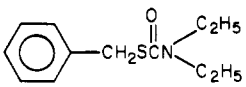
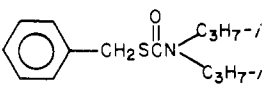


Table II

Compound	Herbicidal act. ^a GR ₅₀ , lb/acre
	0.1
8	0.5
	0.3
1	0.9

^a See text for details.

The vinylbenzyl chloride (VBC) is a monomer of the Dow Chemical Company which is a mixture of the meta (60%) and para (40%) isomers of vinylbenzyl chloride. It is not possible to separate the vinylbenzyl chloride isomers nor compounds 1 through 14 by gas chromatography on

the instrument used for this work; therefore, the assumption was made that the products obtained were of the same meta (60%) and para (40%) isomer composition as the vinylbenzyl chloride. All amines were freshly distilled.

Supplementary Material Available: Details of the synthetic procedures and physical properties for the new compounds discussed (9 pages). Ordering information is given on any current masthead page.

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Synthesis and Spectroscopic and Gas Chromatographic Behavior of Isomeric Chlorinated Terphenyls

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The synthesis and spectroscopic and chromatographic properties of 22 polychlorinated terphenyl (PCT) isomers are reported. Diazo coupling of a biphenylamine with an excess of a symmetrical chlorobenzene gave a single chloroterphenyl product; coupling with unsymmetrical chlorobenzenes gave mixtures which in some cases could be purified and identified by the wavelength of their characteristic ultraviolet absorption spectra. Chlorine substitution in the para position gives a characteristic bathochromic shift of the λ_{max} whereas substitution in the ortho positions gives a hypsochromic shift to these values. The gas-liquid chromatographic retention times of the PCT isomers increased with increasing chlorine content, whereas the relative molar electron capture responses tended to be highest with 4-chloro substitution and whereas ortho substitution (2 and 6 positions) gave the lowest response values. Availability of synthetic PCT isomers thus permits comparative evaluation of the environmental and biological impact of PCTs which have already been identified as pollutants.

Polychlorinated terphenyls (PCTs) are industrial chemicals with applications similar to those of the polychlorinated biphenyls (PCBs). PCT residues have been identified in the eggs and fatty tissue of herring gulls (Zitko et al., 1972), Rhine River water, oysters, eel, and human fat (Freudenthal and Greve, 1973; Doguchi and Fukano, 1975), paperboard samples (Thomas and Reynolds, 1973), and silo wall scrapings, silage, and cows' milk (Fries and Marrow, 1973). Chromatographic analysis indicated that this PCT corresponded to commercial Aroclor 5460, a mixture of ortho-, meta-, and para-chlorinated terphenyl isomers (Putnam et al., 1974). It is difficult to investigate the biological properties of a complex mixture and we therefore report the synthesis and chromatographic properties of 22 chlorinated terphenyl isomers. 4-

Chloro-*p*-terphenyl is readily prepared from the corresponding commercially available 4-nitro-*p*-terphenyl and the remaining isomers were all synthesized by the diazo coupling of a biphenylamine and a halobenzene (Cadogan, 1962). In coupling reactions where more than one product was formed the structures were confirmed by spectroscopic and photochemical methods.

MATERIALS AND METHODS

Chemicals. The following compounds were obtained commercially: 1,3-dichlorobenzene, 1,2,3-trichlorobenzene (BDH); 1,2-dichlorobenzene (Anachemia); *p*-terphenyl (Eastman); 4-nitro-*p*-terphenyl, 4-aminobiphenyl, 2-aminobiphenyl, 1,2,4,5-tetrachlorobenzene, 1,2,3,4,5-pentachlorobenzene (Aldrich); 1,3,5-trichlorobenzene (Baker); 1,4-dichlorobenzene, 1,2,4-trichlorobenzene, isoamyl nitrite (Matheson Coleman and Bell); 4-amino-4'-chlorobiphenyl hydrochloride (Burdich and Jackson); 1,2,3,5-tetrachlorobenzene (Schuchardt, Munchen).

