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Correlation of structure with linear retention index for bromo- and bromochlorodibenzo-*p*-dioxins and bromodibenzofurans

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ABSTRACT

A model-correlating structure with gas chromatographic retention index was developed to assist in making positional isomer assignments for dioxins halogenated by bromine and/or chlorine using commercially available standards and synthetic mixtures. Bromodibenzofuran assignments were made using pyrolysate mixtures, assuming the elution order was the same as for chlorinated dibenzofurans. These strategies can be used, on an interim basis, for isomer assignments in environmental monitoring efforts.

INTRODUCTION

Many commonly used commercial products, such as carpets, textiles, and plastics, contain brominated flame retardants in levels up to 20% (w/w) [1]. Brominated dibenzofurans (PBDFs) have recently been found at parts per billion (ppb)[a] levels in decabromodiphenyl ether flame retardant and in commercial thermoplastic resins formulated with brominated diphenyl ether flame retardants [2]. Brominated dibenzofurans at high parts per million (ppm) levels, as well as brominated dioxins (PBDDs) and related compounds (possibly brominated methyldibenzofurans) were found at ppb levels in a pyrolysate of one such resin [2]. PBDFs have been reported in the flame retardant tetrabromobisphenol-A; PBDDs and PBDFs were found in 2,4,6-tribromophenol [3]. Pyrolysates of tri- and pentabromophenols were found to contain PBDDs; tetra- and pentabromodiphenyl ether pyrolysates were reported to contain PBDDs and PBDFs; polybromobiphenyl (PBB) pyrolysates contained PBDFs [4,5]. PBDDs and PBDFs have also been detected in vehicular exhaust [6]. Recent studies of municipal and hazardous waste incinerator fly

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[a] Throughout this article, the American billion (10^9) is meant.

ash have shown the presence of numerous bromochloro-dibenzo-*p*-dioxins and -dibenzofurans (PBCDDs, PBCDFs) [7–12]. Soot from an accidental fire in a building was also found to contain PBDFs and PBCDFs [13].

The environmental occurrence of dioxins and furans, halogenated by bromine and/or chlorine (HDDs, HDFs), is a matter of concern since available toxicological data indicate that their toxicities are similar to those of the chlorinated dioxins and furans (PBDDs, PCDFs) [14–17]. Analytical methodology has recently been elaborated for routine environmental monitoring of these analytes [2,9,18,19]. Recently, an international consensus was reached in assigning toxicity equivalency factors (TEFs) to individual PCDD and PCDF isomers with 2,3,7,8-substitution for health-risk assessment [20]. The U.S. Environmental Protection Agency (EPA) considers these TEFs to be interim guidance for making risk assessments and regulations [21]. One provision within the Toxic Substances Control Act (TSCA) is the "Test Rule" under which manufacturers of specified commercial products supply the EPA with analytical results for halogenated dibenzo-*p*-dioxins and dibenzofurans in those products [22]. While available methodology using high-resolution gas chromato-graphy–mass spectrometry (HRGC–MS) can provide good isomer specificity to address that need in TEF calculations, standards are not available for most of the bromine-containing congeners of concern. Therefore, an immediate need exists for alternative means to establish retention time windows for routine monitoring of HDDs and HDFs.

Models which correlate structure to GC retention index (*I*) have been proposed and tested for PCDDs [23] and PCDFs [24]. Thus, the retention index–structure relationship could be used to identify synthetic products and unknown PCDDs and PCDFs found during environmental monitoring efforts, reducing the need for a large number of expensive, hazardous standards. The problems regarding number, cost, availability, and potential toxicity of standards exist to similar or greater extends for the structurally similar brominated and bromochlorinated analogues. Because of these problems, the development and extension of these models to bromine-containing HDDs and HDFs would be very advantageous.

This report presents the successful development of those features needed for application of retention index modelling to the 75 PBDD, 75 PCDD, 135 PBDF and 1550 PBCDD congeners. To develop the HDD model, numerous compounds were synthesized to supplement the few commercially available standards. Once developed, the HDD retention index model was used to assign structures of individual synthetic products in a manner that was also consistent with the known mechanistic chemistry of the synthetic methods.

EXPERIMENTAL

Available standards were purchased from Cambridge Isotope Labs. (Woburn, MA, U.S.A.) or from Chemsyn Science Labs. (Lenexa, KS, U.S.A.). Some PBDD and PBDF mixtures had been synthesized by electrophilic bromination of dioxin and dibenzofuran [25,26]. However, this technique was of limited utility for determination of retention index contributions from the nine possible brominated single rings because the bromine atoms appeared to be introduced in a specific sequence, providing only a limited number of major and minor products. In general, halogens were

introduced in the 2-, 3-, 7-, and 8-positions in preference to the 1-, 4-, 6-, or 9-positions. Further, the synthetic scheme was not completely unambiguous in positional selectivity. Therefore, other synthetic procedures were applied to the preparation of PBDDs and PBCDDs, including the self-condensation of halogenated phenolates [27] and the coupling of halogenated catechols with halonitrobenzenes under basic conditions [28]. The phenolate self-condensation was convenient and effective except when fully halogenated bromochlorophenols were required because isomer specificity of products was difficult to control. In such instances, the coupling of appropriate catechols and nitrobenzenes was utilized. To minimize the possibility of errors in the structural assignment of products, with resulting errors in retention index–structure relationships, it was essential that the synthetic reactions yield a minimum number of products, having rational structural relationships based upon the synthetic route. The harzardous nature of these compounds precluded the large-scale syntheses and the extensive purifications and analyses traditionally used to elucidate organic compound structures. During the syntheses, it was noted that bromine, unlike chlorine, could be lost under the reaction conditions. Thus, HDD products with fewer bromines than expected were sometimes encountered as by-products. Through careful choice of reactants and synthetic route, all 26 bromochloro single rings were accessed through synthesis [27,28]. Six of the nine possible bromo single rings were accessed through commercial standards, and three (1,2; 1,4; 1,2,4) were synthesized.

Access to most PBDF congeners was gained through several pyrolysates of polybutylene terephthalate (PBT) thermoplastic resins [2]. Commercially available standards were purchased, allowing bracketing of retention indices found in the pyrolysates with those of available standards.

