Characterization of Four Major Components in a Technical Polychlorinated Biphenyl Mixture

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■ Polychlorinated biphenyls (PCB's) have recently been recognized as contaminants of the environment. Technical PCB preparations are complicated mixtures of compounds with different structures and degrees of chlorine substitutions. The exact structures of some major constituents (two hexachlorobiphenyls and two heptachlorobiphenyls) of a commercial PCB preparation have been determined by synthesis. The pure compounds may be useful for toxicity studies.

Polychlorinated biphenyls (PCB's) have a wide spectrum of industrial application. The compounds are used as plasticizers, insulation fluids, and as additives to hydraulic fluids, lubricants, paints, protective coatings, and adhesives. PCB's are quite stable and chemically inert compounds. Their widespread use has been found to give rise to environmental pollution (Gustafson, 1970). PCB residues in wildlife samples were first reported in Sweden (Jensen, 1966) and afterward in several European countries and in North America. PCB's have a tendency to accumulate in fatty animal tissues like some of the persistent organochlorine pesticides. PCB residues have been detected by gas chromatography in sludge from sewage purification works (Holden, 1970); in fish, mussels, and birds (Bagley et al., 1970; Holmes et al., 1967; Koeman et al., 1969), seals and porpoises (Holden and Marsden, 1967); in food (Bailey et al., 1970; Westöö et al., 1970); and in human milk (Acker and Schulte, 1970; Westöö et al., 1970) The compounds are industrially prepared by chlorination of biphenyl. Several fractions of different degrees of chlorination are manufactured. Gas chromatograms of PCB residues found in Dutch birds and fish (Koeman et al., 1969) show a pattern comparable to that of a commercial PCB mixture containing about 60% of chlorine (corresponding to an average number of six chlorine atoms per molecule).

In the technical chlorination process, many chlorinated biphenyls are formed with different arrangements of the chlorine atoms in the molecule. Molecular weight and numbers of chlorine atoms per molecule have been determined for several components from PCB mixtures by gas chromatography combined with mass spectrometry (Bagley et al., 1970; Koeman et al., 1969).

To our knowledge, however, the actual structure of one or more of these compounds has not been reported so far. The knowledge of the structure may be important for toxicity studies. It has been found that the evaluation of animal tests on PCB is made difficult by the presence of traces of toxic chlorinated dibenzofurans in some commercial PCB preparations (Vos et al., 1970). For the evaluation of the actual PCB toxicity, it is necessary to have pure compounds of known structures available.

In this paper, the structure is reported of four major components of a commercial PCB preparation named Phenochlor DP 6 (Figure 1*A*) This French product (manufactured by Prodelec) is comparable to Clophen A 60 (Bayer, Ger Figure 1*B*), and Arocior 1260 (Monsanto, U S . Figure 1*C*)

Experimental

The technical mixture was fractionated by preparative glc and the purity of the fractions corresponding to the numbered peaks (Figure 1) was further tested by electron capture glc and by a tlc system with improved resolution under published conditions (de Vos and Peet, 1971). Fractions 6, 8, 11, and 12 proved to contain essentially one component and were further investigated by nmr spectroscopy, giving evidence on the positions of the chlorine atoms in the aromatic nuclei

The compounds having the inferred structures were synthesized by the Ullmann reaction with activated copper powder at 215–225°C and 2.5 hr reaction time ("Organic Reactions," 1944) with the appropriate polychloroiodobenzenes as the starting materials. When two different polychloroiodobenzenes were used, the two symmetrical PCB's were also formed. The reaction products were then isolated by glc

The polychloroiodobenzenes were prepared from the corresponding amino compounds by diazotation and reaction with KI.

By comparing nmr and ir spectra, the retention times on two different analytical glc columns and the R_f values in tlc of both the fractions mentioned above and the synthesized PCB's, the identity of the following components could be ascertained.

Peak 6: 2,2',4,4',5,5'-hexachlorobiphenyl
Peak 8: 2,2',3,4,4',5'-hexachlorobiphenyl
Peak 11: 2,2',3,4,4',5,5'-heptachlorobiphenyl
Peak 12: 2,2',3,3',4,4',5-heptachlorobiphenyl

Instrumental and Other Data

Preparative glc was performed with an Aerograph Model 705; column: aluminum, 5 meters × 6 mm i.d., packed with 20% SF 96 on Chromosorb W/AW, temp 225°C, flow 75 ml N_2/ min.

