AN ABSTRACT OF THE THESIS OF

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        (Major)   (Date)

Title: THE CRYSTALLOGRAPHY OF ALDRIN AND

DIELDRIN INSECTICIDES

Abstract approved: _____
                              Max B. Williams

The object of this investigation was to determine a number of
physical constants for the crystals of two commonly used insecti-
cide compounds. The compounds chosen were Aldrin and Dieldrin,
which are chlorinated cyclodiene compounds. These compounds are
in considerable use today, and show promise of heavy continued use.
The data collected includes crystal system and structure, unit cell
dimensions, refractive indices, optical directions, and fusion data.
This data should allow determination of the identity of these com-
pounds by use of the techniques of chemical microscopy, although
admittedly, the work reported here does not include the complete
amount of crystallographic and optical information possible.

The two compounds were investigated and the following
information was obtained.

Dieldrin crystallizes into two forms, depending presumably

upon the polarity of the solvent used. One form (benzene) is tetragonal, and was found to be uniaxial negative in character. The other was orthorhombic and biaxial positive.

Aldrin crystallizes in the monoclinic system and is also biaxial positive. Both Aldrin and Dieldrin have rather large unit cells.

The author had considerable difficulty in obtaining the proper sized crystals for analysis. Nevertheless, it was demonstrated that the commercial and rather crude product could be recrystallized a few times using ordinary techniques, and the crystals obtained could be used to provide a fairly specific identification.

The Crystallography of Aldrin
and Dieldrin Insecticides

by

Donald Alan Griffin

A THESIS

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Professor of Chemistry
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THE CRYSTALLOGRAPHY OF ALDRIN
AND DIELDRIN INSECTICIDES

INTRODUCTION

The object of this investigation was to determine a number of
physical constants for the crystals of two commonly used insecticide
compounds. The compounds chosen were Aldrin and Dieldrin, which
are chlorinated cyclodiene compounds, and are in considerable use
today. The data collected includes crystal system and structure,
unit cell dimensions, refractive indices, optical directions, and
fusion data.

The investigation was undertaken to add these compounds to the
list of compounds for which data is available. Since these compounds
are both highly toxic and will be used for many years, one should be
able to identify them by general methods. The author wanted to
develop a knowledge of the techniques required to obtain this data.

The compounds chosen are two commonly used organochlorine
insecticides that show promise of heavy continued use. Dieldrin has,
in particular, been of interest on this campus. Several different
research groups have been carrying out studies with this compound
as part of a large Public Health Service grant.

The data collected should allow determination of the identity of
these compounds by use of the techniques of chemical microscopy,

although admittedly, the work reported here does not include the complete amount of crystallographic and optical information possible. This data is important because chemists and laboratories are not equipped with the specialized techniques, equipment, and reference chemicals available to a pesticide analyst. A chemist faced with an unknown chemical will apply a general method of analysis to try to determine the identity. Chemical microscopy and X-ray diffraction are two commonly used, general, unknown identification methods. Chemical microscopy in particular is used in many criminology laboratories for study and identification.

A word of caution should be added at this point. These compounds are highly toxic and very stable. They should be handled with care. They are stable to strong base and mild acids, but are destroyed by concentrated strong acids.
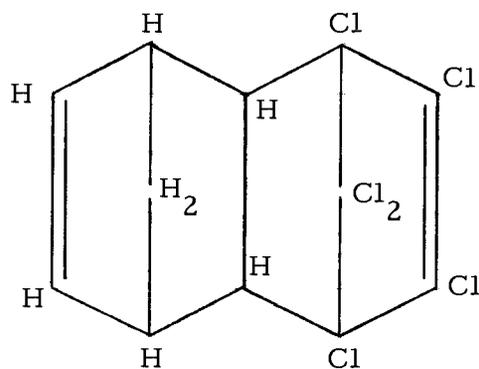
GENERAL INFORMATION ON COMPOUNDS

Aldrin and Dieldrin are chlorinated cyclodiene insecticide compounds. The structure of Aldrin is shown in Figure 1 as a planar and a three-dimensional representation (4). The I. U. P. A. C. system chemical name is also given. The compound is also known as compound 118, "Octalene", and HHDN. The name "Aldrin" applies to material containing not less than 95% of the compound. The chemical was developed by J. Hyman and Company, and first described in the literature by Kearns in 1948 (3). The manufacture of the compound is protected by U. S. Patent 2, 635, 977, which presently belongs to the Shell Oil Company. Aldrin is produced by the dehydrochlorination by alcoholic potash of the Diels Alder condensation product of cyclopentadiene and vinyl chloride to yield bicyclo [2, 2, 1] -2, 5 - heptadiene. The condensation of this compound with hexachlorocyclopentadiene yields Aldrin (Figure 2).