Retention indices for PBDDs, PCDDs and PBCDDs were determined relative to the normal hydrocarbons, using a Hewlett-Packard 5880A gas chromatograph with splitless injection, a Restek 30 m × 0.25 mm I.D., 0.25-μm film RT$_x$-5 column, helium carrier gas at 25 p.s.i., and flame ionization detection. The column was temperature-programmed with 1 min at 170°C followed by 2°C/min to 320°C. This column and temperature program yielded moderate retention times suitable for routine environmental monitoring efforts. Retention indices for PBDF were determined using a Hewlett-Packard 5890 gas chromatograph with on-column injection, a 60 m × 0.25 mm I.D., 0.25-μm film RT$_x$-5 column, helium carrier gas at 31 p.s.i., and a temperature program from 170°C (no initial hold) at 1°C/min to 320°C. The longer GC column and temperature program were necessary to achieve separation of the numerous PBDF present in the pyrolysates. Detection was accomplished with a VG 70-250 SE mass spectrometer, 300°C transfer line, 270°C source, in electron ionization mode. Retention indices were calculated using the linear retention index scale for linear temperature-programmed GC, as suggested by Van Den Dool and Kratz [29].

DISCUSSION

Features of the I model

Retention indices for the PBDDs and PBCDDs were successfully calculated and effectively applied by modifying and extending a model which was developed for the PCDD series [23]. In this study of PBDDs and PBCDDs, the strategy was employed of expressing the retention index as the sum of five contributors: (1) the index of
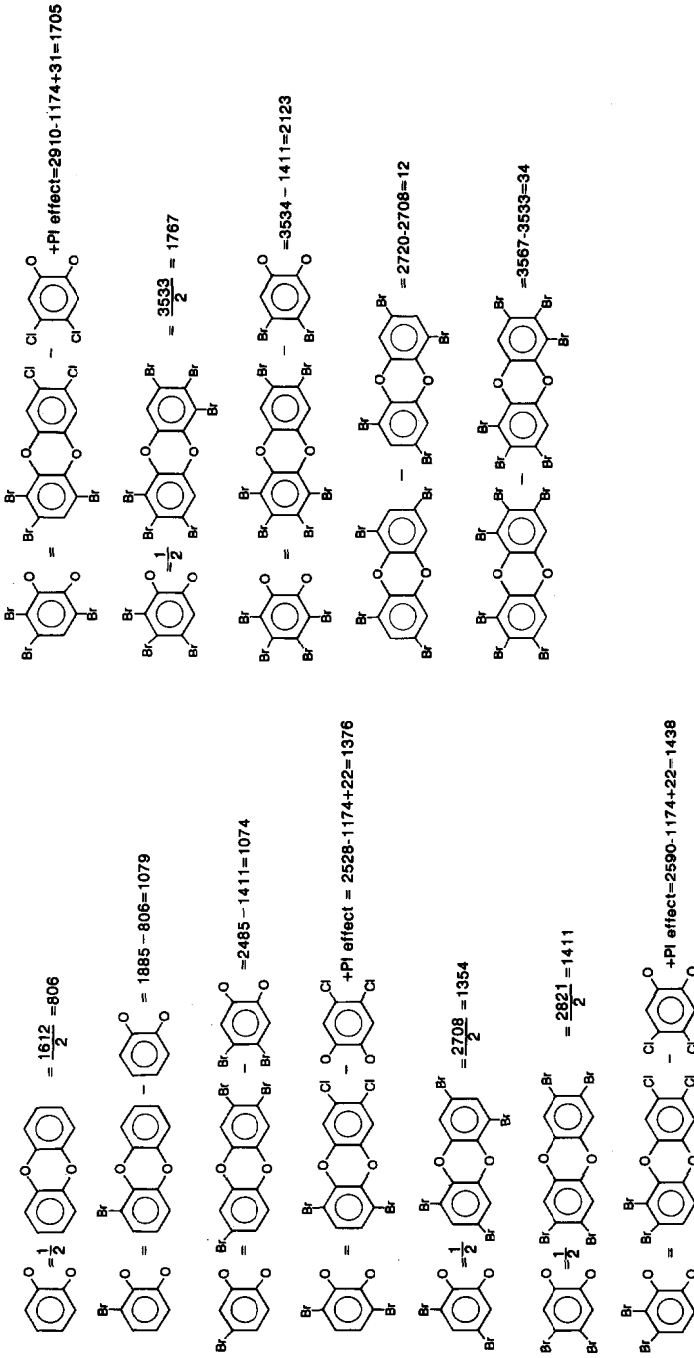
Fig. 1. Calculation procedures for single-ring indices of PBDDs.

single-ring A; (2) the index of single-ring B; (3) the index of a "ring interaction" effect or "1,9-effect"; (4) the index increment from "buttressing" the 1,9-effect with additional substitution at the 2-, 3-, 7-, and 8-positions; and (5) the index of a "phase interaction" (PI) effect. The calculation procedures for the single-ring retention indices (SRRI) of HDDs are presented in Figs. 1 and 2. Values of the PI effect are calculated in Table I. For the PCDDs, a simpler approach employing contributors (1), (2), and (3) provided calculated indices for the PCDDs which agreed with the measured values within 4–6 *I* units for most congeners [23].