Thin-Layer Chromatography. Preparative and analytical thin-layer chromatography (TLC) was carried out on glass plates (20 × 20 cm, 20 × 50 cm, and 20 × 100 cm) coated with MN-Kieselgel G/UV₂₅₄ silica at a

Guelph Waterloo Centre for Graduate Work in Chemistry, University of Guelph, Guelph, Ontario, Canada (B.C., S.S., L.O.R.), Milieuchemie, University of Amsterdam, Amsterdam, The Netherlands (O.H.), and Environment Canada, Biology Station, St. Andrews, New Brunswick, Canada (V.Z.).

Table I. Synthesis and Spectroscopic Properties of Isomeric Chlorinated Terphenyls

Starting materials	Amount, g	Chlorinated terphenyl products	Yield, mg	R_f	Mp, °C	M ^a	UV maxima of products, nm $\epsilon \times 10^{-3}$
4-Nitro- <i>p</i> -terphenyl	0.10	4-Chloro- <i>p</i> -terphenyl	70	1.33	218-220	264	277 (26.8)
{4-Aminobiphenyl 1,3-Dichlorobenzene	0.30	2,4-Dichloroterphenyl (II)	80	1.76	119-121	298	269 (25.4)
	20.0	2,6-Dichloroterphenyl (III)	48	1.38	72-73	298	261 (25.2)
		3,5-Dichloroterphenyl (IV)	17	2.14	115-117	298	276 (35.0)
{4-Aminobiphenyl 1,4-Dichlorobenzene	0.30	2,5-Dichloroterphenyl (V)	150	1.86	128-130	298	267 (30.4)
	20.0						
{4-Aminobiphenyl 1,2,3-Trichlorobenzene	0.20	2,3,4-Trichloroterphenyl (VI)	33	1.29	162-164	332	270 (28.4)
	15.0	3,4,5-Trichloroterphenyl (VII)	17	1.57	145-146	332	277 (36.8)
	0.20	2,3,6-Trichloroterphenyl (VIII)	51	1.48	71-73	332	262 (25.2)
1,2,4-Trichlorobenzene	15.0	Mixture ^a	73	1.86		332	
	0.30	2,4,6-Trichloro- <i>p</i> -terphenyl (IX)	161	1.86	134-136	332	261 (28.4)
1,3,5-Trichlorobenzene	20.0						
	0.30	2,4,4''-Trichloro- <i>p</i> -terphenyl (X)	35	2.14	122-124	332	271 (30.8)
4-Amino-4'-chlorobiphenyl HCl	20.0	2,6,4''-Trichloro- <i>p</i> -terphenyl (XI)	32	1.81	112-114	332	264 (27.2)
	0.20	3,5,4''-Trichloro- <i>p</i> -terphenyl (XII)	4	2.48	119-121	332	280 (34.2)
4-Amino-4'-chlorobiphenyl HCl	0.30	2,5,4''-Trichloro- <i>p</i> -terphenyl (XIII)	37	2.24	88-90	332	270 (31.4)
	20.0						
4-Amino-4'-chlorobiphenyl HCl	0.20	2,3,4,4''-Tetrachloro- <i>p</i> -terphenyl (XIV)	52	1.52	147-149	366	271 (33.2)
	20.0	3,4,5,4''-Tetrachloro- <i>p</i> -terphenyl (XV)	5	1.86	154-156	366	281 (28.6)
4-Amino-4'-chlorobiphenyl HCl	10.0						
	0.20	2,3,6,4''-Tetrachloro- <i>p</i> -terphenyl (XVI)	34	1.76	135-137	366	267 (26.6)
1,2,4-Trichlorobenzene	10.0	Mixture ^b	35	2.24		366	
	0.30	2,4,6,4''-Tetrachloro- <i>p</i> -terphenyl (XVII)	26	2.43	107-109	366	266 (34.8)
1,3,5-Trichlorobenzene	20.0						
	0.50	2,3,4,6-Tetrachloro- <i>p</i> -terphenyl (XVIII)	156	1.86	145-147	366	265 (25.2)
1,2,3,5-Trichlorobenzene	10.0	2,3,5,6-Tetrachloro- <i>p</i> -terphenyl (XIX)	336	1.81	153-155	366	264 (24.8)
	10.0	2,3,5,6,4''-Pentachloro- <i>p</i> -terphenyl (XX)	94	2.33	185-187	400	266 (27.6)
4-Amino-4'-chlorobiphenyl HCl	0.50	2,3,4,5,6-Pentachloro- <i>p</i> -terphenyl (XXI)	75	2.05	208-209	400	262 (25.6)
	10.0	2,5-Dichloro- <i>o</i> -terphenyl (XXII)	178	1.71	63-65	298	226 (21.6) ~248 (14.0)
1,2,3,4,5-Pentachlorobenzene	0.50						
	10.0	<i>p</i> -Terphenyl					276 (25.2)

