ISOMER IDENTIFICATION OF NON-LATERALLY TETRACHLORINATED DIBENZO-p-DIOXIN ISOMER GROUPS BY GAS CHROMATOGRAPHY/ FOURIER TRANSFORM INFRARED SPECTROSCOPY

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ABSTRACT

Vapor phase infrared spectra are reported for the mono-, di-, and trichlorinated dibenzo-p-dioxin isomer groups. The spectrum of each chlorinated dibenzo-p-dioxin congener is unique. Individual model aromatic rings in the molecule can be distinguished on the basis of their characteristic aromatic skeletal stretching bands while the number of chlorine sustituents can be estimated by the maximum aromatic skeletal stretch/ether linkage asymmetric stretching frequency ratio. The structures for individual isomers in each isomer pair were assigned by empirically derived quantitative valence-bond estimations of ether linkage assymmetric stretching frequencies.

INTRODUCTION

Chlorinated dibenzo-p-dioxins (CDDs) have been subjected to intense analytical scrutiny[1-15] in recent decades due to extreme animal toxicities[11] and to the extent of environmental contamination[12]. The laterally (2,3,7, and 8) tetrachlorinated dibenzo-p-dioxin (LTCDD) isomer groups [tetrachlorodibenzo-p-dioxin (TCDD) through octachlorodibenzo-p-dioxin (OCDD)] have been the primary targets of these investigations since they contain the most toxic isomers. There is very little published information on structural characterization of the non-laterally tetrachlorinated (nLTCDD) isomer groups. Gas chromatography/ Fourier transform infrared spectroscopy (GC/FTIR)[4,5,6,9,14,15], proton nuclear magnetic resonance (^{1}H NMR)[7] and carbon-13 nuclear magnetic resonance (^{13}C NMR)[13] have been utilized to systematically identify CDD congeners by chromatographically independent assignment techniques. In this presentation, the empirically determined infrared valence-bond parameters[5,6,9] used in isomer differentiation of laterally tetrachlorinated isomer groups are extended to mono-, di-, and trichlorinated dibenzo-p-dioxins.

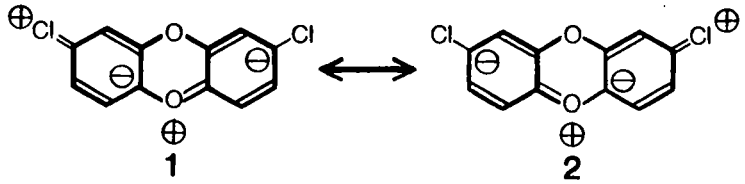
EXPERIMENTAL

Isomer Preparation. The CDD isomers were prepared at the Centers for Disease Control and Prevention by methods previously described[7]. The isomer mixture components were separated from the residual starting materials by silica gel chromatography, followed by high performance liquid chromatography (HPLC) when necessary.

GC/FTIR Instrumentation. A Nicolet (Madison, WI.) Model 170SX Fourier transform infrared spectrometer equipped with an array processor and a mercury-cadmium-telluride detector was used for all GC/FTIR measurements. Chromatographic separations were performed by a Hewlett-Packard (Palo Alto, CA) 5880A gas chromatograph containing a J & W Scientific (Rancho Cordova, CA) 1um DB5 film (30m X .52mm) fused silica capillary column (FSCC). The end of the FSCC was passed through an insulated transfer line maintained at 280° C to a 1mm X 15 cm light pipe maintained at 285° C. Vapor phase spectra were recorded at 4cm^{-1}.