It was observed in this study that each additional bromine substitution incremented the *I* about 1.5 times as much as a chlorine substitution did. This effect could be noted by comparing the spacings among *I* values for the single rings. In addition to PBDDs and PBCDDs, selected PCDD standards were also analyzed in the current study to provide *I* values for chlorinated single rings under the same experimental conditions as for PBDDs and PBCDDs (see Table III). These data were needed for calculations of *I* for PBCDD containing chlorine but no bromine atoms on one of the rings.
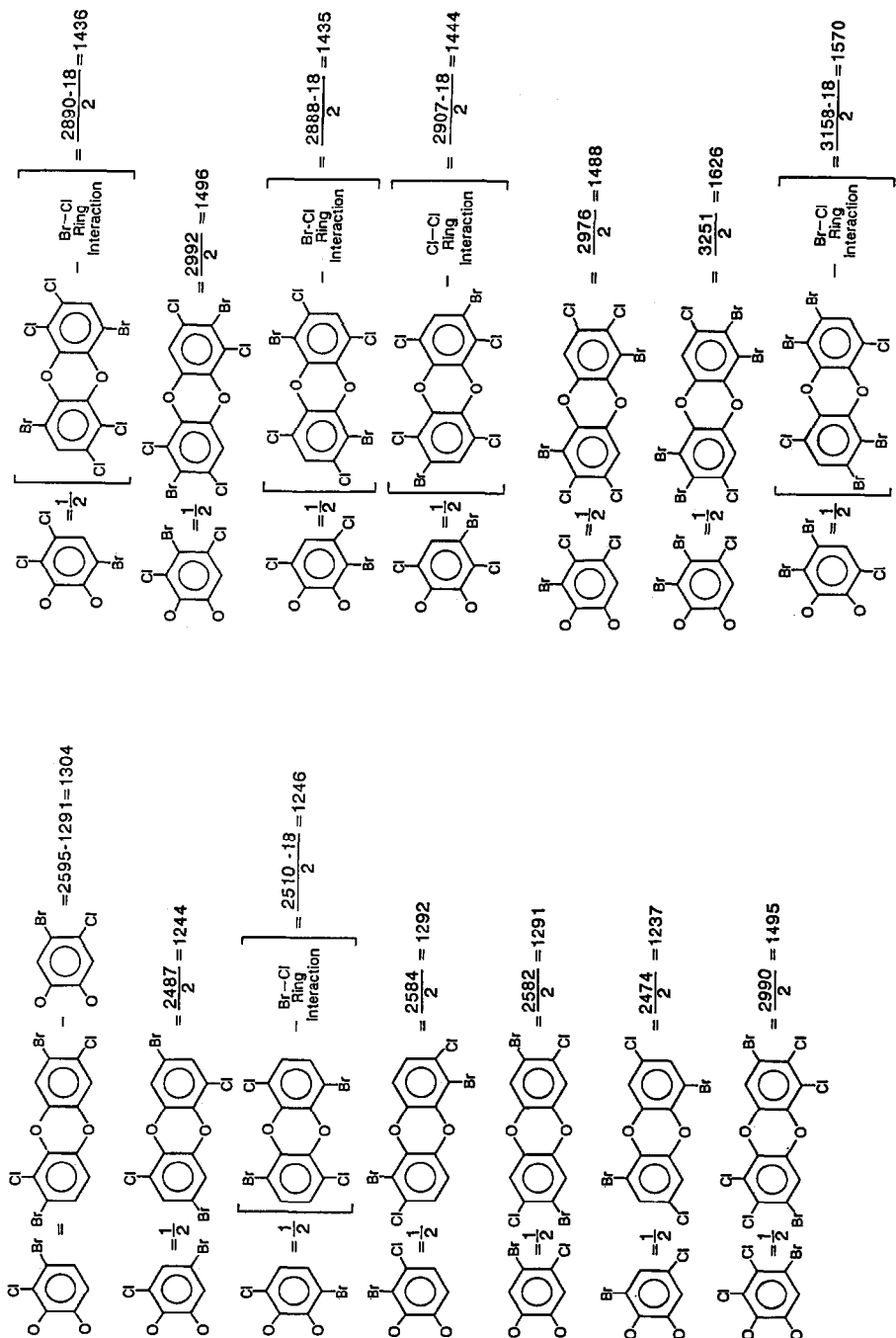
Ring–ring interactions

In the present study of HDDs, the 1,9-dichloro ring interaction was found to average 12 *I* units; when two 1,9-effects were present (*i.e.* all four 1-, 4-, 6-, and 9-positions were occupied by chlorine atoms), the total ring–ring effect was found to be 1.5 times that of a single ring–ring effect, or 18 units.

The magnitude of the 1,9-dibromo ring interaction was found to be approximately 12 *I* units, the same as for 1,9-chlorines. However, buttressing with halogen substitutions at the 2- and 8-positions resulted in increased magnitude of the effect. This buttress effect was not observed in the PCDD series and was not observed for 1-bromo-9-chloro interactions either. Possibly the steric requirements of 1,9-dibromo substitutions are necessary for buttressing. When 1,9-dibromo substitutions were buttressed with bromine atoms in the 2-, 3-, 7-, and 8-positions, the ring–ring interaction effect increased to 34 *I* units; buttressing with 2,8-dibromo-3,7-dichloro substitution gave the ring–ring interaction effect a magnitude of 22 *I* units. Buttressing of 1,9-dibromo substitution at the 2- and 8-positions with chlorine atoms, or with one bromine and one chlorine, resulted in an effect of approximately 18 *I* units. A similar buttress effect has been invoked to explain variations in PCDF infrared spectral ether linkage asymmetric stretching frequencies [30].

For those HDD molecules with two ring–ring interaction effects, the full value of the larger effect was added to the halved value of the second effect, to calculate the total ring–ring effect for the molecule. For example, the total ring–ring interaction effect for octabromodibenzo-*p*-dioxane (OBDD) was calculated to be 34 *I* units plus (0.5) (34) *I* units, for a total of 51 *I* units.

Molecule to GC phase interactions

The retention index contribution of the unsubstituted ring was found to have some dependence upon the overall character of the molecule (see Table I). If the other single ring was heavily halogenated, the unsubstituted ring incremented the *I* less than if the other single ring was monohalogenated or also unsubstituted. In the PBDD series, this *I* difference for the unsubstituted ring contribution was significant (a

