

Synthesis, Structure Verification, and Chromatographic Relative Retention Times for Polychlorinated Diphenyl Ethers

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Fifty-four polychlorinated diphenyl ether (PCDEs) congeners were synthesized, and their structures were confirmed by mass spectrometry and proton magnetic resonance spectroscopy. The gas chromatographic relative retention times (RRT) for the PCDEs were determined relative to a reference standard, [¹³C-3,3',4,4']-tetrachlorobiphenyl (PCB 77) on the fused silica capillary columns of SE-54 and OV-1701. The retention times for PCDEs increased with the increasing number of vicinal chlorines within a series of isomers. The chlorine substitution patterns of PCDEs were used to develop a method for predicting RRTs for congeners that were not synthesized.

Introduction

Polychlorinated diphenyl ethers (PCDEs) are becoming of great concern because of their structural and toxicological similarity to polychlorinated biphenyls (PCBs) (1). However, very little toxicity data are available for PCDEs, which makes the estimation of the environmental hazard of PCDEs difficult. Howie *et al.* have determined ED₅₀ values for immunotoxicity and AHH and EROD induction for eight PCDE congeners (2). The toxic equivalence factor (TEF) proposed by Safe for non- and mono-*ortho*-substituted PCDEs is 0.001 (3), which is the same as for mono-*ortho*-coplanar PCBs.

PCDEs arise as impurities in technical chlorophenol preparations and in chlorinated phenoxyacetic acids (4-7). In addition PCDEs have also been identified in emissions from municipal waste incinerators (8). PCDE residues have been found in several environmental samples including sediments, fish, wildlife, and human tissues (9-14). The levels of PCDEs are often higher than those of polychlorinated dibenzofurans (PCDFs). For example, the levels of PCDEs in fish have been measured 10-50 times higher (15). A recent study of PCDEs and other organochlorines in white-tailed eagles from the Baltic Sea environment showed the presence of about 30 PCDE congeners (of the 50 studied here) at levels ranging from 5 to 13 000 ng/g of lipid weight (16). The major congeners of identified PCDEs were 47, 99, 147/153 (coeluting), 196, 180/181 (coeluting), 182 and 197 [numbered as PCBs according to the system of Ballschmiter and Zell (17)].

The synthesis of about 100 congeners of the 209 possible PCDEs have been published (including congeners synthesized in this work) (18) so far. Some studies on synthetic routes to PCDEs have been reviewed (19, 20). The coupling reaction between diphenyliodonium salt and chlorophenol is the most convenient route for the synthesis of PCDEs (21). This paper reports the synthesis, mass spectra, and proton magnetic resonance (¹H NMR) spectra and the relative retention times (RRT) of 54 PCDE

Table 1. Diphenyliodonium Salts Synthesized

diphenyliodonium salt		anion	yield (%)
diphenyl-	I	Br ⁻	57
4,4'-dichloro-	II	Cl ⁻	57
2,2',4,4'-tetrachloro-	III	Cl ⁻	39
3,3',4,4'-tetrachloro-	IV	Cl ⁻	38
2,2',3,3',4,4'-hexachloro-	V	HSO ₄ ⁻	48
2,2',4,4',5,5'-hexachloro-	VI	HSO ₄ ⁻	62
2,2',4,4',6,6'-hexachloro-	VII	HSO ₄ ⁻	12
2,2',3,3',4,4',5,5'-octachloro-	VIII	HSO ₄ ⁻	50
2,2',3,3',4,4',6,6'-octachloro-	IX	HSO ₄ ⁻	4

congeners. In addition, a model is developed describing the relationship between the RRTs and the chlorine substitution pattern of PCDEs. This model could be useful for identifying synthetic products as well as unknown PCDEs found in environmental analysis.

Materials and Methods

Chemicals. The PCDE congeners were synthesized from the respective chlorinated diphenyliodonium salt and chlorinated phenol by a procedure analogous to that of Nilsson *et al.* using 3 mmol quantities of reactants (21). The products were purified by a silica gel column chromatography eluting with *n*-hexane. Chlorinated diphenyliodonium salts (Table 1) were prepared by the oxidative coupling of iodyl sulfate with a chlorobenzene as previously described (21, 22). The decachloroDE (209) was prepared by direct chlorination of octa- and nonachlorinated diphenyl ethers in CCl₄ using AlCl₃ as catalyst. For the preparation of diphenyliodonium bromide, the following modified procedure was used (23, 24).

Synthesis of Diphenyliodonium Bromide. A total of 20 mmol (4.3 g) of potassium iodate was introduced into 17 mL of concentrated sulfuric acid, and 7 mmol (1.8 g) of iodine was added at 15-20 °C. After being stirred for 15 h, the iodyl sulfate was filtered. The obtained iodyl sulfate was suspended in 25 mL of concentrated sulfuric acid kept below 10 °C. To this mixture was added 15 mL of acetic anhydride and then 20 mL of benzene. After 2 h, the reaction mixture was cooled in an ice bath and treated with 200 mL of water and filtered. The filtrate was extracted three times with ethyl acetate and three times with ether. The addition of 10 g of sodium bromide in water precipitated diphenyliodonium bromide as small needles.

NMR and Mass Spectra. The chemical structures of the individual PCDE congeners synthesized were confirmed by mass spectrometry and proton magnetic resonance (¹H NMR) spectra. The ¹³C NMR data of 28 PCDE congeners have been published previously (25). The starting materials, yields, and melting points of PCDEs synthesized are shown in Table 2. The ¹H NMR spectra