^a Most likely a mixture of 2,4,5- and 2,3,5-trichloro-*p*-terphenyl. ^b Most likely a mixture of 2,4,4'',5- and 2,3,4'',5-tetrachloro-*p*-terphenyl. ^c Relative to *p*-terphenyl.

Table II. Relative Retention Times and Electron-Capture Detector Responses of Some Chloroterphenyls^a

Compound	Retention time			Electron-capture detector response ^c
	Column A ^b	Column B ^b	Column C ^c	
4-Chloro- <i>p</i> -terphenyl	1.84	1.83	0.37	0.048
2,4-Dichloro- <i>p</i> -terphenyl	2.00	2.22	0.42	0.451
2,5-Dichloro- <i>p</i> -terphenyl	2.05	1.67	0.43	0.339
2,6-Dichloro- <i>p</i> -terphenyl	1.79	1.83	0.35	0.314
3,5-Dichloro- <i>p</i> -terphenyl	2.47	2.56	0.60	0.465
2,3,4-Trichloro- <i>p</i> -terphenyl	4.05	3.67	0.90	1.190
2,3,6-Trichloro- <i>p</i> -terphenyl	2.95	2.89	0.60	0.663
2,4,6-Trichloro- <i>p</i> -terphenyl	2.21	2.56	0.45	0.672
3,4,5-Trichloro- <i>p</i> -terphenyl	4.89	4.44	1.21	0.989
2,4,4''-Trichloro- <i>p</i> -terphenyl	3.79	3.50	0.87	0.944
2,5,4''-Trichloro- <i>p</i> -terphenyl	3.79	3.33	0.83	0.561
2,6,4''-Trichloro- <i>p</i> -terphenyl	3.26	2.94	0.66	0.417
3,5,4''-Trichloro- <i>p</i> -terphenyl	4.84	4.28	1.23	0.380
2,3,4,6-Tetrachloro- <i>p</i> -terphenyl	4.32	4.50	0.95	1.758
2,3,5,6-Tetrachloro- <i>p</i> -terphenyl	3.89	4.11	0.94	1.061
2,3,4,4''-Tetrachloro- <i>p</i> -terphenyl	7.89	8.00	1.89	0.644
2,3,6,4''-Tetrachloro- <i>p</i> -terphenyl	5.47	6.00	1.23	1.325
2,4,6,4''-Tetrachloro- <i>p</i> -terphenyl	4.11	4.11	0.95	0.922
3,4,5,4''-Tetrachloro- <i>p</i> -terphenyl	10.10	9.00	2.62	0.587
2,3,4,5,6-Pentachloro- <i>p</i> -terphenyl	7.00	6.78	1.73	1.842
2,3,5,6,4''-Pentachloro- <i>p</i> -terphenyl	7.63	8.00	1.94	0.917
2,5-Dichloro- <i>o</i> -terphenyl	0.74	1.11	0.10	0.595

^a For conditions, see Experimental Section. ^b Retention times relative to *p*-terphenyl; see Materials and Methods for column packings. ^c Retention times and detector response relative to decachlorobiphenyl.

thickness of 0.8 mm. In all cases petroleum ether (bp 30–60 °C) (Fisher U.S.P.) was used as the solvent system and the developed plates were viewed under a short-wave UV lamp.

