the region below 600 cm^{-1}, is sensitive to polymorphic variations (*10*). The Raman spectra of the four samples were, therefore, recorded, and they are compared in Fig. 2, in which it is clear that although the spectrum of cellulose IV is quite similar to that of cellulose II, the spectrum of I-R is almost identical to that of the native cellulose I. There is thus very little question that the sample recovered at 170°C is a high crystallinity cellulose in the native lattice.

In view of the questions raised above concerning the problem of residues in previous studies, it is well to consider the possibility in the present instance. We believe that a number of our observations exclude this possibility. The SEM micrographs of the I-R sample revealed structures that are spongy and stringy, and they are much larger than the pore sizes of the filters used for clarification of the solutions. Furthermore, the structures had no similarity to the morphological features of the native fiber. The DP of sample I-R is 60; it is unlikely that cellulose of such low DP would resist dissolution in 85 percent phosphoric acid. Indeed, sample I-R can be redissolved in phosphoric acid quite readily. Finally, and perhaps most convincing, if we were observing an artifact due to residues it would be difficult to explain recovery of celluloses II and IV from the same solutions when they are regenerated respectively at room temperature and at 150°C.

Although the implications of our observations are manifold, they cannot be developed fully here. It seems clear that the native lattice can no longer be regarded as attainable only through biosynthesis. The conditions under which it was regenerated, although quite remote from those prevailing during synthesis of the cell walls in a living plant, must have factors in common with the biosynthetic process. The thermodynamic condition of the regenerated material is not clear; the conditions of regeneration involve heterogeneities in temperature and solvent environment. Whether they are as dispersive as the conditions thought to generate structure in biological systems (*11*) remains an open question. The role of phosphate ester groups must also be considered, for their rapid hydrolysis in regeneration may contribute to the energetics of the process.

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4 April 1974; revised 24 May 1974

Mirex: An Unrecognized Contaminant of Fishes from Lake Ontario

Abstract. A perchlorinated, cage-structured hydrocarbon, $C_{10}Cl_{12}$, also known as mirex or Dechlorane, has been identified in fish samples from the Bay of Quinte, Lake Ontario, Canada. The compound coelutes with polychlorinated biphenyls (PCB's) in residue cleanup procedures and under standard gas chromatographic conditions. Mirex has never been registered for use as an insecticide in Canada, nor does it appear to be in use in any area of the United States discharging water into Lake Ontario or its tributaries. It seems likely, therefore, that this compound is another widespread environmental contaminant of extremely high geochemical stability and as yet only superficially investigated biological activities. Under standard gas chromatographic conditions its peak is superimposed on that of the PCB's, and, as a result, the presence of mirex may have been unrecognized and it may therefore have been misinterpreted as a PCB isomer.

In recent years, pesticides in general and the DDT group (*1*) in particular have been of increasing concern to environmental protection agencies around the world. A wide variety of aquatic and terrestrial samples have been and are still being monitored for residual contaminants, and the results indicate that the evidence of pesticides is widespread. Until 1966, neither the presence of polychlorinated biphenyls (PCB's) (*2*) nor their interference with the DDT analysis was recognized. However, analytical cleanup techniques were rapidly developed to permit differentiation between the DDT group and PCB's, primarily column chromatographic separations of the more polar pesticides from the less polar PCB fractions. It is ironic to find now that still another compound may be hidden under the PCB peaks.

I report here the detection of a perchlorinated hydrocarbon, $C_{10}Cl_{12}$, commonly known as mirex (*3*), in fish samples distinctly remote from areas of any field application of this insecticide (*4*) and its presence in the PCB fraction of residues treated by approved standard procedures (*5, 6*). Two fish

Table 1. Sample data for PCB and mirex residues from two fishes from the Bay of Quinte, Lake Ontario, Canada; ppm, parts per million; N.D., value not determined.

Part	Weight (g)	PCB's as Aroclor (ppm)			Mirex (ppm)
		1242	1254	1260	
Northern longnose gar [Lepisosteus osseus (L.)], 902 g					
Gonads	32	2.09	1.18	0.44	0.020
Viscera, fat	62	3.14	2.95	0.90	0.041
Liver	19	0.68	1.31	0.88	0.047
Northern pike [Esox lucius (L.)], 2930 g					
Pectoral to pelvic fin	930	N.D.	N.D.	N.D.	0.025
Post-anal fin	280	0.89	1.01	0.48	0.050

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samples from the Bay of Quinte, located on the northern side of Lake Ontario, were investigated. The Bay of Quinte receives waters from agricultural, industrial, and urban areas and shows significant eutrophication. The samples were taken in May and July 1973, respectively, and were digested with sulfuric acid. The purified extracts were analyzed for their PCB contents by two parallel means: (i) quantitative determination of PCB's by gas chromatography with electron capture detectors (*5, 6*) and (ii) qualitative investigation of the gas chromatographic peaks by computerized gas chromatography–mass spectrometry (*7–9*). The sample and analytical data obtained are summarized in Table 1.