Table 2. Starting Materials, Yields, and Melting Points of PCDEs Synthesized

PCDE	R	R'	iodonium salt	chloro-phenol	yield (%)	mp (°C)
8	2-	4-	II	2-	33	oil
13	3-	4-	II	3-	87	oil
15	4-	4-	II	4-	56	oil
22	2,3-	4-	II	2,3-	56	oil
28	2,4-	4-	II	2,4-	29	oil
32	2,6-	4-	II	2,6-	41	oil
37	3,4-	4-	II	3,4-	57	oil
47	2,4-	2,4-	III	2,4-	90	69-70
49	2,4-	2,5-	III	2,5-	46	oil
51	2,4-	2,6-	III	2,6-	62	oil
62	2,3,4,6-		I	2,3,4,6-	47	oil
66	2,4-	3,4-	III	3,4-	74	oil
68	2,4-	3,5-	III	3,5-	62	oil
71	2,6-	3,4-	IV	2,6-	12	86-8
74	2,4,5-	4-	II	2,4,5-	55	62-3
77	3,4-	3,4-	IV	3,4-	51	69-71
85	2,3,4-	2,4-	V	2,4-	54	65-7
89	2,3,4-	2,6-	V	2,6-	37	109-10
90	2,3,5-	2,4-	III	2,3,5-	60	57-8
99	2,4,5-	2,4-	VI	2,4-	54	oil
100	2,4,6-	2,4-	III	2,4,6-	67	45-6
101	2,4,5-	2,5-	VI	2,5-	56	oil
105	2,3,4-	3,4-	V	3,4-	40	64-6
116	2,3,4,5,6-		I	2,3,4,5,6-	79	138-9
118	2,4,5-	3,4-	VI	3,4-	47	oil
119	2,4,6-	3,4-	IV	2,4,6-	28	oil
126	3,4,5-	3,4-	IV	3,4,5-	44	68-70
128	2,3,4-	2,3,4-	V	2,3,4-	24	141-2
137	2,3,4,5-	2,4-	III	2,3,4,5-	90	78-80
138	2,3,4-	2,4,5-	VI	2,3,4-	71	69-70
140	2,3,4-	2,4,6-	V	2,4,6-	17	120-2
147	2,3,5,6-	2,4-	III	2,3,5,6-	24	110-1
153	2,4,5-	2,4,5-	VI	2,4,5-	52	113-5
154	2,4,5-	2,4,6-	VI	2,4,6-	62	94-6
156	2,3,4,5-	3,4-	VIII	3,4-	82	134-6
157	2,3,4-	3,4,5-	V	3,4,5-	35	157-8
163	2,3,5,6-	3,4-	IV	2,3,5,6-	57	119-20
167	2,4,5-	3,4,5-	VI	3,4,5-	53	104-5
170	2,3,4,5-	2,3,4-	V	2,3,4,5-	39	105-6
172	2,3,4,5-	2,3,5-	VIII	2,3,5-	22	108-10
177	2,3,5,6-	2,3,4-	V	2,3,5,6-	36	156-7
180	2,3,4,5-	2,4,5-	VI	2,3,4,5-	51	88-90
181	2,3,4,5,6-	2,4-	III	2,3,4,5,6-	54	113-4
182	2,3,4,5-	2,4,6-	VIII	2,4,6-	25	136-8
187	2,3,5,6-	2,4,5-	VI	2,3,5,6-	68	117-9
190	2,3,4,5,6-	3,4-	IV	2,3,4,5,6-	35	117-9
194	2,3,4,5-	2,3,4,5-	VIII	2,3,4,5-	24	125-8
195	2,3,4,5,6-	2,3,4-	V	2,3,4,5,6-	30	166-7
196	2,3,4,6-	2,3,4,5-	VIII	2,3,4,6-	36	147-9
197	2,3,4,6-	2,3,4,6-	IX	2,3,4,6-	43	124-6
203	2,3,4,5,6-	2,4,5-	VI	2,3,4,5,6-	58	167-8
204	2,3,4,5,6-	2,4,6-	VII	2,3,4,5,6-	9	142-4
206	2,3,4,5,6-	2,3,4,5-	VIII	2,3,4,5,6-	29	176-7
209	2,3,4,5,6-	2,3,4,5,6-			90	220-2

were recorded on a JEOL GSX 270 FT NMR spectrometer in acetone- d_6 or in $CDCl_3$. The chemical shifts are referenced to internal tetramethylsilane (TMS). The EI mass spectra were recorded at 70 eV using a Hewlett-Packard 5970 mass selective detector system. A 25-m SE-54 column (HP-5; 0.2-mm i.d., 0.33- μ m film thickness) was connected to the HP 5890 gas chromatograph. The temperature was programmed from 100 °C after 1 min isothermal time at 20 °C/min to 180 °C, then at 5 °C/min to 290 °C, and was held there 15 min. Mass spectra and 1H NMR data are summarized in Tables 3 and 4.

Chromatography. The high-resolution capillary gas chromatography was performed on a Micromat HRGC 412 (Nordion Instruments Oy Ltd) gas chromatograph equipped with two ^{63}Ni electron capture detectors and

two 25-m fused silica capillary columns. Columns coated with SE-54 and OV-1701 were used to separate the PCDE isomers and congeners. The temperature program was from 150 °C at 5 °C/min to 250 °C and held for 20 min. The injector temperature was 250 °C. The temperature program was not optimized for low chlorinated congeners. The relative retention times for the PCDEs were expressed relative to the [^{13}C -3,3',4,4']-tetrachlorobiphenyl (PCB 77). This compound was selected because it had been used as an internal standard in an earlier work (26).

Results and Discussion

Synthesis. The coupling reaction of diphenyliodonium salts with chlorinated phenols was described earlier by Crowder *et al.* (27). It has proven to be the most successful route to these compounds, because the majority of PCDEs can be prepared via this route (20). The method for the preparation of diphenyliodonium salts was originally published by Beringer *et al.* (22), and it was afterwards modified to a simplified and less time-consuming procedure by Nilsson *et al.* (21). Theoretically, the possibility of forming different isomers of diphenyliodonium salts exists, but in all cases synthesis gave only one symmetrical iodonium salt. In the coupling reaction, chlorinated iodobenzene was formed as a side product, and in some cases other iodinated compounds such as chlorinated iododiphenyl ethers were formed. In most cases, PCDEs were obtained in the pure state after silica gel column chromatography.