Gas-Liquid Chromatography. Gas-liquid chromatography (GLC) using a flame ionization detector (FID) was carried out using a Hewlett Packard 5710A gas chromatograph fitted with a 183 × 0.64 cm glass column packed with either 3% OV-255 on Gas-Chrom Q, 80–100 mesh (column A), or 3% SE-30 on Chromosorb W, 60–80 mesh (column B). Both injection port and detector temperatures were 300 °C; oven temperature using either column was 250 °C.

GLC using an electron capture detector (ECD), tritium at 220 °C, was carried out using a Packard A7901 gas chromatograph fitted with a 200 × 0.40 cm glass column packed with 3% OV210 on Chromosorb W, 60–80 mesh (column C). Oven temperature was 200 °C and the carrier gas used was nitrogen at 50 ml/min.

Recording of Spectra. Mass spectra of all chloroterphenyls were obtained using a Varian MAT CH-7 low-resolution mass spectrometer operated at 70 eV and equipped with electrical detection. The samples were inserted into the ion source at 20 °C and the temperatures increased as required. The UV spectra of 5 × 10⁻⁵ M solutions of the chloroterphenyls in cyclohexane (Fisher Spectroanalyzed) were measured on a Unicam SP800 UV spectrophotometer. The 220-MHz NMR spectra were recorded on a Varian HR220 instrument using carbon tetrachloride or deuteriochloroform as solvent. With few exceptions the spectra were highly complex and not amenable to interpretation.

Synthetic Procedures. The primary synthetic method used was as previously described (Cadogan, 1962) involving a one-step diazotization using isoamyl nitrite as the diazotizing agent. The appropriate biphenylamine and chlorobenzene, in the amounts given in Table I, were placed in a 100-ml round-bottomed flask fitted with reflux apparatus. This mixture was then heated to 120 °C in an oil bath. Isoamyl nitrite (0.5 ml) was then added and the solution stirred for approximately 50 h. The resultant mixture was then vacuum distilled until approximately 1

g of material remained. From this fraction the chloroterphenyl was isolated and purified using preparative TLC as described.

RESULTS AND DISCUSSION

Synthesis. A summary of the diazo coupling reaction products, melting points, molecular ions, and ultraviolet (UV) absorption maxima is given in Table I. Diazo coupling of the amine (i.e., 4-biphenylamine, 2-biphenylamine, or 4'-chloro-4-biphenylamine) with an excess of a symmetrical chlorobenzene (i.e., 1,4-dichloro-, 2,4,6-trichloro-, 1,2,3,5-tetrachloro-, 1,2,4,5-tetrachloro-, or pentachlorobenzene) gave only the single expected chlorinated terphenyl product (compounds V, IX, XIII–XV, and XVII–XXII). Diazo coupling of the amines with unsymmetrical chlorobenzenes can yield more than one expected product and compounds II–IV, VIII, and XIV–XVI were prepared using this route.

The structure proof for the unsymmetrical diazo coupling products was given by their corresponding UV absorption spectra and photochemical lability. Examination of the UV spectra of the symmetrical diazo coupling products indicated that (i) the wavelengths of the absorption peaks were in the order 4-chloro > 3-chloro > *p*-terphenyl and (ii) chlorination at the 2 (or 6) position results in a hypsochromic shift of the absorption maxima. These observations correlated well with previous data (Iguchi et al., 1963) and were also similar to results obtained for a series of isomeric chlorinated biphenyls (MacNeil et al., 1976). Preliminary work (Chittim et al., 1976) has also shown that photolysis of chlorinated terphenyls in cyclohexane readily gives dechlorination products in which the ease of dechlorination was 2(or 6)-chloro >> 3-chloro > 4-chloro. This relative ease of dechlorination was also observed for the comparable photodecomposition of several isomeric PCBs (Ruzo et al., 1974).