The compound is a white, crystalline, odorless solid with a melting point of 104-104. 5° C. The commercial grade is a dark tan solid, which melts at 50 to 60° C. It is insoluble in water, moderately soluble in mineral oils, and readily soluble in acetone, benzene, xylene and methanol (1). It is stable to alkali and to mild acid; oxidizing agents and strong acids attack the unchlorinated ring. The planar formula would suggest four possible stereoisomers.

1, 2, 3, 4, 10, 10 - hexachloro - 1, 4, 4a - 5, 8, 8a -

hexahydro - _endo_ - 1, 4 - _exo_ - 5, 8 - dimethanonapthalene

planar representation
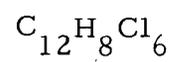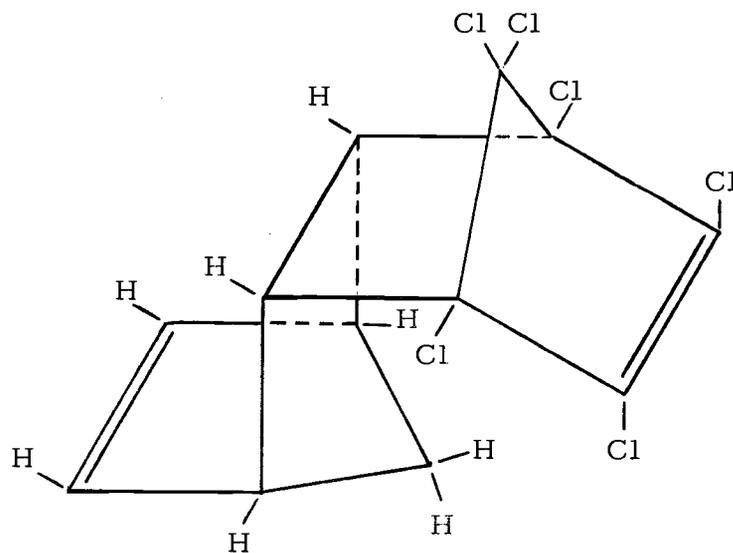

3 dimensional representation

$C_{12}H_8Cl_6$

Figure 1. Molecular structure of Aldrin.

cyclopentadiene

$+$ H$_2$C $=$ CHCl $\xrightarrow[\text{Alder}]{\text{Diels}}$

bicyclo (2, 2, 1)-2, 5-heptadiene

hexachlorocyclopentadiene

$\xrightarrow[\text{Alder}]{\text{Diels}}$
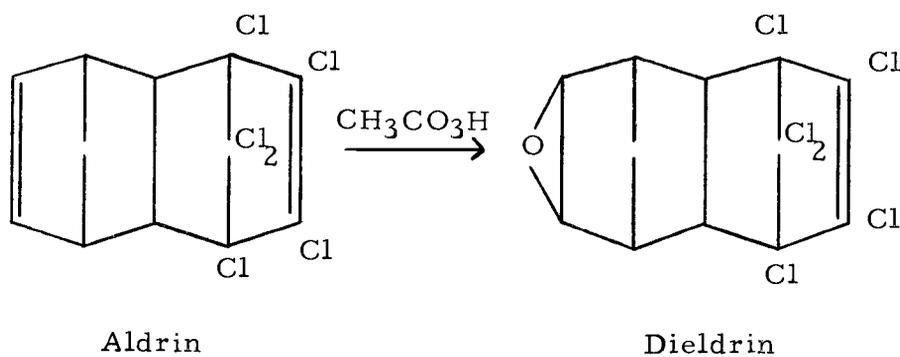
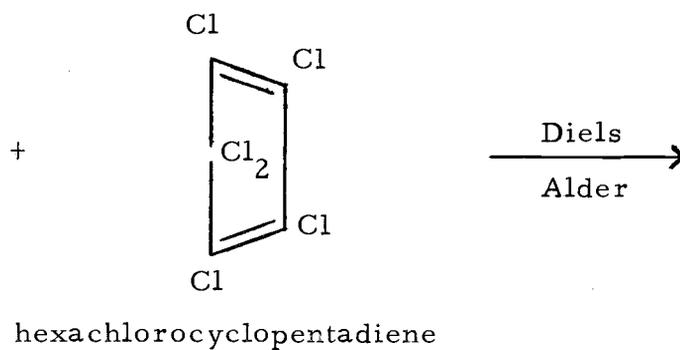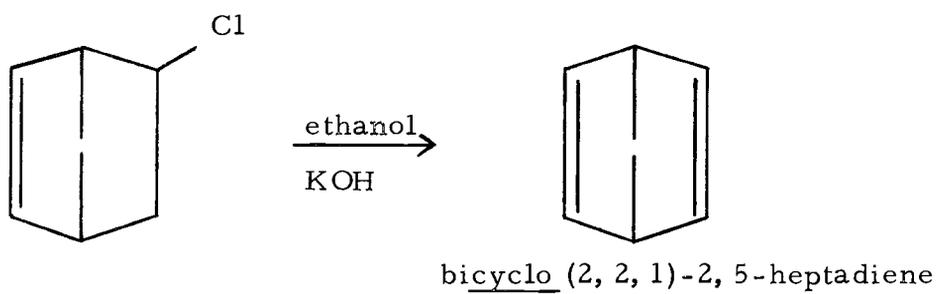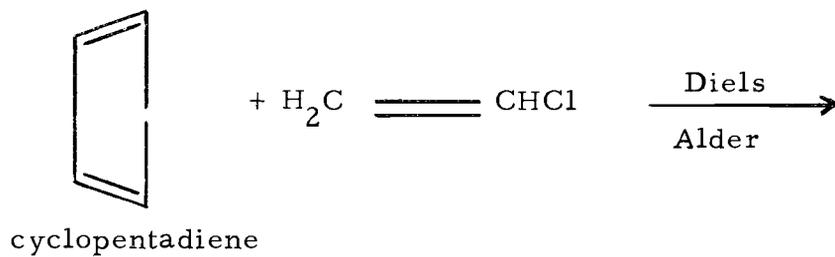Aldrin $\xrightarrow{\text{CH}_3\text{CO}_3\text{H}}$ Dieldrin