Mass Spectra of PCDEs. The individual PCDE isomers have very similar spectral patterns to one another, except for the difference of chlorine number in the molecule. Therefore, the structural difference cannot be determined by the mass spectral patterns. The characteristic features of the mass spectra of PCDEs are the chlorine clusters of molecular ion M^{*+} and fragment ion ($M - 2Cl$; $M - 70$) $^{*+}$ (28). The latter was the base peak for all PCDEs studied except those having no *ortho* chlorines in their molecule. In such cases, the base peak was M^{*+} and instead of ($M - 2Cl$) $^{*+}$, the ($M - COCl$; $M - 63$) $^{*+}$ ion was observed as a major fragment ion. Also in some 2,4- or 2,4,6-substituted congeners, including PCDEs 28, 47, 51, 99, 100, 119, 140, 154, and 184, the base peak was M^{*+} , or it was almost as intense as the fragment ($M - 2Cl$) $^{*+}$. Some typical minor fragment ions were ($M - HCl - COCl$; $M - 99$) $^{*+}$, ($M - 2Cl - COCl$, $M - 133$) $^{*+}$, and ($M - 4HCl - COCl$; $M - 207$) $^{*+}$. Two examples of the EI mass spectra of PCDEs are presented in Figure 1. Mass spectral fragmentation results are in good agreement with those reported previously by Humppi (29). Congeners with one ring unsubstituted gave intense fragments at $m/e = 51$ and $m/e = 77$ (C_6H_5). Congeners with a *p*-chlorine as the only substituent at one ring gave fragments at $m/e = 75$ and $m/e = 111$ (C_6H_4Cl), as was previously reported (30). The fragments at $m/e = 74$ and $m/e = 109$ were typical for all other PCDEs. PCDEs can interfere with the MS detection of polychlorinated dibenzofurans (PCDFs) with two less chlorine atoms by the fragment ion ($M - 2Cl$) $^{*+}$, that corresponds to the M^{*+} ion for PCDFs (28).

1H NMR Spectra. Protons of PCDEs occur in the shift region $\delta = 6.3$ -8.1 ppm. Shifts of *ortho* protons to the etheral oxygen are at higher field region than those in the *meta* and *para* positions. The smallest 1H chemical shifts are found for *ortho*-hydrogens of tri-*ortho*-substituted

Table 3. Mass Spectral Data for PCDEs

PCDE	exact mass of M ⁺	molecular formula	mass spectra ^a m/e (rel. int., %)
8	237.9952	C ₁₂ OCl ₂ H ₈	168 (100), 238 (80), 203 (35), 75 (33), 139 (17), 111 (10)
13	237.9952	C ₁₂ OCl ₂ H ₈	238 (100), 175 (70), 75 (45), 168 (30), 111 (17), 139 (15)
15	237.9952	C ₁₂ OCl ₂ H ₈	238 (100), 175 (70), 75 (45), 168 (30), 139 (15), 111 (17)
22	271.9562	C ₁₂ OCl ₃ H ₇	202 (100), 272 (60), 75 (27), 237 (20), 173 (10), 139 (8), 111 (8)
28	271.9562	C ₁₂ OCl ₃ H ₇	202 (100), 272 (90), 75 (30), 111 (15), 237 (12), 173 (9), 139 (8)
32	271.9562	C ₁₂ OCl ₃ H ₇	202 (100), 272 (80), 75 (28), 237 (17), 111 (12), 173 (10), 139 (8)
37	271.9562	C ₁₂ OCl ₃ H ₇	272 (100), 209 (32), 75 (27), 202 (25), 111 (12), 139 (8), 173 (7)
47	305.9173	C ₁₂ OCl ₄ H ₆	308 (100), 236 (75), 109 (27), 133 (25), 75 (25), 173 (10), 271 (5)
49	305.9173	C ₁₂ OCl ₄ H ₆	236 (100), 308 (45), 75 (22), 109 (20), 133 (18), 271 (10), 173 (10)
51	305.9173	C ₁₂ OCl ₄ H ₆	308 (100), 236 (90), 75 (18), 133 (15), 109 (15), 173 (10), 271 (5)
62	305.9173	C ₁₂ OCl ₄ H ₆	236 (100), 77 (68), 51 (55), 308 (38), 271 (12), 133 (12), 173 (10)
66	305.9173	C ₁₂ OCl ₄ H ₆	236 (100), 308 (86), 109 (41), 75 (40), 133 (23), 271 (20), 173 (13)
68	305.9173	C ₁₂ OCl ₄ H ₆	236 (100), 308 (68), 271 (38), 109 (16), 75 (16), 133 (12), 173 (8)
71	305.9173	C ₁₂ OCl ₄ H ₆	236 (100), 308 (70), 109 (18), 75 (17), 271 (17), 133 (12), 173 (8)
74	305.9173	C ₁₂ OCl ₄ H ₆	236 (100), 308 (85), 75 (28), 111 (15), 271 (13), 173 (10)
77	305.9173	C ₁₂ OCl ₄ H ₆	308 (100), 243 (32), 109 (25), 75 (24), 236 (17), 133 (10), 173 (7)
85	339.8783	C ₁₂ OCl ₅ H ₅	272 (100), 342 (82), 109 (12), 74 (12), 307 (7)
89	339.8783	C ₁₂ OCl ₅ H ₅	272 (100), 342 (57), 74 (25), 109 (23), 307 (6)
90	339.8783	C ₁₂ OCl ₅ H ₅	272 (100), 342 (40), 74 (19), 109 (17), 307 (11)
99	339.8783	C ₁₂ OCl ₅ H ₅	272 (100), 342 (97), 109 (15), 74 (12), 307 (6)
100	339.8783	C ₁₂ OCl ₅ H ₅	272 (100), 342 (97), 109 (15), 74 (12), 307 (6)
101	339.8783	C ₁₂ OCl ₅ H ₅	272 (100), 342 (65), 109 (22), 74 (19), 307 (14)
105	339.8783	C ₁₂ OCl ₅ H ₅	272 (100), 342 (58), 109 (16), 74 (14), 307 (12)
116	339.8783	C ₁₂ OCl ₅ H ₅	272 (100), 77 (57), 51 (43), 342 (38), 307 (9)
118	339.8783	C ₁₂ OCl ₅ H ₅	272 (100), 342 (80), 109 (18), 307 (15), 74 (10)
119	339.8783	C ₁₂ OCl ₅ H ₅	272 (100), 342 (87), 109 (22), 74 (18), 307 (15)
126	339.8783	C ₁₂ OCl ₅ H ₅	342 (100), 279 (28), 109 (20), 74 (15), 272 (13)
128	373.8393	C ₁₂ OCl ₆ H ₄	306 (100), 376 (47), 169 (9), 109 (9), 74 (9), 341 (5)
137	373.8393	C ₁₂ OCl ₆ H ₄	306 (100), 376 (58), 133 (12), 109 (10), 74 (10), 341 (6)
138	373.8393	C ₁₂ OCl ₆ H ₄	306 (100), 376 (70), 169 (12), 109 (11), 74 (10), 341 (6)
140	373.8393	C ₁₂ OCl ₆ H ₄	376 (100), 306 (95), 169 (17), 109 (15), 74 (12), 341 (6)
147	373.8393	C ₁₂ OCl ₆ H ₄	306 (100), 376 (47), 133 (17), 109 (15), 74 (12), 341 (6)
153	373.8393	C ₁₂ OCl ₆ H ₄	306 (100), 376 (57), 109 (14), 169 (13), 74 (12), 341 (6)
154	373.8393	C ₁₂ OCl ₆ H ₄	376 (100), 306 (92), 169 (20), 109 (15), 74 (12), 341 (6)
156	373.8393	C ₁₂ OCl ₆ H ₄	306 (100), 376 (40), 109 (17), 74 (10), 341 (9)
157	373.8393	C ₁₂ OCl ₆ H ₄	306 (100), 376 (60), 341 (15), 109 (12), 74 (11), 169 (10)
163	373.8393	C ₁₂ OCl ₆ H ₄	306 (100), 376 (23), 109 (18), 341 (13), 153 (9), 74 (9)
167	373.8393	C ₁₂ OCl ₆ H ₄	data not available
170	407.8004	C ₁₂ OCl ₇ H ₃	340 (100), 410 (37), 375 (10), 169 (7), 74 (5)
172	407.8004	C ₁₂ OCl ₇ H ₃	340 (100), 410 (34), 375 (12), 169 (8), 109 (7), 74 (6)
177	407.8004	C ₁₂ OCl ₇ H ₃	340 (100), 410 (45), 375 (13), 169 (10), 109 (7), 74 (6)
180	407.8004	C ₁₂ OCl ₇ H ₃	340 (100), 410 (40), 375 (7), 169 (7), 109 (6), 74 (5)
181	407.8004	C ₁₂ OCl ₇ H ₃	340 (100), 410 (54), 109 (21), 133 (15), 74 (13), 375 (6)
182	407.8004	C ₁₂ OCl ₇ H ₃	340 (100), 410 (42), 169 (11), 109 (8), 375 (6), 74 (5)
187	407.8004	C ₁₂ OCl ₇ H ₃	340 (100), 410 (57), 169 (12), 375 (10), 109 (10), 74 (6)
190	407.8004	C ₁₂ OCl ₇ H ₃	340 (100), 410 (34), 109 (20), 74 (14), 375 (10)
194	441.7614	C ₁₂ OCl ₈ H ₂	374 (100), 446 (30), 311 (12), 409 (6)
195	441.7614	C ₁₂ OCl ₈ H ₂	374 (100), 446 (38), 311 (11), 409 (8)
196	441.7614	C ₁₂ OCl ₈ H ₂	374 (100), 446 (41), 311 (12), 409 (6)
197	441.7614	C ₁₂ OCl ₈ H ₂	374 (100), 446 (67), 311 (10), 409 (3)
203	441.7614	C ₁₂ OCl ₈ H ₂	374 (100), 446 (46), 311 (9), 409 (5)
204	441.7614	C ₁₂ OCl ₈ H ₂	374 (100), 446 (52), 204 (12), 409 (3)
206	475.7224	C ₁₂ OCl ₉ H	408 (100), 480 (40), 345 (17), 445 (6)
209	509.6834	C ₁₂ OCl ₁₀	444 (100), 514 (41), 237 (22), 379 (13), 479 (6)