RESULTS AND DISCUSSION

Vapor phase infrared spectra representative of non-laterally tetrachlorinated isomer groups are presented in Figure 1. The most prominent features of the spectra are (1) aromatic skeletal stretching [$Vcc_{(arom)}$] bands (1400-1500 cm^{-1}) that provide distinctive patterns characteristic of individual ring substitution; (2) ether linkage asymmetric stretching frequency [$Vcoc_{(asym)}$] bands (1280-1321 cm^{-1}) that correlate with model ring electron-withdrawing capacities and contributions from laterally stabilized delocalizations and (3) ether linkage symmetric stretching frequency [$Vcoc_{(sym)}$] bands (800-900 cm^{-1}). The infrared spectrum of each isomer is unique. The spectra of the 2,7- and 2,8-dichlorodibenzo-p-dioxin (DCDD) isomers (Figure 1.) both exhibit $Vcc_{(arom)}$ values (1483 and 1486 cm^{-1}, respectively) characteristic of the 2-monochlorodibenzo-p-dioxin (2-MCDD) model ring(1489 cm^{-1}). The two isomers can be distinguished on the basis of the $Vcoc_{(asym)}$ values where two laterally stabilized delocalization contributions for the 2,8-DCDD isomer generate more ether linkage partial double bond character (resulting in a larger $Vcoc_{(asym)}$ value) than for the 2,7-DCDD isomer where no contributions of this type are possible.



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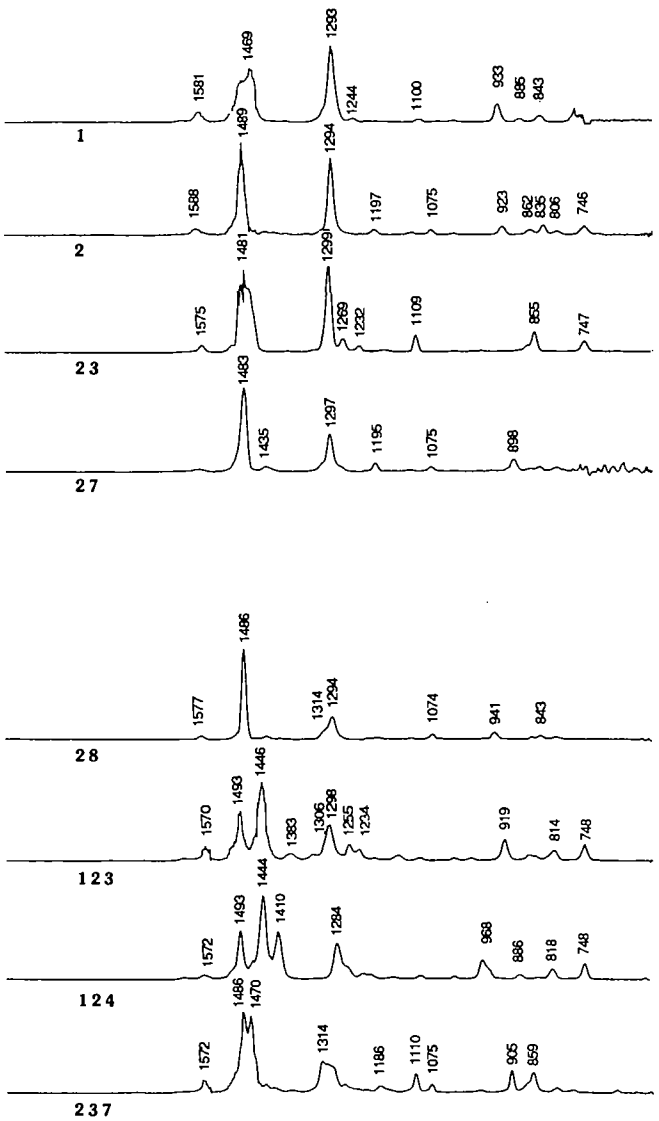
The relative strengths of ether linkages in CDD isomer pairs have been quantitatively estimated by a valence-bond approach employing a linear combination of wave functions that correspond to specific laterally stabilized ether linkage delocalizations. The wave function describing the cumulative effect of these

