amplitude butterfly vibration, natural-abundance istope effects, and Fermi resonances. None of the first two possibilities, as described below, solves the problem. They do, however, contribute to the understanding of the molecular structure and vibrations of TCDDs. For instance, the large-amplitude butterfly vibration probably contributes to the slight systematic deviations between the calculated and experimental frequencies. The knowledge of isotope frequencies is useful because isotopes are used to calibrate the quantitative determination of TCCDs by IR spectroscopy.

(c) **Effect of the Large-Amplitude Vibration.** The simplest way to account for the effects of the butterfly vibration is to consider **1**, on the average, to be nonplanar. The lowering of the symmetry shifts the band and, more importantly, changes the selection rules, rendering some inactive modes active. A more sophisticated treatment considers these new bands combination modes between skeletal vibrations and the butterfly mode. We have calculated the potential energy curve for the butterfly angle, defined in Figure 7, by fixing this angle and optimizing all other degrees of freedom. The potential curves are shown in Figure 8. In spite of the floppy nature of the butterfly motion, the potential for both **1** and **2** is almost quadratic up to a deformation of 30°, corresponding to about 1.5 kcal/mol, i.e. well above the thermal energy at room temperature. We have estimated the thermally averaged frequencies of the small-amplitude vibrations by the Boltzmann distribution:

$$\bar{\nu}_j = \int \nu_j(\theta) e^{-\epsilon(\theta)/kT}\, d\theta \Big/ \int e^{-\epsilon(\theta)/kT}$$

Here $\epsilon(\theta)$ is the total energy at a given butterfly angle θ and $\nu_j(\theta)$ is the *j*th vibrational frequency at this angle. The integral was evaluated numerically, using vibrational frequencies calculated at $\theta = 0$, ±10°, ±20°, and ±30°, and using a polynomial fit in the range $\theta = -40$ to 40°. Calculating vibrational frequencies at non-equilibrium geometries yields values which depend on the coordinate system,[18] although this is not serious if internal coordinates are used as in the present work.[18] The average absolute value of the butterfly angle was calculated similarly as 13.5° for **1** and 15° for **2** at 373 K, the temperature of the gas-phase spectra. Although averaging over the large-amplitude vibration shifts the bands somewhat at this temperature, the differences are too small to be seen in the simulated spectra. The largest differences for 2,3,7,8-TCDD are the decrease of the intensity of vibration 46 and the increase of vibration 53. Therefore, the effect of the large-amplitude vibration cannot be responsible for the appearance of extraneous

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[18] Pulay, P. In *Applications of Electronic Structure Theory*; Schaefer, H. F., Ed.; Plenum: New York, 1977; p 153.

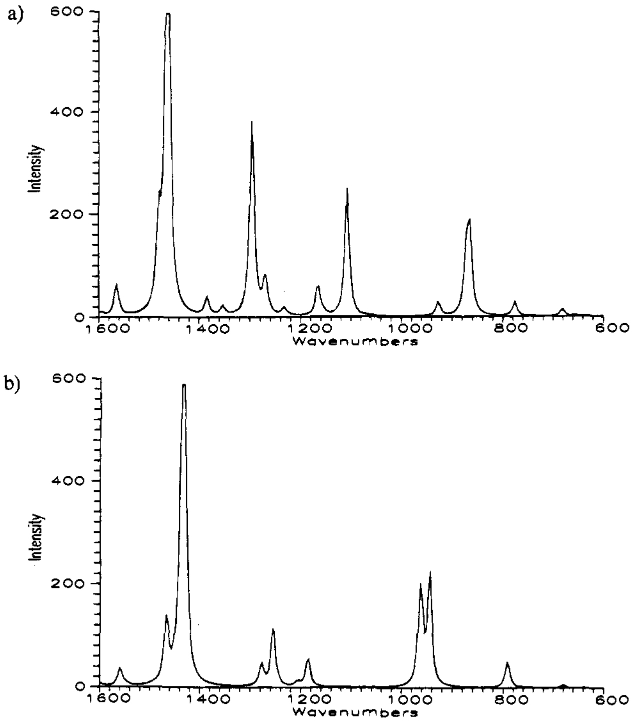

Figure 9. The vibrational spectra of 100% ^{13}C monosubstituted 2,3,7,8-TCDD (a) and 1,4,6,9-TCDD (b). See the caption for Figure 3 for the intensity scale.

bands in the IR spectrum of **1**. The thermally averaged spectra at the temperature given above (373 K) are given in the supplementary material as Table A.

(d) Isotope Effects. Symmetrical TCDD isomers contain a number of equivalent chlorine and carbon atoms. This enhances the effect of isotopes in natural abundance (^{37}Cl 27%, ^{13}C 1.1%). Isotope effects offer a possible explanation of band splittings. We looked first for ^{37}Cl isotope effects, but the isotope shifts are too small, of the order of 1−2 cm^{-1} for the bands in question. Carbon-13 is more promising, on account of the larger relative change in the effective mass. Only isotopomers with a single ^{13}C nucleus are present in appreciable quantity. There are three possible ^{13}C positions in **1**, of which the position next to the hydrogen atom (C-1,4,6,9) causes the largest changes in the spectrum. The spectrum of the pure $^{13}C_1$ isotopomers of **1** is shown in Figure 9a, and the analogous spectrum for **2** in Figure 9b; the harmonic frequencies and intensities are given in the supplementary material as Table B. As these figures show, the spectrum of **2** changes much less upon isotope substitution than that of **1**. In the latter, a new peak appears at 1363 cm^{-1} and a very strong peak at 1472 cm^{-1}. It is tempting to identify the latter with the experimental band observed at 1489 cm^{-1}, but the first peak cannot be explained this way. However, the intensities of both peaks are too low if we consider only the natural abundance of ^{13}C (supplementary material: Figure A, Table C). Therefore the band splittings observed in the IR spectrum cannot be explained by ^{13}C isotope effects either, despite the fact that we found a peak at the right position if we consider a 100% isotopic substitution.

We have also calculated the deuterium substitution spectra of **1** and **2**. They may be useful to predict spectra of calibration standards (supplementary material: Table D).

Conclusions

Density functional theory with moderate basis sets and Becke's 3-parameter exchange-correlation functional reproduces the experimental infrared spectra of chlorinated dibenzodioxins very well, allowing the indentification of isomers and the assignment of observed bands. 2,3,7,8-TCDD shows splittings in three bands which are not reproduced by the calculations even after considering the effects of large-amplitude vibrations and natural-isotope effects and are probably due to Fermi resonance.

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Supplementary Material Available: Tables of vibrational frequencies and IR intensities and vibrational spectra for 2,3,7,8-TCDD and 1,4,6,9-TCDD (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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