^a Only the most abundant peak of each molecular cluster shown.

PCDEs. The tri-*ortho*-substituted PCDEs adopt a skew conformation (31) where the *ortho* aromatic hydrogen lies below the adjacent ring and is shielded by the ring current effect of the neighboring ring. The *ortho* coupling constants (³J_{HH}) vary from 7.8 to 9.2 Hz. The largest couplings were found in the 2,3,4-substituted ring (³J_{H-5,H-6} > 9 Hz). The *meta* couplings (⁴J_{HH}) range from 1.6 to 3.0 Hz.

Chromatographic Properties and Prediction of Relative Retention Times (RRTs). The RRTs for isomeric homologues are highly dependent on the structure. The RRT for any given PCDE can be predicted using only a knowledge of its chlorine substitution pattern. The calculated 1/2(RRT) values are useful in checking gas chromatographic retention data for internal consistency. It can aid in structure assignment of a specific

congener, whether obtained from synthesis or found in environmental monitoring. The PCDE molecule can be thought to be composed of 20 basic *chloro*-substituted phenyl groups each with its own half relative retention time 1/2(RRT). This approach was applied successfully for the calculation of retention indices (RI) to chlorinated biphenyls (32).

The RRT for each specific isomer can be expressed as the sum of these 1/2(RRT) values. The 1/2(RRT) values were determined by multiple linear regression analysis for all possible chlorination patterns except for the 2,3,6-substituted ring, because that pattern was absent from the rings of 54 PCDE congeners studied here. Each of the 19 chlorine substitution variables appearing in the PCDEs studied takes the values 0, 1, and 2, depending on whether that pattern does not occur, occurs once, or occurs twice