$$= \frac{2890 \cdot 18}{2} = 1436$$

Br—Cl Ring Interaction

$$= \frac{2992}{2} = 1496$$

$$= \frac{2888 \cdot 18}{2} = 1435$$

Br-Cl Ring Interaction

$$= \frac{2907 \cdot 18}{2} = 1444$$

Cl-Cl Ring Interaction

$$= \frac{2976}{2} = 1488$$

$$= \frac{3251}{2} = 1626$$

$$= \frac{3158 \cdot 18}{2} = 1570$$

Br-Cl Ring Interaction

$$= \frac{1}{2}$$

$$= 2595 \cdot 1291 = 1304$$

$$= \frac{2487}{2} = 1244$$

$$= \frac{2510 \cdot 18}{2} = 1246$$

Br—Cl Ring Interaction

$$= \frac{2584}{2} = 1292$$

$$= \frac{2582}{2} = 1291$$

$$= \frac{2474}{2} = 1237$$

$$= \frac{2990}{2} = 1495$$
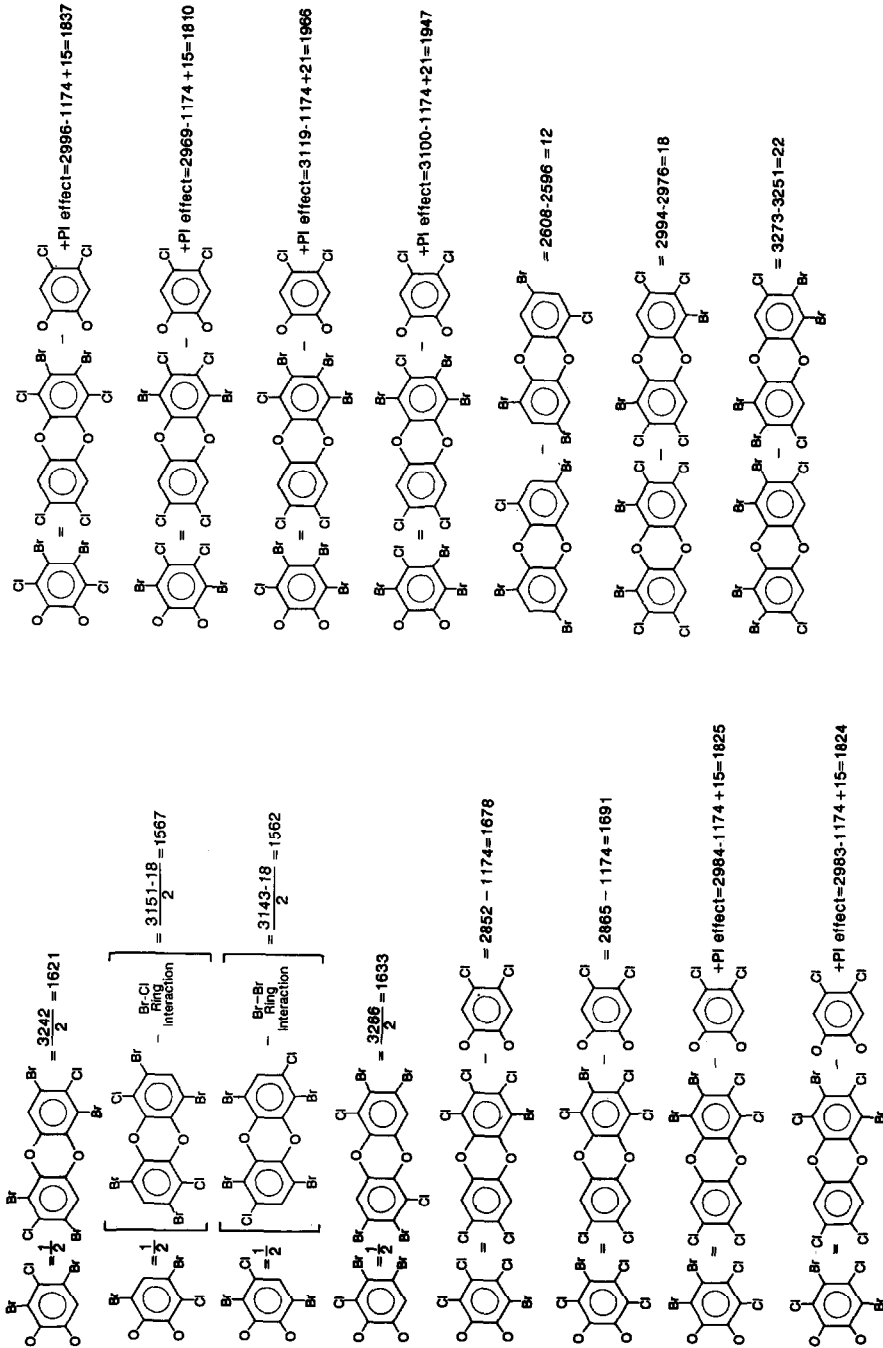
$$= \frac{1}{2}$$

Fig. 2. Calculation procedures for single-ring indices of PBCDDs.

TABLE I

I CALCULATIONS USED TO DETERMINE THE MAGNITUDE OF THE PHASE INTERACTION (PI) EFFECT

I values were obtained under experimental conditions specified for HDD: 30 m Restek RT_x-5 column, 1 min at 170°C, 2°C/min to 320°C.

Source compound	*I* Calculation	*I* Value derived	Single ring calculated	PI Effect magnitude *I* units
Dioxin	1612/2	806	Unsubst.	
2,3,7,8-TBDD	2821/2	1411	2,3-Br$_3$	
2,3,7,8-TCDD	2348/2	1174	2,3-Cl$_2$	
2,3,7-TrCDD	2160 − 1174	986	2-Cl	
2,3-Br$_2$-7-Cl-HDD	2375 − 986	1389	2,3-Br$_2$	
	1411 − 1389		Δ(2,3-Br$_2$)	22
1,2,3,6,7,8-HxBDD	3533/2	1767	1,2,3-Br$_3$	
1,2,3-Br$_3$-7,8-Cl$_2$-HDD	2910 − 1174	1736	1,2,3-Br$_3$	
	1767 − 1736		Δ(1,2,3-Br$_3$)	31
1,2,3,4,7,8-HxBDD	3534 − 1411	2123	1,2,3,4-Br$_4$	
1,2,3,4-Br$_4$-7,8,-Cl$_2$-HDD	3244 − 1174	2070	1,2,3,4-Br$_4$	
	2133 − 2070		Δ(1,2,3,4-Br$_4$)	53
1,2,3,4-TBDD	2811 − 2123	688	Unsubst.	
	806 − 688		Δ(1,2,3,4-Br$_4$)	118
1,4,9-Br$_3$-2,7-Cl$_2$-HDD	1562 + 1237 + 12	2811	Calcd. *I*	
	2811 − 2800		Calcd. − exptl.	11
2-Br-1,4,6,9-Cl$_4$-HDD	1444 + 1145 + 18	2607	Calcd. *I*	
	2607 − 2596		Calcd. − exptl.	11
2,3-Br$_2$-1,7,8-Cl$_3$-HDD	1633 + 1174	2807	Calcd. *I*	
	2807 − 2792		Calcd. − exptl.	15
4-Br-1,2,6,7-Cl$_4$-HDD	1436 + 1186 + 12	2634	Calcd. *I*	
	2634 − 2627		Calcd. − exptl.	07

TABLE II

SINGLE-RING INDICES FOR PCDD

All *I* values were determined under experimental conditions specified for HDD: 30 m Restek RT_x-5 column, 1 min at 170°C, 2°C/min to 320°C.

