SOME TENTATIVE RULES FOR PREDICTING BIOLOGICAL REFRACTIVITY OF HALOGENATED AROMATICS

Q. E. Thompson

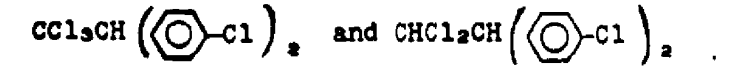
Evidence to date indicates that among chlorinated biphenyls those molecules containing 4 or more chlorine atoms per molecule are the chief offenders insofar as biological contamination is concerned. The higher Aroclors are thus said to be "refractive" with respect to natural degradative processes. The extent to which lower chlorinated biphenyls are refractive remains to be determined.

A considerable literature exists concerning the biodegradability of chlorinated hydrocarbon pesticides. Several recent papers (1,2,3) give results which may be of use in predicting biodegradability of Aroclors and some possible Aroclor substitutes. In brief, the findings may be summarized as follows.

A. Aliphatic Hydrocarbons: Aliphatic materials containing one chlorine atom are not refractive. Additional chlorine substitution markedly increases refractiveness (Dieldrin, Aldrin, Heptachlor, DDT) although the latter may still be somewhat degradable under anaerobic conditions.

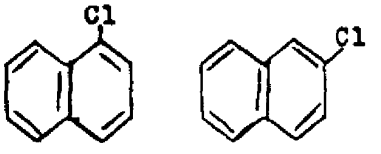
B. A Benzene Nucleus

1. When not substituted with at least one C-atom or one O-atom, a benzene ring becomes refractory with only one Cl-atom attached. DDT and DDD seem to be special cases in which refractiveness is increased by the high degree of chlorination in the aliphatic portion of the molecule, i.e.

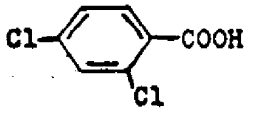


2. A benzene nucleus substituted by one C-atom or one O-atom generally requires at least two chlorines before it becomes refractive.

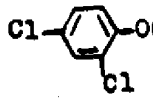
Examples:

a) 

not refractive

b) 

almost but not quite refractive

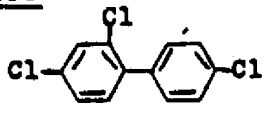
d)  not refractory while the 2,4,6 trichloro analog is.

d) Ar-O substitution alleviates refractivity more than Ar-C substitution (cf b vs. c)

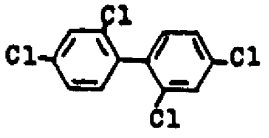
e) An isomer with chlorine closest to the point of substitution will metabolize slower than one with chlorine substitution farther away (1-chloronapthalene slower than 2-chloro isomer, o-chlorobenzoic acid slower than p-chlorobenzoic acid).

Applying the preceding observations to the Aroclor situation permits the following predictions.

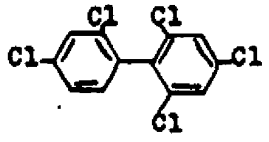
A. Aroclors

1.  probably not refractory - neither ring has more than two chlorines.

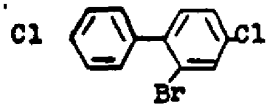
~1242 (41% Cl)

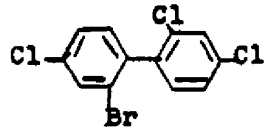
2.  borderline - probably not completely refractory.

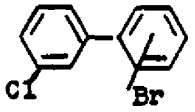
~1248 (48.5% Cl)

3.  refractory -

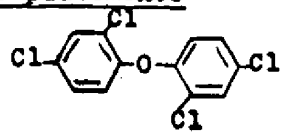
B. Bromochlors - Would conform to the same rules.

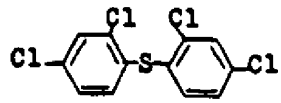
1.  equivalent to Aroclor 1248 would no longer be borderline but should be at least as degradable as the $(Cl)_3$-biphenyl.

2.  equivalent to 1254 in physical properties but approximately the same as Aroclor 1248 in refractivity.

3.  equivalent to 1242 in physical properties but less refractive.

C. Other possible Aroclor replacements

1. Diphenyl ethers -  less refractory than $(Cl)_4$-biphenyl

2. Diphenyl sulfides -  probably still less refractory than the corresponding oxygen ether since -S- is more electron releasing than -O-.

Undoubtedly, additional factors such as water solubility, hydrolytic stability as well as oxidative and light stability also influence the extent of environmental refractiveness. Thus, for example, highly chlorinated materials which could hydrolyze readily to chlorophenols (pentachlorophenol, etc.) might be expected to be substantially less serious long term contaminants than a material of similar or lesser chlorine content which resists the initial hydrolytic attack. Specific data on these points are however lacking at present.

October 6, 1969

REFERENCES:

1. R. W. Okey and R. H. Bogan, "The Apparent Involvement of Electronic Mechanisms in Limiting the Microbial Metabolism of Pesticides", J. Water Pollution Control Federation, 37, 692 (1965)

2. D. W. Hill and P. L. McCarty, "Anaerobic Degradation of Selected Chlorinated Hydrocarbon Pesticides", ibid., 39, 1259 (1967).

3. H. G. Schwartz, "Microbial Degradation of Pesticides in Aqueous Solutions", ibid., 39, 1701 (1967).