The magnitudes of the PCB residues observed were comparable to those of other fishes from Lake Ontario (*10*). The samples were also found to contain several other insecticides, particularly of the DDE group (*1*), but no effort was made to quantify these. One "PCB" peak was found with a mass spectrometric fragmentation pattern different from that of known PCB isomers. The base peak of this compound had a mass-to-charge ratio (*m/e*) of 272 with an isotope cluster centered on this peak, unambiguously indicating a $(C_5Cl_4)^+$ moiety. Mass spectrometric fragmentations showing this cluster are derived from compounds containing a perchlorocyclopentadiene unit in their molecular structure or, for a very few cases, from similar, highly chlorinated hydrocarbons (*11*). Compounds of this kind include such insecticides (*12*) as aldrin, chlordane, dieldrin, endrin, endosulfan, heptachlor, Kepone, mirex, Pentac, and toxaphene.

The identification of the unknown in the fish samples as mirex was established by a combination of certain gas chromatographic and mass spectrometric techniques. For several gas chromatographic conditions (*7*) the retention volumes of the compounds aldrin, chlordane, endrin, dieldrin, heptachlor, and toxaphene were considerably smaller than that of mirex. The retention volume of mirex was identical with that of the observed compound, and endosulfan cannot be chromatographed under these conditions. The differentiation between mirex, Kepone, and Pentac was achieved by combined gas chromatography–mass spectrometry with a computer-controlled system (Pentac has a mass spectrum quite different from those of mirex and Kepone and can therefore be eliminated). To enhance the system's sensitivity, a selective ion-monitoring program (*8*) was used under the same gas chromatographic conditions as for the previous PCB investigation. Thus a constant retention time for the unknown compound was assured. The mass spectrometer was set to observe seven small mass ranges, five of which are relevant to mirex or Kepone fragments, or both. The *m/e* ranges were as follows: 220 to 225, 235 to 241, 253 to 258, 270 to 275, 353 to 361, 451 to 465, and 505 to 517, with integration times for each atomic mass unit of 30 msec (*9*). Table 2 lists the observed intensities together with those of mirex and Kepone standards (*13*).

For $m/e < 360$ the mass spectra of mirex and Kepone are quite similar. Both compounds have base peaks of *m/e* 272 due to the $(C_5Cl_4)^+$ ion. Mirex, however, has a different fragmentation pattern at the high mass end which is substantially demonstrated by the mass spectrum of the fish samples: peaks due to Kepone (*m/e* 451 to 463) are absent, and those due to mirex (*m/e* 505 to 517) are observed. The molecular ions of mirex (*m/e* 540 to 544) are of very low relative intensities and were not investigated. All gas chromatographic and gas chromatographic–mass spectrometric data for the observed compound were in good agreement with those of authentic mirex.

Table 2. Mass spectra of mirex observed in fish samples and of mirex and Kepone standards (*13*). Only major peaks with $m/e \geq 235$ are presented.

m/e	Relative intensities		
	Fish samples	Mirex	Kepone
235	50	28	24
236	7	4	3
237	77	55	38
238	8	6	4
239	49	30	25
240	4	4	3
241	15	10	9
270	54	52	50
271	7	5	5
272	100	100	100
273	10	7	7
274	80	76	80
275	6	6	6
276	36	36	35
277	3	3	3
278	9	9	9
353	6	6	6
355	11	11	11
356	2	2	2
357	13	13	12
358	3	1	2
359	4	3	7
360	3	1	4
361	2	1	3
451	0	0	2
453	0	0	7
455	0	0	8
457	0	0	6
459	0	0	4
461	0	0	2
463	0	0	1
507	1	2	0
509	1	3	0
511	1	4	0
513	1	2	0

The identification of mirex and Kepone and their differentiation between PCB's and mirex (*14*). This is especially true for laboratories outside the areas of direct insecticide application where mirex contamination has hitherto not been observed. In fact, in the ordinary analytical procedure, the mirex peak is exactly superimposed on one of the major Aroclor 1260 peaks. Since with the use of the electron capture detector it is impossible to differentiate between a PCB and coeluting mirex, there is a strong likelihood that the presence of mirex in many environmental samples has not been recognized. As a result, the gas chromatographic spectra of PCB samples containing mirex may have been misinterpreted, for example, in the lack of any report of mirex as part of Reynolds' PCB peak XII (*5*).