Control glc was effected by using a Carlo Erba Fractovap GV; columns: (a) glass, 1.9 meters × 3 mm i.d., packed with 3% OV-1 on gaschrom Q, 80–100 mesh, temp 190°C, flow 80 ml N_2/min, and (b) a column of identical size packed with 1.8% OV-1 and 2.7% QF-1 on gaschrom Q, 80–100 mesh

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under the same conditions. Retention times were calculated relative to aldrin.

Ir spectra were recorded either with a Perkin-Elmer 13 or with a Hilger and Watts H-1200 apparatus. The samples were supplied either as a thin layer on NaCl tablets or mulled and pressed in KBr tablets. Absorptions are given at cm^{-1} values.

Nmr spectra were recorded with a Jeol A-60 apparatus, TMS being the internal standard and $CDCl_3$ the solvent.

Mass spectra were recorded with an Atlas CH4 apparatus.

2,4,5-Trichloroiodobenzene was prepared, using 2,4,5-trichloroaniline (obtained from Fluka, Switz.) as base. Mol wt: 306; three Cl atoms (from mass spectrum); mp: 106–107°C; bp: 97–100°C/0.5 mm; ir spectrum: Figure 2*A*.

2,3,4-Trichloroiodobenzene was prepared from 2,3,4-trichloroaniline, which was synthesized from 1,2,3-trichlorobenzene (obtained from BDH, Eng.) by nitration and catalytic reduction (PtO_2 in ethanol). Mol wt: 306; three Cl atoms (from mass spectrum); mp: 65–66°C; bp: 97–98°C/0.5 mm, ir spectrum: Figure 2*B*.

2,3,4,5-Tetrachloroiodobenzene was prepared from 2,3,4,5-tetrachloroaniline as base. The latter compound was prepared from 2,3,4,5-tetrachloronitrobenzene (obtained from Fluka, Switz.) by catalytic reduction (PtO_2 in ethanol). Mol wt: 340; four Cl atoms (from mass spectrum); mp: 89–90°C; bp: 115–118°C/0.5 mm; ir spectrum: Figure 2*C*.

2,2',4,4',5,5'-Hexachlorobiphenyl was prepared from 2,4,5-trichloroiodobenzene. Mp: 102–103°C. R_f value of 2,2',4,4',-

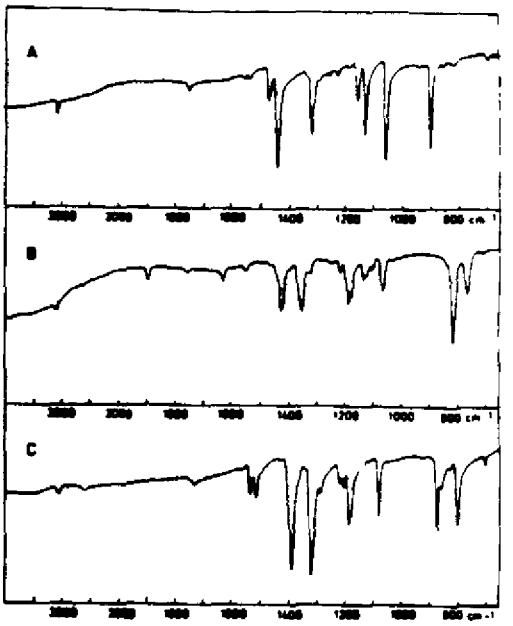

Figure 2. Infrared spectra of *A*. 2,4,5-trichloroiodobenzene (in KBr), *B* 2,3,4-trichloroiodobenzene (supercooled liquid), *C* 2,3,4,5-tetrachloroiodobenzene (in KBr)