Source compound	*I* Calculation	*I* Value derived	Single ring
Dioxin	1612/2	806	Unsubst.
1,2,3,6-TCDD	2340 − 1359	981	1-Cl
2,3,7-TrCDD	2160 − 1174	986	2-Cl
2,3,7,8-TCDD	2348/2	1174	2,3-Cl$_2$
1,3,6,8-TCDD	2260/2	1130	1,3-Cl$_2$
1,4,7,8-TCDD	2319 − 1174	1145	1,4-Cl$_2$
1,2,6,7-TCDD	2372/2	1186	1,2-Cl$_2$
1,2,4,7-TCDD	2305 − 986	1319	1,2,4-Cl$_3$
1,2,3,7-TCDD	2345 − 986	1359	1,2,3-Cl$_3$
1,2,3,4-TCDD	2340 − 806	1534	1,2,3,4-Cl$_4$

maximum of 118 *I* units; see Table I). A similar unsubstituted-ring effect has been reported and discussed by Albro *et al.* [31] and by Ballschmiter and Zell [32] for polychlorinated biphenyls (PCBs).

It is postulated that the ability of the unsubstituted ring to interact with the column phase was diminished because of its greater than optimum distance for interaction with the phase, caused by the other (dibromo, tribromo or tetrabromo) single ring forcing the planar dioxin molecule to assume the larger molecule–phase distance for halogen–phase interactions. The large radius of bromine compared to hydrogen might be predicted to cause such a PI effect which would have significant, observable magnitude.

A similar effect of reduced magnitude might be expected for cases where one ring was bromine-substituted and the other was chlorinated. A PI effect was invoked to explain retention index shifts observed in cases where one ring was di-, tri- or tetrabrominated and the other was only chlorinated (22, 31 and 53 *I* units, respectively). In those bromochlorodioxins where one bromochloro ring contained at least two bromines and one or two chlorines, but the second ring contained only chlorines, this PI effect magnitude was about two thirds as large (*i.e.* 15 or 21 *I* units for dibromo and tribromo, respectively) as for cases with only bromine on one ring and only chlorine on the other. When one bromochloro single ring contained two bromines, and the other single ring was 1,2- or 1,3-disubstituted with one bromine and one chlorine, a reduction in retention index, ascribed to a PI effect, was observed at one half (0.5 × 22 = 11) the amount seen in cases with one single brominated and the other chlorinated. In cases where one ring had one bromine and two chlorines, and the other single ring had two chlorines, the reduction in retention index or PI effect, was observed to be dependent upon the substitution pattern of the chlorinated single ring. Six compounds having a single ring with non-*ortho* (1,3 or 1,4) chlorines exhibited a reduction of about 11 *I* units from that predicted by summing contributors (1) through (4). The one available compound with a 1,2-dichloro single ring exhibited a reduction of 7 *I* units. The six synthetic products having a 2,3-dichloro-substituted single ring did not exhibit a retention index reduction from that predicted by summing the single-ring indices. These findings have been summarized in Table I and Figs. 1 and 2.

Tests of the retention index model for HDDs

In this study of HDDs, 70% of the 63 HDDs which tested the model (60 PBCDD and PCDD synthetic products and 3 PBDD commercial standards; see Table III) were found to agree with the predicted *I* value within 3 *I* units, over a molecular *I* range of *ca.* 2500–4300 units; 89% were within 5 *I* units, and no predictions varied from the experimental values by more than 7 *I* units. In a few instances, reactions of different starting materials generated, *inter alia*, a common product HDD. These products are listed separately along with their independently measured *I* values.

The retention index model for HDDs was also applied to check the substitution pattern assignments for the synthetic products from electrophilic bromination of dibenzo-*p*-dioxin [25]. The minor pentabromodibenzo-*p*-dioxin (PeBDD) product obtained in that synthesis was probably 1,2,4,6,8- or 1,2,4,7,9-PeBDD, not 1,2,4,7,8-PeBDD as originally assigned; using the model developed in the present study, the early-eluting minor hexabromodibenzo-*p*-dioxin (HxBDD) product *I* value correlated

TABLE III

EXAMPLES OF AGREEMENT BETWEEN CALCULATED AND EXPERIMENTAL RETENTION
INDICES FOR HDD

Substituents		I		Δ(Experimental − calculated)
Br	Cl	Experimental	Calculated	
2	1,3,7,9	2625	2627	−2
1,4	7,8	2528	2528	0
1,2	3,7,8	2786	2785	1
3	1,2,7,8	2669	2669	0
2	1,3,7,8	2669	2670	−1
1,3,8	4,9	2872	2872	0
1,3,8	4,7	2854	2858	−4
1	3,8	2217	2223	−6
3,9	1,2,6,7	2945	2943	2
1,2	3,4,7,8	2982	2984	−2
1	2,3,7,8	2659	2662	−3
4	1,2,7,8	2612	2610	2
	2,3,7,8	2350	2348	2
	1,3,6,8	2260	2260	0
	1,3,7,9	2271	2272	−1
1	2,4,7,9	2567	2566	1
2	1,3,6,8	2612	2615	−3
3	1,2,7,8	2668	2669	−1
2,3,8	1,6	2861	2866	−5
2,3,7	1,9	2875	2878	−3
1,2,7	4,9	2814	2815	−1
3,7	1,9	2500	2500	0
3,8	1,6	2487	2488	−1
1,6	3,8	2471	2474	−3
1,9	3,7	2482	2486	−4
1,2,6	3,8	2850	2852	−2
1,2,9	3,7	2864	2864	0
1	3,4,6,9	2686	2588	−2
3	1,2,6,9	2638	2641	−3
4	1,2,6,7,9	2769	2773	−4
2	1,4,6,7,9	2779	2781	−2
1,2	3,4,7,8	2984	2984	0
1,9	3,7	2483	2486	−3
3,7	1,9	2500	2500	0
1,3,8	6	2596	2598	−2
3,6,8	1,2,9	3067	3074	−7
3,7,9	1,2,6	3067	3074	−7
1,3,6,8	4,9	3152	3152	0
1,3,7,9	4,6	3152	3152	0
3,7	1,2,8,9	3000	3002	−2
1,3,6,8	2,9	3205	3200	5
1,3,7,9	2,6	3205	3200	5
1,3,7,9	2,8	3261	3260	1
1,6	2,3,8,9	2940	2936	4
1,9	2,3,6,7	2940	2936	4
2,9	1,3,6,8	2943	2943	0
2,6	1,3,7,9	2943	2943	0
1,6	2,9	2555	2550	5