Diazo coupling of 4-biphenylamine with 1,3-dichlorobenzene gave the three expected products which were separated by preparative TLC (see Table II). One of the products (*R_f* 1.76) was identical with the major photo-dechlorination product of 2,4,6-trichloro-*p*-terphenyl

(Chittim et al., 1976) and could be assigned the 2,4-dichloro-*p*-terphenyl structure. Comparison of the UV absorption spectra of the R_f 1.38 and 2.14 products showed maxima at 261 and 276 nm clearly indicating ortho substitution for the R_f 1.38 component. The UV spectrum of this compound was similar to that of the 2,4,6-trichloro isomer and therefore the 2,6-dichloro-*p*-terphenyl structure was assigned. The λ_{\max} 276 nm product (R_f 2.14) was assigned the 3,5-dichloro-*p*-terphenyl structure which is the only other possible product of this unsymmetrical diazo coupling synthesis. Diazo coupling of 4'-chloro-4-biphenylamine with 1,3-dichlorobenzene can also yield three expected products, namely the 2,4,4''-, 2,6,4''-, and 3,5,4''-trichloro-*p*-terphenyl isomers. Three trichloroterphenyl isomers were isolated from the reaction by preparative TLC (R_f 2.14, 1.81, and 2.48); the R_f 2.14 component was identical with the major photodechlorination of 2,4,4''-6-tetrachloro-*p*-terphenyl (Chittim et al., 1976) and was assigned the 2,4,4''-trichloro-*p*-terphenyl structure. Comparison of the UV absorption spectra of the R_f 1.81 and 2.48 products supported the assignment of the 2,4'',6- and 3,4'',5-trichloro-*p*-terphenyl structures, respectively. Diazo coupling of 4-biphenylamine and 1,2,3-trichlorobenzene can yield only two possible products, namely 2,3,4- and 3,4,5-trichloro-*p*-terphenyl. Two products were isolated from this reaction (R_f 1.29 and 1.57) and the structures assigned on the basis of their corresponding ultraviolet spectra in which the R_f 1.29 product (assigned the 2,3,4-trichloro-*p*-terphenyl structure) exhibited an absorption maximum at 270 nm which was 7 nm lower than the R_f 1.57 component. Similarly, the two products isolated from the diazo coupling of 4'-chloro-4-biphenylamine and 1,2,3-trichlorobenzene were identified as 2,3,4,4'-tetrachloro-*p*-terphenyl (λ_{\max} 271 nm) and 3,4,4'',5-tetrachloro-*p*-terphenyl (λ_{\max} 281 nm). Diazo coupling of 4-biphenylamine with 1,2,4-trichlorobenzene can yield three possible isomers; however, only two bands could be separated by preparative TLC. The UV absorption of the R_f 1.48 product exhibited a λ_{\max} at 262 nm and was assigned the 2,3,6-trichloro-*p*-terphenyl structure; the UV absorption of the R_f 1.86 band was at 270 nm and presumably a mixture of the 2,4,5- and 2,3,5-trichloro-*p*-terphenyl isomers. Similar results were observed with the coupling of 4'-chloro-4-biphenylamine and 1,2,4-trichlorobenzene in which only the 2,6-disubstituted product, i.e. 2,3,4'',6-tetrachloro-*p*-terphenyl, could be purified and identified.

Chromatographic Data. A summary of the GLC retention times of the chlorinated terphenyl isomers using three column packings and their relative molar responses

using an electron capture detector are summarized in Table II. An increase in the chlorine content generally increases the relative retention times of the PCT isomers although there are minor variations which depend on both the column used and the chlorine substitution pattern. Comparison of the relative electron-capture response of 2,5-dichloro-*o*- and -*p*-terphenyl clearly shows a significantly higher response by the ortho isomer. In addition, the relative electron-capture response is markedly increased with 4-chloro substituents and tends to be reduced with substitution at the ortho (2 and 6) positions. These results were comparable to the data obtained for several isomeric PCBs (Zitko et al., 1971).

The reported synthetic studies have thus yielded 22 chlorinated terphenyl isomers and research on the photochemical, metabolic, and biological properties of both commercial PCT and PCT isomers is in progress. Commercial PCTs, which are formed by direct chlorination procedures, contain isomers with chlorine substituents in all three phenyl rings. Due to the unavailability of appropriate chlorobiphenylamines, this paper does not include the synthesis of chloroterphenyls substituted in the central phenyl group. Studies on the synthesis of some of these intermediates are also in progress.

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