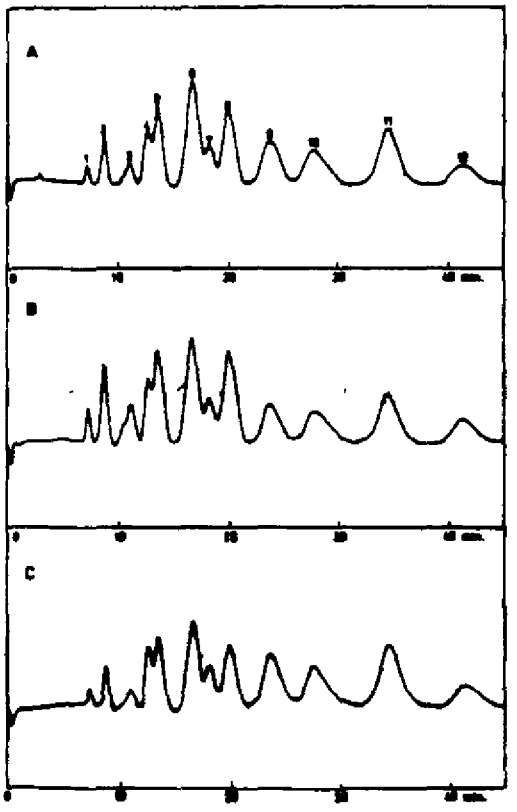

Figure 1. Gas chromatograms of *A* Phenochlor DP 6 (Prodelec, Fr), *B* Clophen (Bayer, Ger.), *C*, Aroclor 1260 (Monsanto, U.S.)

Column: glass, 1.5 meters × 3 mm i.d., packed with 3% OV-1 on gas-chrom Q, 80–100 mesh, temp 180°C, flow 60 ml N_2/min. Detection: electron capture

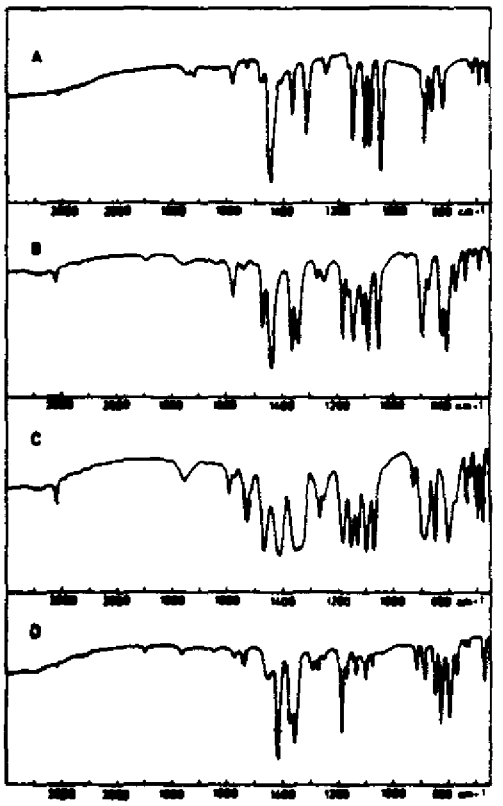

Figure 3. Infrared spectra of *A*: 2,2',4,4',5,5'-hexachlorobiphenyl (in KBr), *B*: 2,2',3,4,4',5'-hexachlorobiphenyl (supercooled liquid), *C*: 2,2',3,4,4',5,5'-heptachlorobiphenyl (supercooled liquid), *D* 2,2',3,3',4,4',5-heptachlorobiphenyl (in KBr)

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5,5'-hexachlorobiphenyl on (a) 3.18, on (b) 3.21. R_t value of peak 6 on (a) 3.19; on (b) 3.22. Ir spectrum: Figure 3A. Nmr spectrum: 2H (d), $\delta = 7.61$, $J \simeq 0.3$ cps; 2H (d), $\delta = 7.36$, $J \simeq 0.3$ cps.

2,2',3,4,4',5'-Hexachlorobiphenyl was prepared from an equimolecular amount of 2,4,5-trichloroiodobenzene and 2,3,4-trichloroiodobenzene. Mp: 78.5–80°C. R_t value of 2,2',3,4,4',5'-hexachlorobiphenyl on (a) 3.75; on (b) 3.88. R_t value of peak 8 on (a) 3.77; on (b) 3.90. Ir spectrum: Figure 3B. Nmr spectrum: 1H (d), $\delta = 7.62$, $J \sim 0.3$ cps; 1H (d), $\delta = 7.50$, $J = 8.25$ cps; 1H (d), $\delta = 7.35$, $J \sim 0.3$ cps; 1H (d), $\delta = 7.10$, $J = 8.25$ cps.