Figure 1. Infrared Spectra (2000 - 600 cm^{-1}) for Representative Mono-, Di-, and Trichlorinated Dibenzo-p-dioxins



delocalizations has been expressed as:

$$\Psi = c_1\phi_1 + c_2\phi_2 + \ldots + \sum c_n\phi_n \qquad (1)$$

where ϕ represents a wavefunction for a specific canonical form where an oxonium ion is stabilized by an electron pair delocalization from a lateral chlorine and where c represents a weighting coefficient that qualitatively correlates with model ring electron-withdrawing capacities[5]. Quantitative estimations of $Vcoc_{(asym)}$ using empirically derived parameters for delocalization and steric effects have been established for laterally tetrachlorinated CDD isomer groups.[6,9,14,15] The estimated values [$V'coc_{(asym)}$] have been expressed as:

$$V'coc_{(asym)} = V^0coc_{(asym)} + \sum nS + F + Q \qquad (2)$$

where $V^0coc_{(asym)}$ is the value for the dominant model compound, S is the value for laterally stabilized delocalizations for the dominant ring, F is a steric parameter for 1,9- substituent steric interactions with the ether linkage, and Q is a 1,4-substituent interaction with the ether linkages. Estimated and observed Vcoc(asym) values for nLTCDD isomer groups are presented in Tables 1 and 2.

Table 1. Comparison of Experimentally Determined MCDD and DCDD $V_{COC(asym)}$ Values with $V_{COC(asym)}$ Values Obtained From Empirically Derived Parameters and Molecular Geometry.

Dioxin	α (°)	V^0 COC(asym)	nS_i	1,9 Interactions F(cm^{-1})	1,4 (αα) Rings Q(cm^{-1})	COC(asym) Estimated (cm^{-1})	COC(asym) Observed (cm^{-1})
1	115.2	1293	0(2)	0	0	1293	1293
2	116.1	1294	0(2)	0	0	1294	1294
12	115.5	1297	0(2)	0	0	1297	1297
13	111.0	1292	0(1)	0	0	1292	1292
14	112.1	1290	0(2)	0	-8	1282	1282
16	112.0	1293	0(2)	0	0	1293	1291
17	113.0	1294	1(2)	0	0	1296	1297
18	112.7	1294	0(2)	0	0	1294	1294
19	113.0	1293	0(2)	-3	0	1290	1291
23	120.8	1299	0(2)	0	0	1299	1299
27	116.8	1294	0(2)	0	0	1294	1297
28	114.1	1294	2(2)	0	0	1298	1304

Table 2. Comparison of Experimentally Determined TrCDD $V_{COC(asym)}$ values with $V_{COC(asym)}$ Values Obtained From Empirically Derived Parameters and Molecular Geometry.

Dioxin	(°)	COC(asym)	ΣS_i	1,9 Interactions F(cm^{-1})	1,4 ($\alpha\alpha$) Rings Q(cm^{-1})	COC(asym) Estimated (cm^{-1})	COC(asym) Observed (cm^{-1})
123	114.8	1302	0(2)	0	0	1302	1302
124	110.1	1284	0(1)	0	0	1284	1284
126	112.2	1297	1(2)	0	0	1299	1298
127	116.6	1297	1(2)	0	0	1299	1296
128	118.6	1297	2(2)	0	0	1301	1302
129	115.9	1297	0(2)	-3	0	1294	1294
136	111.4	1293	0(1)	0	0	1293	1296
137	111.6	1294	3(1)	0	0	1297	1296
138	111.6	1294	0(1)	0	0	1294	1296
139	111.7	1293	1(1)	-3	0	1291	1292
146	111.7	1293	0(1)	0	-8	1285	1287
147	115.6	1294	1(2)	0	-8	1288	1287
178	113.6	1299	1(2)	0	0	1301	1302
237	116.3	1299	2(2)	0	0	1303	1303

CONCLUSIONS

Isomer structural assignments for non-laterally tetrachlorinated dibenzo-p-dioxin groups were determined by evaluating model aromatic skeletal stretching bands and from qualitative valence-bond calculations of ether linkage asymmetric stretching frequency values. The calculated values are in good agreement with experimentally determined values and with the steric, delocalization and inductive parameters established for the laterally tetrachlorinated dibenzo-p-dioxin isomer groups.

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