Figure 2.   Synthesis of Aldrin and Dieldrin.

Aldrin is thought to be the endo-exo structure shown in Figure 1. The endo-endo isomer is known as Isodrin, and would be found as an impurity of Aldrin. Isodrin has some toxicity, but is not a registered pesticide. Aldrin is a potent and persistent insecticide, both by contact and ingestion, and is especially effective against soil insects.

Dieldrin is the 6, 7 exo epoxide of Aldrin. The structural representation and I. U. P. A. C. name are given in Figure 3. Dieldrin is the approved name for material containing at least 85% of the compound. Other names for Dieldrin are HEOD, compound 497, and "Octalox". It was also developed by Julius Hyman and Company and first described in 1948 by Kearns (3). It is produced by oxidation of Aldrin with peracetic or perbenzoic acid (Figure 2). The manufacture is governed by the same patent as Aldrin.

Dieldrin is a white, crystalline, and odorless solid with a melting point of $175-176^{\circ}$ C and a density of 1. 75 (4). The commercial product is light brown in color with a melting point of 95° C or above. It is insoluble in water, slightly soluble in mineral oils, moderately soluble in acetone and methanol, and soluble in aromatic solvents. The planar formula yields eight possible stereo isomers. Dieldrin is thought to be the exo-epoxide of the endo-exo isomer shown in Figure 3. The corresponding oxidation product of Isodrin is known as Endrin. Endrin is a registered pesticide with equal

1, 2, 3, 4, 10, 10 – hexachloro – <u>exo</u> – 6, 7 – epoxy –

1, 4, 4a, 5, 6, 7, 8, 8a – octahydro – 1, 4 – <u>endo</u>, <u>exo</u> –

5, 8 – dimethanonapthalene

planar representation

3 dimensional
representation

$C_{12}H_8Cl_6O$
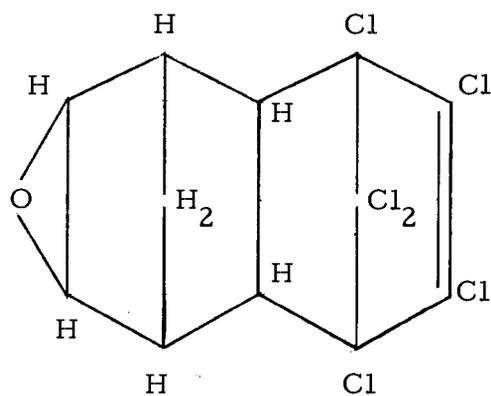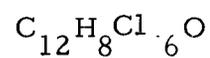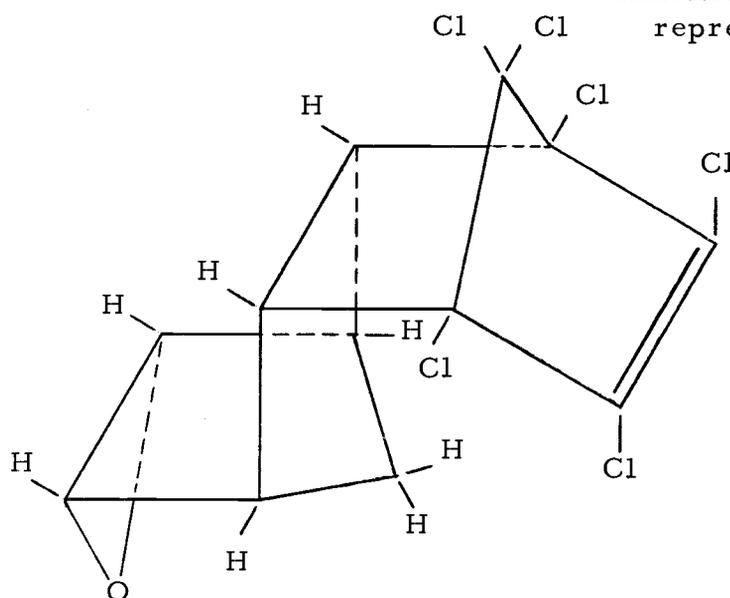
Figure 3.   Molecular structure of Dieldrin.