By-products: 2,2',4,4',5,5'-hexachlorobiphenyl and 2,2',-3,3',4,4'-hexachlorobiphenyl. Mp: 145.5–146.5°C. R_t value on (a) 4.44; on (b) 4.69. Ir spectrum (KBr): strong 1430, 1353, 1185, 792; medium 1370, 1168, 881, 830, 819, 751. Nmr spectrum: 2H (d), $\delta = 7.50$, $J = 8.25$ cps; 2H (d), $\delta = 7.10$, $J = 8.25$ cps.

2,2',3,4,4',5,5'-Heptachlorobiphenyl was prepared from an equimolecular amount of 2,4,5-trichloroiodobenzene and 2,3,4,5-tetrachloroiodobenzene. Mp: 109–110°C. R_t value of 2,2',3,4,4',5,5'-heptachlorobiphenyl on (a) 6.48; on (b) 6.52. R_t value of peak 11 on (a) 6.49; on (b) 6.53. Ir spectrum: Figure 3C. Nmr spectrum: 1H (d), $\delta = 7.64$, $J \sim 0.3$ cps; 1H (d), $\delta = 7.35$, $J \sim 0.3$ cps; 1H (s), $\delta = 7.30$.

By-products: 2,2',4,4',5,5'-hexachlorobiphenyl and 2,2',-3,3',4,4',5,5'-octachlorobiphenyl. Mp: 152–153°C. R_t value of 2,2',3,3',4,4',5,5'-octachlorobiphenyl on (a) 13.18; on (b) 13.18. Ir spectrum: strong 1401, 1341; medium 1181, 1097, 880, 848, 831, 782, 686. Nmr spectrum: 2H (s), $\delta = 7.31$.

2,2',3,3',4,4',5-Heptachlorobiphenyl was prepared with an equimolecular amount of 2,3,4-trichloroiodobenzene and 2,3,4,5-tetrachloroiodobenzene. Mp: 134.5–135.5°C. R_t value of 2,2',3,3',4,4',5-heptachlorobiphenyl on (a) 7.73; on (b) 7.92. R_t value of peak 12 on (a) 7.68; on (b) 7.89. Ir spectrum: Figure 3D. Nmr spectrum: 1H (d), $\delta = 7.51$, $J = 8.25$ cps; 1H (s), $\delta = 7.32$; 1H (d), $\delta = 7.09$, $J = 8.25$ cps.

By-products: 2,2',3,3',4,4'-hexachlorobiphenyl and 2,2',-3,3',4,4',5,5'-octachlorobiphenyl.

Results and Discussion

From the obtained nmr, ir, and glc data, it can be conclu that the two hexachlorobiphenyls and two heptachlor phenyls are major constituents of the investigated Phenoc DP 6 chlorinated biphenyl mixture. Moreover, the mel points of the isolated fractions showed no depression w mixed with the corresponding synthetic material. The s metric compound 2,2',4,4',5,5'-hexachlorobiphenyl can obtained in a pure form by a relatively simple synthesis, will be used for toxicity studies. The identification study been restricted to the Phenochlor mixture. As far as the chromatograms are concerned, comparable products of ot manufacturers have been found similar (Koeman et al. 19 Figure 1).

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A Smog Chamber Study Comparing Blacklight Fluorescent Lamps with Natural Sunlight

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■ Photochemical smog is commonly studied in irradiation chambers by using blacklight fluorescent lighting, which differs in several respects from natural sunlight. A direct comparison of the effects of artificial and natural sunlight has been obtained in a glass chamber. Since only slight discrepancies are observed in comparable experiments with blacklight or sunlight irradiation, the differences between blacklight lamps and natural sunlight do not dramatically influence photochemical smog formation with the systems investigated. This finding justifies the conventional use of blacklight irradiation in laboratory investigations of photochemical smog.

Much of the present knowledge about photochemical smog comes from studies conducted in irradiation chambers with either fluorescent lamps (Altshuller, 1966; Altshuller and Bufalini, 1965, 1971; Heuss and Glasson, 1968; Katz, 1970) or actual sunlight (Altshuller et al., 1970). Artificial sunlight obtained from fluorescent lamps differs appreciably from natural sunlight, and these differences in the light source conceivably could affect photochemical smog formation. One comparison of the effects of artificial and natural sunlight was presented by Stephens et al. (1967), who used gas-liquid chromatography (glc) to follow hydrocarbon disappearance with a sample of urban air in two glass vessels. One vessel was exposed to the sun for an entire day, and the

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