TABLE III *(continued)*

Substituents		*I*		Δ(Experimental–
				calculated)
Br	Cl	Experimental	Calculated	
1,9	2,6	2555	2550	5
1,9	2,8	2605	2602	3
1,2,8,9	4,6	3168	3168	0
2,3,8,9	1,6	3222	3215	7
2,3,6,7	1,9	3222	3215	7
2,3,7,8	1,9	3282	3278	4
1,2,6,9	3,8	3211	3206	5
1,2,6,9	3,7	3200	3200	0
2,9	1,4,6,7	2899	2898	1
2,6	1,4,8,9	2899	2898	1
4,9	1,2,6,7	2887	2890	−3
4,6	1,2,8,9	2887	2890	−3
1,3,7,8		2765	2765	0
1,2,3,7,8		3171	3178	−7
Octa		4303	4297	6

well with 1,2,4,6,7,9- and 1,2,4,6,8,9-HxBDD, but not well with 1,2,3,4,7,8-HxBDD, the structure which was previously assigned. The present study has established that 1,2,3,4,7,8-HxBDD would coelute with 1,2,3,6,7,8-HxBDD, at the *I* value of the major-product chromatographic peak from that synthesis: commercial standards of these two HxBDDs, not available at the time of the synthetic study, eluted at *I* values of 3534 and 3533, respectively. Their melting points have been reported as 339–341°C and 385–388°C, respectively [33]. These revised structural assignments for electrophilic bromination products are reasonable for the proposed synthetic ordering of substitutions and are in agreement with the observed *I* values of the products.

Thus, the significance of the model for HDD is that it is an effective tool for predicting elution order and relative retention times when relatively slow, linear temperature programs are employed with a non-polar or very slightly polar GC column. The model also provides good estimates of the retention index spacing between isomers within a congener group.

Retention indices of PBDF

In the PBDF series, only four standards were commercially available: 2,3,7,8-tetrabromodibenzofuran (TBDF); 1,2,3,7,8- and 2,3,4,7,8-pentabromodibenzofurans (PeBDFs), and 1,2,3,4,7,8-hexabromodibenzofuran (HxBDF). Octabromodibenzo-furan (OBDF) was available from recent electrophilic bromination synthetic efforts [26]. Other synthetic products structure assignments made in that report could not be completely unambiguous, due to the lack of authentic standards [26]. Fortunately, several pyrolysates of a PBT thermoplastic resin, which had been flame-retarded with decabromodiphenyl ether, were available and contained a great number of chromatographically separable PBDF.

The substitution patterns *versus* retention indices for the PBDFs were assigned to the observed pyrolysate PBDF chromatographic peaks (see Table IV and Fig. 3) in

TABLE IV

RETENTION INDICES FOR PCDF AND PBDF

Congener	I (PCDF) model [24]	I (PCDF) exptl. [24]	Δ (Exptl. − model)	I (PCDF) exptl. [34,35]	I (PBDF) exptl.
1-	1728	1739	11		1837
3-	1745	1749	4		1849
2-	1751	1749	−2		1851
4-	1761	1760	−1		1865
1,3-	1875	1884	9		2098
1,7-	1908	1910	2		2122
2,4-	1914	1912	−2		2122
1,4-	1901	1913	12		2122
1,8-	1913	1925	12		2130
1,6-	1923				2130
3,7-	1925	1930	5		2137
2,7-	1931	1930	−1		2137
1,2-	1936	1934	−2		2146
2,8-	1936	1935	−1		2147
2,3-	1954	1939	−15		2150
3,6-	1941	1944	3		2156
2,6-	1946	1946	0		2156
4,6-	1947	1953	6		2158
3,4-	1964	1959	−5		2176
1,9-	1982	1975	−7		2182
1,3,7-	2055	2057	2		2396
1,3,8-	2060	2070	10		2401
1,3,6-	2071	2072	1		2401
2,4,9-	2076	2082	6		2409
1,2,4-	2084	2085	1		2418
1,4,7-	2081	2086	5		2418
1,3,4-	2079	2088	9		2424
1,4,6-	2087	2094	7		2437
2,4,8-	2099	2097	−2		2441
2,4,7-	2094	2099	5		2452
1,4,8-	2087	2100	13		2452
2,4,6-	2100	2101	1		2452
1,2,7-	2116	2109	−7		2459
2,3,9-	2116	2111	−5		2462
1,2,3-	2123	2113	−10		2462
1,3,9-	2129	2124	−5		2466
3,4,9-	2126	2125	−1		2466
1,2,6-	2132	2125	−7		2466
1,2,8-	2121	2129	8		2470
2,3,8-	2139	2132	−7		2478
2,3,7-	2134	2134	0		2478
2,3,6-	2149	2141	−8		2479
2,3,4-	2156	2148	−8		2490
3,4,7-	2144	2150	6		2491
3,4,8-	2149	2151	2		2491
1,4,9-	2155	2151	−4		2491
3,4,6-	2150	2152	2		2491
1,2,9-	2190				2518
1,3,6,8-	2224	2227	3	2278	2688