The question of the source of mirex in environmental samples remains. The chemical has been used as an insecticide in the southern United States and is promoted as a flame retardant additive for polymer formulations. The following hypotheses as to its source in the fish samples are offered: (i) discharge into waterways connected with the sample location; (ii) impurities in other chemicals used or manufactured near the sample location; and (iii) environmental distribution of the contaminant through the atmosphere. The third pathway particularly seems to predominate for other compounds of low water solubility (*15*). A decision on the source of the compound cannot be made at this time. Both the first and the second pathways, however, could easily be eliminated if other samples from remote areas can be shown to contain the contaminant.

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1. Abbreviations: DDT, 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane; DDE, 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene.
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5 March 1974; revised 10 April 1974

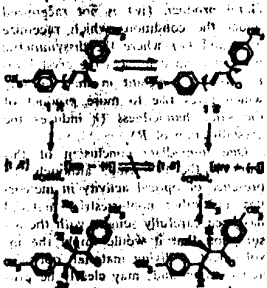
Mechanism for the Autocatalytic Formation of Optically Active Compounds under Abiotic Conditions

Abstract. The bromination of chiral crystalline samples of 4,4'-dimethylchalcone was reinvestigated. In the presence of the optically active, reaction product, (+)- or (−)-chalcone dibromide, crystallization from solutions of the achiral chalcone is specifically directed toward one handedness. A feedback mechanism can thus be envisaged where optically active compounds are formed, generate additional material of the same chirality, and communicate this chirality to other regions, simply by cycles of solidification, reaction, and liquefaction.

Crystals of 4,4'-dimethylchalcone, **1**, space group $P2_12_12_1$, belong to the class of chiral (enantiomorphic, dissymmetric, optically active) crystals. In solution or in the melt, rotation about single bonds causes rapid interconversion between the right- and left-handed conformations, *R* and *S*. In the crystal, however, the conformations are locked in and cannot interconvert; further, as a result of the chiral crystal structure, all of the molecules in any single crystal have the same chiral conformation (*1*). Penzien and Schmidt found that the addition of bromine to monocrystals of **1** afforded optically active dibromide, **2**, some crystals yielding (+)-**2** and some yielding (−)-**2** in excess (*2*).

Penzien and Schmidt also noted inoculation effects. As a result of the more rapid growth of the initially formed precursors of (+) or precursors of (−) crystal of **1** and their subsequent inoculation effects, polycrystalline samples of **1** also afforded **2** with varying degrees of optical activity. The spontaneous generation of optical activity by crystallization, of which this is a striking example, has been reported in other, widely different chemical systems (*3*, *4*).

When solutions of **1** in ethyl acetate were slowly evaporated, the resulting



(+)-**2** (−)-**2**

polycrystalline samples yielded, on treatment with bromine vapor, optically active dibromide, **2** (*5*). Both dextrorotary (+) and levorotary (−) material were formed (Fig. 1a) and, although the data show bias in favor of (+) material, this is most likely a result of the relatively small number of samples (*6*).

When solutions containing **1** and 3.97 mole percent of optically active (+)-dibromide [(+)-**2**] were evaporated, polycrystalline samples of **1** (containing some **2**) again resulted. But bromination of these samples as above now gave only levorotary [(−)-**2**] material (Fig. 1b) (*7*). The dibromide initially added was 62 percent optically pure, so that the solution contained only 0.025 mole of excess pure (+)-enantiomer per mole of **1** [or 0.042 g of pure (+)-enantiomer per gram of **1**] prior to crystallization.

The same experiment was repeated with (−)-**2** to induce crystallization of **1**. Twelve solutions of **1** and (−)-**2** (3.97 mole percent) in ethyl acetate were evaporated, and the resulting solids were powdered and brominated (*8*). All afforded (+)-**2** (Fig. 1c). In this experiment the (−)-**2** used to induce chirality was only 17 percent optically pure so that only 0.0067 mole of excess pure enantiomer was present per mole of dimethylchalcone, **1**.

In order to show that the presence of racemic (±)-**2** cannot direct the chirality of the crystallization of **1**, we evaporated and brominated solutions of the chalcone containing 5.2 mole percent of (±)-**2**. As we expected, both (+)- and (−)-dibromide were produced during the gas-solid reaction (Fig. 1d).

Another example illustrating that the crystallization of compounds which appear in chiral crystal structures can be profoundly affected by the presence of chiral materials is provided by Pincock *et al.*, who have found that the crystallization of a racemic melt of 1,1'-binaphthyl is directed toward the formation of (−)-samples in the presence of *l*-mandelic acid, while *d*-mandelic acid induces the crystallization of (+)-material (*6*). The resolution of racemates by chiral solvents is a related phenomenon (*9*). Our results indicate that the influence of even small quantities of optically active material in directing the chirality of crystals may be general. Further, the possibility of a feedback mechanism leading to the autocatalytic formation of optical activity is raised.

MONS 069539