Table 4. ¹H NMR Spectra of PCDEs

PCDE	¹ H NMR, δ (ppm from TMS)
8	7.42 (H-3, dd, $J = 7.8, 1.6$ Hz), 7.06 (H-4, t, $J = 7.8$ Hz, d, $J = 1.6$ Hz), 7.19 (H-5, t, $J = 8.0$ Hz, d, $J = 1.6$ Hz), 6.96 (H-6, dd, $J = 8.0, J = 1.6$ Hz), 6.85 (H-2',4', d, $J = 8.8$ Hz, t, $J = 2.8$ Hz), 7.24 (H-3',5', d, $J = 8.8$ Hz, t, $J = 2.8$ Hz)
13	6.95 (H-2, t, $J = 2.0$ Hz), 7.02 (H-4, d, $J = 8.1$ Hz, dd, $J = 1.0, 2.0$ Hz), 7.16 (H-5, t, $J = 8.2$ Hz), 6.81 (H-6, d, $J = 8.2$ Hz, dd, $J = 1.0, 2.3$ Hz), 6.88 (H-2',6', d, $J = 8.6$ Hz, t, $J = 2.7$ Hz), 7.23 (H-3',5', d, $J = 8.6$ Hz, t, $J = 2.7$ Hz)
15	6.91 (H-2',5', d, $J = 8.7$ Hz, t, $J = 2.8$ Hz), 7.28 (H-3',5', d, $J = 8.7$ Hz, t, $J = 2.8$ Hz)
22	7.19 (H-4, dd, $J = 8.2, 1.6$ Hz), 7.09 (H-5, t, $J = 8.2$ Hz), 6.82 (H-6, dd, $J = 8.2, 1.6$ Hz), 6.85 (H-2',6', d, $J = 9.0$ Hz, t, $J = 2.2$ Hz), 7.23 (H-3',5', d, $J = 9.0$ Hz, t, $J = 2.2$ Hz)
28	7.43 (H-3, d, $J = 2.5$ Hz), 7.17 (H-5, dd, $J = 8.7, 2.5$ Hz), 6.89 (H-6, d, $J = 8.7$ Hz), 6.85 (H-2',6', d, $J = 8.9$ Hz, t, $J = 2.7$ Hz), 7.26 (H-3',5', d, $J = 8.9$ Hz, t, $J = 2.7$ Hz)
32	7.34 (H-3,4, d, $J = 8.1$), 7.07 (H-4, t, $J = 8.1$ Hz), 6.75 (H-2',6', d, $J = 9.1$ Hz, t, $J = 2.3$ Hz), 7.21 (H-3',5', d, $J = 9.1$ Hz, t, $J = 2.3$ Hz)
37	7.06 (H-2, d, $J = 2.8$ Hz), 7.36 (H-5, d, $J = 8.9$ Hz), 6.8 (H-6, dd, $J = 8.87, 2.8$ Hz), 6.93 (H-2',6', $J = 9.0$ Hz, t, $J = 2.3$ Hz), 7.31 (H-3',5', $J = 9.0$ Hz, t, $J = 2.3$ Hz)
47	7.47 (H-3,3', d, $J = 2.6$ Hz), 7.18 (H-5,5', dd, $J = 8.9, 2.6$ Hz), 6.79 (H-6,6', d, $J = 2.6$ Hz)
49	7.47 (H-3, d, $J = 2.4$ Hz), 7.20 (H-5, dd, $J = 2.4, 8.9$ Hz), 6.86 (H-6, d, $J = 8.9$ Hz), 7.36 (H-3', d, $J = 8.5$ Hz), 7.05 (H-4', dd, $J = 8.5, 2.3$ Hz), 6.79 (H-6', d, $J = 2.3$ Hz)
51	7.47 (H-3, d, $J = 2.5$ Hz), 7.07 (H-5, dd, $J = 2.5, 8.8$ Hz), 6.37 (H-6, d, $J = 8.8$ Hz), 7.18 (H-4', dd, $J = 8.8, 2.5$ Hz), 7.41 (H-3',5', $J = 7.9$ Hz)
62	7.51 (H-5, s), 6.80 (H-2',6', m), 7.73 (H-3',5', m), 7.50 (H-4, m)
66	7.79 (H-3, d, $J = 2.6$ Hz), 7.40 (H-6, d, $J = 8.7$), 7.59 (H-5, dd, $J = 8.7, 2.6$), 7.72 (H-5', d, $J = 8.9$), 7.36 (H-2', d, $J = 2.9$), 7.13 (H-6', dd, $J = 8.9, 2.9$)
68	7.47 (H-3, d, $J = 2.5$ Hz), 7.24 (H-5, dd, $J = 2.5, 8.7$ Hz), 7.00 (H-6, d, $J = 8.7$ Hz), 7.07 (H-4', t, $J = 1.8$ Hz), 6.79 (H-2',6', $J = 1.8$ Hz)
71	7.39 (H-3,5, dd, $J = 7.7, 8.6$ Hz), 7.17 (H-4, t, $J = 7.9$ Hz), 6.93 (H-2', d, $J = 2.9$ Hz), 7.34 (H-5', d, $J = 8.9$ Hz), 6.70 (H-6', dd, $J = 8.9, 2.9$ Hz)
74	7.55 (H-3, s), 7.02 (H-6, s), 6.91 (H-2',6', d, $J = 8.7$ Hz, t, $J = 2.8$ Hz), 7.32 (H-3',5', d, $J = 8.7$ Hz, t, $J = 2.8$ Hz)
77	7.42 (H-5,5', d, $J = 8.9$ Hz), 7.11 (H-2,2', d, $J = 2.8$ Hz), 6.89 (H-6,6', dd, $J = 8.9, 2.8$ Hz)
85	7.48 (H-3', d, $J = 2.4$ Hz), 7.30 (H-5, d, $J = 9.0$ Hz), 7.23 (H-5', dd, $J = 8.8, 2.4$ Hz), 6.85 (H-6', d, $J = 8.8$ Hz), 6.69 (H-6, d, $J = 9.0$ Hz)