TABLE IV *(continued)*

Congener	*I* (PCDF) model [24]	*I* (PCDF) exptl. [24]	*Δ* (Exptl. − model)	*I* (PCDF) exptl. [34,35]	*I* (PBDF) exptl.
1,4,6,8-	2240	2242	2	2297	2708
2,4,6,8-	2252	2254	2	2313	2725
1,3,4,7-	2259	2257	−2	2310	2727
1,3,4,6-	2265	2262	−3	2322	2730
1,3,7,8-	2264	2263	−1	2313	2730
1,2,4,7-	2264	2264	0	2316	2730
1,2,4,6-	2270	2264	−6	2326	2730
1,3,6,7-	2274	2272	−2	2323	2739
1,3,7,9-	2277	2273	−4	2335	2744
1,2,4,8-	2270	2274	4	2335	2744
1,3,4,8-	2264	2276	12	2332	2745
1,2,6,8-	2284	2281	−3	2339	2748
1,4,6,7-	2290	2288	−2	2340	2750
1,4,7,8-	2290	2290	0	2338	2754
1,2,3,7-	2303	2294	−9	2350	2761
1,3,6,9-	2303	2296	−7	2358	2771
2,3,6,8-	2302	2297	−5	2358	2772
2,4,6,7-	2303	2305	2	2357	2786
1,2,3,6-	2318	2307	−11	2365	2788
1,2,3,8-	2308	2307	−1	2366	2788
2,3,4,9-	2318	2308	−10	2377	2792
1,2,3,4-	2318	2310	−8	2369	2792
1,4,6,9-	2319	2314	−5	2363	2795
1,2,7,8-	2324	2322	−2	2378	2800
1,3,4,9-	2333	2325	−8	2394	2803
1,2,6,7-	2335	2329	−6	2398	2809
1,2,4,9-	2339	2335	−4	2394	2813
2,3,4,7-	2336	2337	1	2394	2816
2,3,7,8-	2342	2338	−4	2391	2816[a]
2,3,4,6-	2342	2339	−3	2406	2816
2,3,4,8-	2342	2340	−2	2397	2816
1,2,7,9-	2338	2341	3	2398	2816
2,3,6,7-	2353	2354	1	2413	2825
3,4,6,7-	2353	2362	9	2423	2829
1,2,6,9-	2364	2364	0	2420	2832
1,2,3,9-	2377	2369	−8	2432	2837
1,2,8,9-	2398	2406	8	2472	2852
1,3,4,6,8-	2418				3015
1,2,4,6,8-	2423				3020
1,2,4,6,7-	2473	2465	−8	2501	3082
2,3,4,7,9-	2466	2467	1	2496	3088
1,3,4,7,8-	2468	2469	1	2502	3092
1,3,4,6,7-	2468	2469	1	2495	3092
1,2,3,6,8-	2471				3094
1,2,4,7,8-	2473			2505	3094
1,3,4,7,9-	2481	2473	−8	2503	3098
2,3,4,6,9-	2482	2476	−6	2511	3100
1,2,4,7,9-	2486	2479	−7		3112
2,3,4,6,8-	2495	2495	0	2530	3133
1,2,3,4,7-	2497	2495	−3	2532	3133

TABLE IV *(continued)*

Congener	*I* (PCDF) model [24]	*I* (PCDF) exptl. [24]	*Δ* (Exptl. − model)	*I* (PCDF) exptl. [34,35]	*I* (PBDF) exptl.
1,3,4,6,9-	2497			2522	
1,2,3,4,6-	2504	2496	−8	2530	3133
1,2,4,6,9-	2502	2497	−5		3133
1,2,3,7,8-	2511	2507	−4	2549	3145[a]
1,2,3,4,8-	2503	2508	5	2541	3150
2,3,4,8,9-	2527	2521	−6	2560	3152
1,2,3,7,9-	2524			2562	3159
1,2,3,6,7-	2522	2540	18	2557	3164
1,3,4,8,9-	2542				3172
1,2,3,6,9-	2551	2546	−5	2575	3185
2,3,4,7,8-	2545	2551	6	2586	3188[a]
2,3,4,6,7-	2545	2555	10	2598	
1,2,4,8,9-	2547	2559	12	2590	
1,2,3,4,9-	2572			2603	
1,2,3,8,9-	2585	2593	8		
1,2,3,4,6,8-	2656	2650	−6		3431
1,3,4,6,7,8-	2660				3437
1,2,4,6,7,8-	2665				3439
1,3,4,6,7,9-	2675				
1,2,4,6,7,9-	2680				
1,2,4,6,8,9-	2685	2686	1		
1,2,3,4,6,7-	2707	2706	−1		3514
1,2,3,4,7,8-	2706	2708	2		3520[a]
1,2,3,6,7,8-	2714				3522
1,2,3,4,7,9-	2719	2720	1		3529
1,2,3,6,7,9-	2728				3521
1,2,3,6,8,9-	2734				
1,2,3,4,6,9-	2736				3548
2,3,4,6,7,8-	2737	2748	11		3548
1,2,3,7,8,9-	2772				
1,2,3,4,8,9-	2780				
1,2,3,4,6,7,8-	2899	2898	−1		3856[b]
1,2,3,4,6,7,9-	2914	2913	−1		
1,2,3,4,6,8,9-	2919	2922	3		
1,2,3,4,7,8,9-	2967	2986	19		
1,2,3,4,6,7,8,9-	3152	3147	−5		4259[b]

[a] Assignment verified with commercial standard.
[b] *I* beyond linear temperature ramp; *I* interpolated using values obtained with faster temperature programs.