89	7.42 (H-3',5', d, $J = 8.1$ Hz), 7.19 (H-4', t, $J = 8.1$ Hz), 7.21 (H-5, d, $J = 9.1$ Hz), 6.33 (H-6, d, $J = 9.1$ Hz)
90	7.47 (H-3', d, $J = 2.5$ Hz), 7.23 (H-5', dd, $J = 2.5, 8.7$ Hz), 7.22 (H-4, d, $J = 2.2$ Hz), 6.93 (H-6', d, $J = 8.7$ Hz), 6.65 (H-6, d, $J = 2.2$ Hz)
99	7.54 (H-3, s), 7.47 (H-3', d, $J = 2.5$ Hz), 7.22 (H-5', dd, $J = 2.5, 8.7$ Hz), 6.89 (H-6', d, $J = 8.7$ Hz), 6.87 (H-6, s)
100 ^a	7.86 (H-3,5, s), 7.78 (H-3', d, $J = 2.6$ Hz), 7.42 (H-5', dd, $J = 2.6, 8.9$ Hz), 6.85 (H-6', d, $J = 8.9$ Hz)
101 ^a	7.99 (H-3, s), 7.76 (H-3', d, $J = 8.6$ Hz), 7.49 (H-6, s), 7.46 (H-4', dd, $J = 8.6, 2.3$ Hz), 7.37 (H-6', d, $J = 2.3$ Hz)
105 ^a	7.76 (H-5,6, t, $J = 9.2$ Hz), 7.47 (H-2', d, $J = 2.9$ Hz), 7.39 (H-5', d, $J = 8.9$ Hz), 7.21 (H-6', dd, $J = 8.9, 2.9$ Hz)
116	6.81 (H-2,6, $J = 8.3$ Hz), 7.30 (H-3,5, $J = 8.3$ Hz), 7.08 (H-4, t, $J = 7.4$ Hz)
118	7.53 (H-3, s), 7.38 (H-5', d, $J = 8.8$ Hz), 7.09 (H-6, s), 7.05 (H-2', d, $J = 2.8$ Hz), 6.81 (H-6', dd, $J = 2.8, 8.8$ Hz)
119	7.41 (H-3.5, s), 6.93 (H-2', d, $J = 2.9$ Hz), 7.34 (H-5', d, $J = 8.9$ Hz), 6.69 (H-6', dd, $J = 8.9, 2.6$ Hz)
126	7.43 (H-5', d, $J = 8.9$ Hz), 7.13 (H-2', $J = 2.8$ Hz), 7.03 (H-2,6, s), 6.88 (H-6', dd, $J = 8.9, 2.8$ Hz)
128 ^a	7.75 (H-5,5', d, $J = 9.1$ Hz), 7.29 (H-6,6', d, $J = 9.1$ Hz)
137 ^a	7.82 (H-3', d, $J = 2.4$ Hz), 7.60 (H-5', dd, $J = 2.4, 8.7$ Hz), 7.42 (H-6', d, $J = 8.7$ Hz), 7.40 (H-6, s)
138 ^a	8.00 (H-3', s), 7.76 (H-5, d, $J = 9.0$ Hz), 7.55 (H-6', s), 7.32 (H-6, d, $J = 9.0$ Hz)
140 ^a	7.88 (H-3',5', s), 7.64 (H-5, d, $J = 9.0$ Hz), 6.90 (H-6, d, $J = 9.0$ Hz)
147	7.56 (H-4, s), 7.48 (H-3', d, $J = 2.6$ Hz), 7.08 (H-5', dd, $J = 2.6, 8.8$ Hz), 6.36 (H-6', $J = 8.8$ Hz)
153 ^a	8.00 (H-3,3', s), 7.58 (H-6,6', s)
154 ^a	7.99 (H-3, s), 7.18 (H-6, s), 7.87 (H-3',5', s)
156	7.06 (H-6, s), 7.40 (H-5', d, $J = 8.8$ Hz), 7.13 (H-2', d, $J = 2.8$ Hz), 6.81 (H-6', dd, $J = 8.8, 2.8$ Hz)
157 ^a	7.80 (H-5, d, $J = 8.9$ Hz), 7.49 (H-6, d, $J = 8.9$ Hz), 7.48 (H-2',6', s)
163	7.56 (H-4, s), 6.94 (H-2', d, $J = 2.9$ Hz), 7.35 (H-5', d, $J = 8.9$ Hz), 6.69 (H-6', dd, $J = 2.9, 8.9$ Hz)
167 ^a	7.98 (H-3, s), 7.72 (H-6, s), 7.48 (H-2',6', s)
170 ^a	7.78 (H-5', d, $J = 9.0$ Hz), 7.57 (H-6, s), 7.42 (H-6', d, $J = 9.0$ Hz)
172	7.32 (H-4', d, $J = 2.3$ Hz), 6.96 (H-6, s), 6.81 (H-6', d, $J = 2.3$ Hz)
177	7.56 (H-4, s), 7.23 (H-5', d, $J = 9.1$ Hz), 6.32 (H-6', d, $J = 9.0$ Hz)
180 ^a	8.01 (H-3', s), 7.68 (H-6', s), 7.62 (H-6, s)
181	7.48 (H-3', d, $J = 2.6$ Hz), 7.08 (H-5', dd, $J = 2.6, 8.9$ Hz), 6.38 (H-6', $J = 8.9$ Hz)
182	6.51 (H-6, s), 7.45 (H-3',5', s)
187	7.60 (H-4, s), 7.58 (H-3', s), 7.51 (H-6', s)
190	6.94 (H-2', d, $J = 3.0$ Hz), 7.35 (H-5', d, $J = 8.9$ Hz), 6.69 (H-6', dd, $J = 3.0, 8.9$ Hz)
194 ^a	7.72 (H-6,6', s)
195 ^a	7.63 (H-5', d, $J = 9.0$ Hz), 7.08 (H-6', d, $J = 9.0$ Hz)
196 ^a	8.10 (H-5, s), 7.36 (H-6', s)
197	7.46 (H-5, s)
203	7.59 (H-3', s), 6.52 (H-6', s)
204	7.33 (H-3',5', s)
206	6.49 (H-6', s)

^a The spectrum is run in acetone-d₆.

for the given PCDE, respectively. The substitution patterns of 2-, 3-, 2,3-, and 3,5- are represented only once in the PCDEs studied, which makes 1/2(RRT) values for these isomers unreliable.

The 1/2(RRT) values for 19 substituent patterns are shown in Table 5, and the measured and calculated RRTs

are presented in Table 6. The calculated RRTs versus the measured RRTs illustrated in Figure 2 were in agreement with correlation coefficients of 0.998 and 0.996 for SE-54 and OV-1707, respectively. The 1/2(RRT) values increase on the SE-54 column in the order: 2- < 3- < 4- < 3,5- < 2,6- < 2,5- < 2,4- < 2,3- = 3,4- < 2,4,6- < 2,3,5-

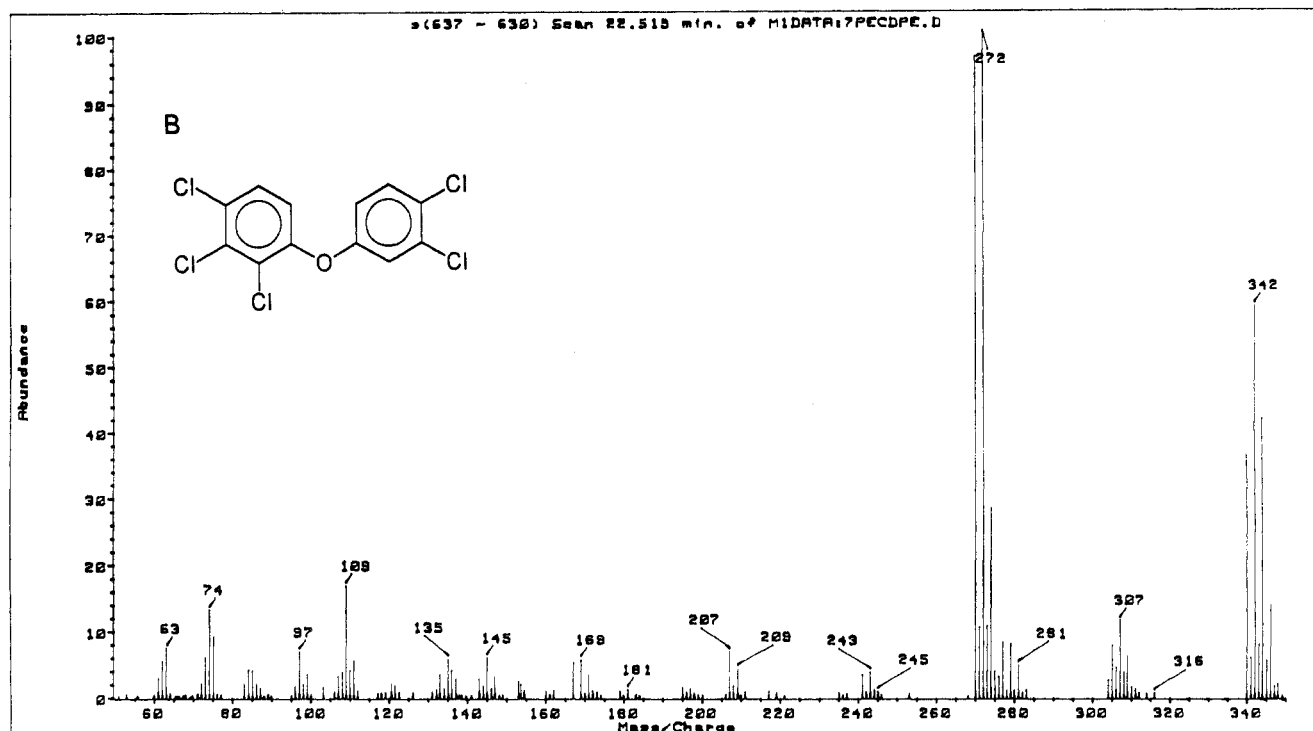
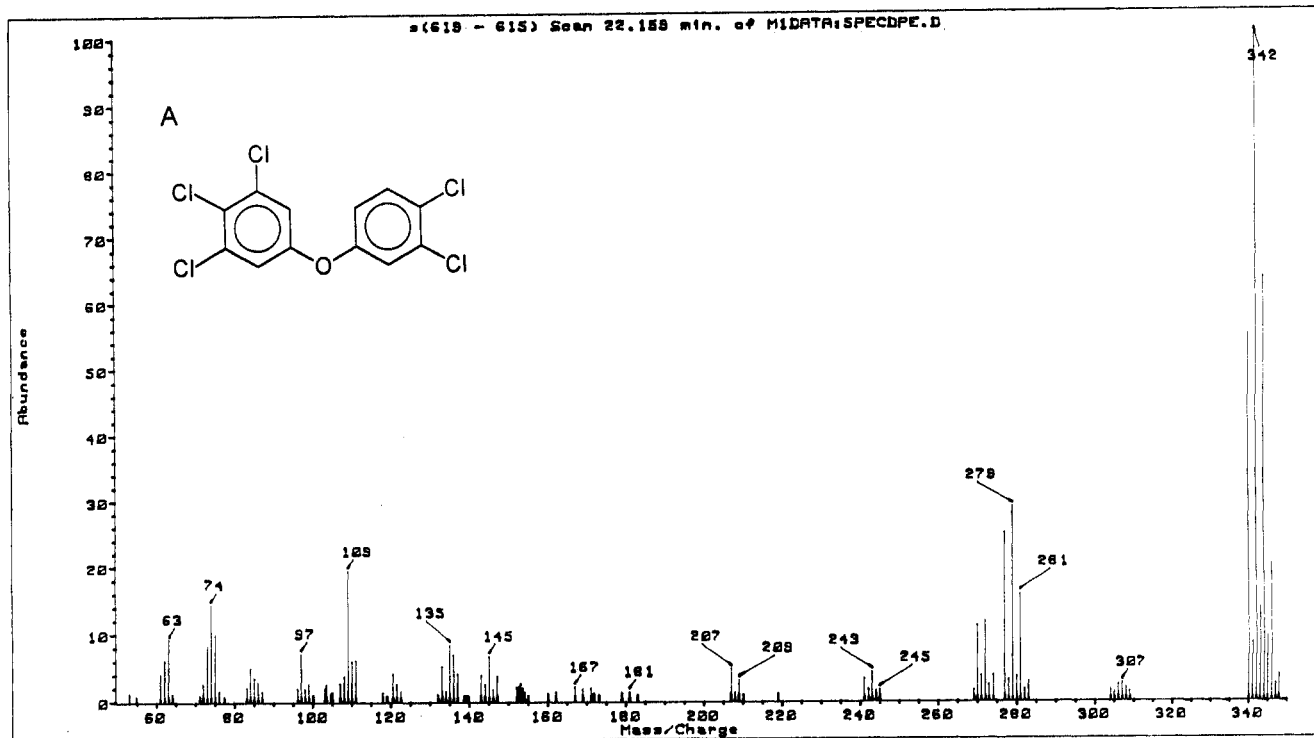


Figure 1. EI mass spectra of 3,3',4,4',5-pentachlorodiphenyl ether 126 (A) and 2,3,3',4,4'-pentachlorodiphenyl ether 105 (B).

< 2,4,5- < 3,4,5- < 2,3,4- < 2,3,5,6- < 2,3,4,6- < 2,3,4,5- < 2,3,4,5,6-, and on the OV-1701 column, the order is same except that 3- < 2- < 4- and 3,4- < 2,3. A significant difference between retention orders of PCDEs and PCBs is that 2,3- and 2,3,4-substitution patterns have the highest $1/2(RRT)$ values, whereas for PCBs the highest retention indices occur in 3,4- and 3,4,5-substitution patterns (32). We can state that the number of vicinal chlorines increases the retention time of PCDE. This is consistent with retention data of chlorobenzenes, whose retention increase in the order: 1,3- < 1,4- < 1,2- < 1,3,5- < 1,2,4- < 1,2,3- < 1,2,3,5- < 1,2,4,5- < 1,2,3,4- (33). The RRTs for congeners 194 and 195 are considerably higher than for

Table 5. $1/2(RRT)$ Values for Chlorine Patterns of PCDEs

ring structure	$1/2(RRT)$ value		ring structure	$1/2(RRT)$ value	
	SE-54	OV-1701		SE-54	OV-1701
phenyl	-0.018	-0.036	2,3,4-	0.717	0.722
2-	0.241	0.246	2,3,5-	0.579	0.553
3-	0.247	0.243	2,4,5-	0.598	0.578
4-	0.271	0.272	2,4,6-	0.525	0.480
2,3-	0.471	0.474	3,4,5-	0.658	0.637
2,4-	0.435	0.423	2,3,4,5-	0.881	0.878
2,5-	0.411	0.405	2,3,4,6-	0.798	0.763
2,6-	0.392	0.390	2,3,5,6-	0.756	0.723
3,4-	0.471	0.463	2,3,4,5,6-	1.054	1.045
3,5-	0.390	0.372			