a manner consistent with the experimentally observed order of elution reported by Hale *et al.* [24]. Retention index predictions and experimentally observed *I* values for PCDFs [24] were included in Table IV for reference; experimental *I* values for tetrachlorodibenzofuran (TCDF) [34] and pentachlorodibenzofuran (PeCDF) [35] obtained by Chittim and co-workers were also included in Table IV. In this study, the assumption was made that the order of elution for PBDFs would follow that of
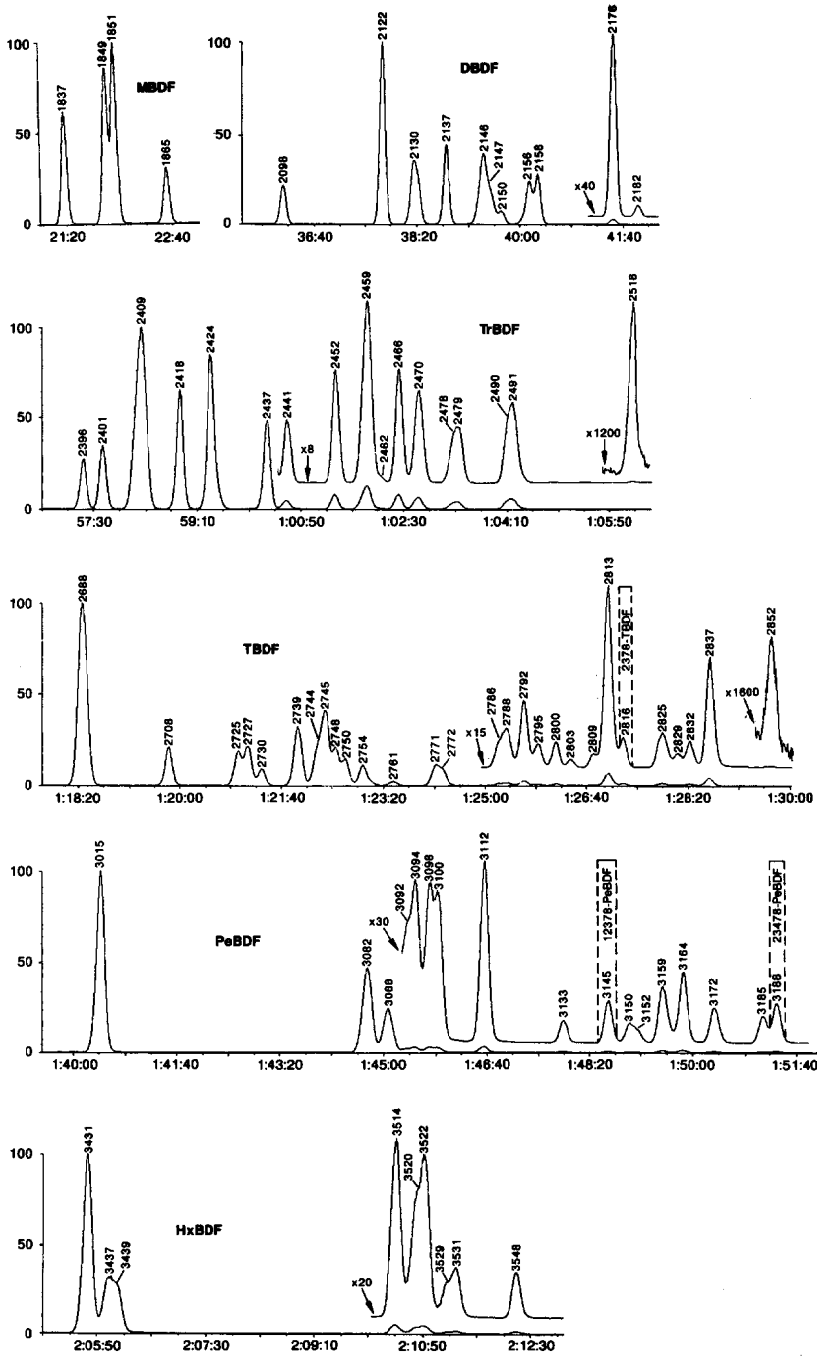
Fig. 3. Mass chromatograms of PBDFs in PBT resin pyrolysates.

PCDFs, and that compounds separated by 1 or 2 I units probably would coelute on the GC column, as was observed for HDD standards. The experimental elution order reported by Hale et al. [24] for 115 of the 135 possible PCDF congeners was used as the basis for PBDF isomer assignments. This elution order varied slightly from that predicted by their model, and also from that reported under somewhat different experimental conditions by Chittim and co-workers [34,35] for a limited number of congeners.

For the lower congeners (mono- through tetrabromodibenzofuran), all expected resolvable or partially resolvable peaks were observed in the pyrolysate, allowing excellent correlation of isomer assignments to observed I values. Isomer-to-isomer spacing of the lower congeners indicated that 1,9-substitution affected the retention index in magnitude similar to that observed in the chloro series. For the penta-, hexa-, and heptabromo (PeBDF, HxBDF, HpBDF) congeners, fewer peaks were observed than would be possible. This observation was valuable when combined with synthetic results [26], discussion in a patent document [36], and X-ray diffraction results [37] that demonstrated the difficulty of obtaining PBDF with 1,9-bromine substitution, particularly when buttressed by bromine substituents at the 2- and 8-positions. The number and spacing of apparently "missing" chromatographic peaks in the higher brominated congeners correlated well with expected I values for 1,9-substituted PBDFs.

In addition to those PBDF I assignments which were verified by standards, some other I values have an increased probability that their isomer assignments are correct. In certain situations, a few chromatographic peaks were bracketed by commercially available standards, or by one standard and the beginning or end of that congener elution profile. For example, four monobromodibenzofurans are possible and were observed; five chromatographically resolved TBDF peaks are expected and were observed after the elution of 2,3,7,8-TBDF; six peaks are expected and were observed between 1,2,3,7,8-PeBDF and 2,3,4,7,8-PeBDF.

The model for the PCDFs might also be applicable (with suitable modifications) to the PBCDFs; standards were not commercially available to test this suggestion.

CONCLUSION

A comprehensive model-correlating structure with GC retention index has been developed and shown to be applicable to brominated, chlorinated, and bromo-chlorinated dioxins (HDDs). The strategy for testing this applicability involved the synthesis of HDD isomer and congener standards and mixtures in addition to the use of commercially available standards. Most members of the PBDF series were prepared efficiently by the pyrolysis of a decabromodiphenyl ether flame-retarded resin, augmenting the few available reference standards for interim retention index assignments. PBDF structural assignments were then correlated with the reported elution order of PCDFs. Because of the current lack of sufficient, authentic standards for the various HDDs and HDFs, the retention index strategy and these interim structural assignments are important to the monitoring of commercial products, synthetic mixtures, environmental samples, and combustion residues for the regulated, high-TEF 2,3,7,8-substituted HDDs and HDFs.

NOTICE

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