Table 6. Observed and Predicted Relative Retention Times (RRT) for PCDEs^a

PCDE no.	RRT of SE-54			RRT of OV-1701		
	observed	predicted	ΔRRT	observed	predicted	ΔRRT
8	0.512	0.512	0.000	0.518	0.518	0.000
13	0.518	0.518	0.000	0.515	0.515	0.000
15	0.539	0.542	-0.003	0.535	0.544	-0.009
22	0.742	0.742	0.000	0.746	0.746	0.000
28	0.699	0.706	-0.007	0.692	0.695	-0.003
32	0.656	0.663	-0.007	0.658	0.662	-0.004
37	0.749	0.742	0.007	0.744	0.735	0.009
47	0.875	0.870	0.005	0.860	0.846	0.014
49	0.843	0.846	-0.003	0.829	0.828	0.001
51	0.840	0.827	0.013	0.837	0.813	0.024
62	0.797	0.780	0.017	0.765	0.727	0.038
66	0.908	0.906	0.002	0.894	0.886	0.008
68	0.825	0.825	0.000	0.795	0.795	0.000
71	0.860	0.863	-0.003	0.850	0.853	-0.003
74	0.885	0.869	0.016	0.862	0.850	0.012
77	0.966	0.942	0.024	0.954	0.926	0.028
85	1.139	1.152	-0.013	1.119	1.145	-0.026
89	1.105	1.109	-0.004	1.094	1.112	-0.018
90	1.037	1.014	0.023	1.000	0.976	0.024
99	1.046	1.033	0.013	1.014	1.001	0.013
100	0.986	0.960	0.026	0.950	0.903	0.047
101	1.012	1.009	0.003	0.982	0.983	-0.001
105	1.173	1.188	-0.015	1.155	1.185	-0.030
116	1.019	1.036	-0.017	0.970	1.009	-0.039
118	1.088	1.069	0.019	1.060	1.041	0.019
119	1.000	0.996	0.004	0.967	0.943	0.024
126	1.153	1.129	0.024	1.124	1.100	0.024
128	1.410	1.434	-0.024	1.419	1.444	-0.025
137	1.282	1.316	-0.034	1.243	1.301	-0.058
138	1.302	1.315	-0.013	1.276	1.300	-0.024
140	1.246	1.242	0.004	1.205	1.202	0.003
147	1.201	1.191	0.010	1.154	1.146	0.008
153	1.206	1.196	0.010	1.162	1.156	0.006
154	1.134	1.123	0.011	1.078	1.058	0.020
156	1.326	1.352	-0.026	1.301	1.341	-0.040
157	1.349	1.375	-0.026	1.332	1.359	-0.027
163	1.223	1.227	-0.004	1.174	1.186	-0.012
167	1.257	1.256	0.001	1.217	1.215	0.002
170	1.594	1.598	-0.004	1.610	1.600	0.010
172	1.437	1.460	-0.023	1.408	1.431	-0.023
177	1.486	1.473	0.013	1.466	1.445	0.021
180	1.454	1.479	-0.025	1.432	1.456	-0.024
181	1.447	1.489	-0.042	1.408	1.468	-0.060
182	1.370	1.406	-0.036	1.312	1.358	-0.046
187	1.337	1.354	-0.017	1.283	1.301	-0.018
190	1.473	1.525	-0.052	1.444	1.508	-0.064
194	1.818	1.762	0.056	1.863	1.756	0.107
195	1.873	1.771	0.102	1.909	1.767	0.142
196	1.674	1.679	-0.005	1.653	1.641	0.012
197	1.589	1.596	-0.007	1.500	1.526	-0.026
203	1.629	1.652	-0.023	1.607	1.623	-0.016
204	1.569	1.579	-0.010	1.469	1.525	-0.056
206	1.979	1.935	0.044	1.880	1.923	-0.043
209	2.108	2.108	0.000	2.158	2.090	0.068

^a RRT vs PCB 77 (3,3',4,4'-tetrachlorobiphenyl).

other nonachloro-congeners, and their predicted RRTs deviate notably from observed values.

Several pairs of isomers and congeners exhibited similar or identical retention times on the SE-54 column (see Table 6). The RRT values were generally longer on the SE-54 column than on the OV-1701 column, especially for tetra-*ortho*-isomers 197 and 204 and for isomer 119. The retention times on the SE-54 column are shorter than on the OV-1701 column for congeners 170, 194, 195, and 206. The retention order for 14 PCDE congeners (same as in this study) obtained by Humppli and Heinola is in good agreement with retention order measured here (7).

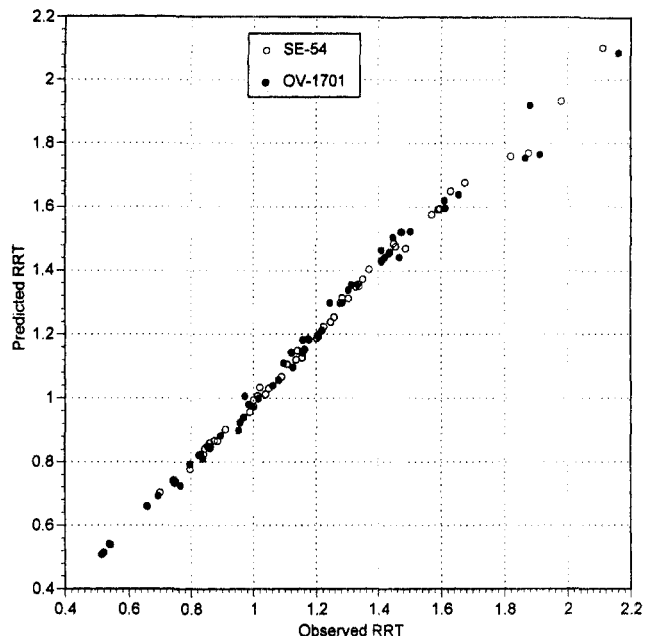


Figure 2. Observed vs predicted relative retention times for PCDE congeners on SE-54 and OV-1701 column.

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