toxicity to insects and greater toxicity to mammals than Dieldrin.
Dieldrin is stable to alkali and mild acids. The epoxide group is
particularly stable. Dieldrin has high contact and stomach toxicity
to most insects, and is highly persistent and effective.

Many organisms present in the environment are capable of con-
verting Aldrin to Dieldrin. Dieldrin is the more toxic of the two
compounds. This is especially true for insects; for mammals they
are about the same in toxicity.

EQUIPMENT USED

The microscope used for most of this work was a Spencer polarizing microscope manufactured by American Optical Company. The instrument was equipped with mechanical stage, first order red plate, quartz wedge and two objectives. The fusion work was done using a Kofler hot stage in conjunction with a Bausch and Lamb microscope.

The X-ray investigations were carried out on a General Electric XRD-1 unit. The powder diffraction patterns were obtained using an oscillating wedge sample holder.

The rotating crystal studies were made using a Unicam Instruments Single Crystal Goniometer in conjunction with the General Electric unit.

The gas chromatographic purity determinations were made on a Varian Aerograph model 1520, equipped with an electron-capture detector.

RECRYSTALLIZATION

Both compounds were recrystallized from the commercial grade material. The Aldrin was manufactured by Julius Hyman and Company and the Dieldrin by Shell Agricultural Chemicals. Two separate methods were used; the first being used on Dieldrin only. This first method consisted of making up a warm, saturated solution of Dieldrin in redistilled benzene. This was done by heating on a steam bath, and filtering through a fine porosity, sintered glass, filter funnel. The solution was warmed slightly to remove any remaining crystals. The solution in an Erlenmyer flask was immersed in a container of warm water. The water provided more heat capacity so that cooling was slower. The water was allowed to cool to room temperature. The crystals were held in solution for several days prior to filtration on the sintered glass funnel. The recrystallization was done four times to produce the crystals used. This method seemed to inherently produce very small crystals.

The second method was used for both Aldrin and Dieldrin. This consisted of dissolving the material in nearly boiling redistilled methanol, until near saturation. The solution was allowed to cool slowly by immersion in water. The crystals were filtered off, using a fritted glass funnel as before. The crystallization was

repeated four times to produce the final crystals used. The solution

was allowed to sit a day or two prior to filtration. This delay

allowed for better crystal formation due to aging, and for obtaining

an equilibrium crystalline state.

It would be appropriate to mention here that the author experi-

enced considerable difficulty in obtaining crystals of a proper size

to be used for this work. The first method tended to supersaturate

and crystallize almost instantly into a solid mass of fine crystals,

and generally gave fine crystals if control could be achieved on the

speed of crystallization. The second method did not give much

problem from supersaturation. The problem here was one of elong-

ated crystals. If crystallized quickly, they were shaped like thick

hair with striations, and were not useable for observation. Letting

the crystallization proceed slowly caused the crystals to be thicker,

although still needle-like. The crystals then were generally too

thick for good observation. However, these latter crystals were

used, since they did offer good form, and enough cross section to

allow observation of interference figures.

Purity of Crystals

The crystals were checked for purity by gas chromatography.

Each batch was checked for the percent impurity present. This

was done by dissolving a known amount of sample in high purity

hexane and diluting by a factor of 10^4.

The hexane was injected into the gas chromatograph and the peaks compared with standard solutions of known identity and concentration to determine the purity. The gas chromatograph used was equipped with a 5' x 1/8 pyrex column packed with a mixture of 5% Dow Corning 11 silicone grease and 5% QF-1 flourinated silicone coated on 100-120 mesh Gas Chrom Q.

The instrument was equipped with an electron capture detector of concentric tube design. The linear analytical range was from approximately 10^{-9} to 10^{-12} g per injection. Typical results are shown in Figures 4 and 5 for each type of crystal studied. The purity of the crystals was better than 97% in all cases; the main impurity of each compound being the other, plus a little Isodrin and Endrin. The instrument is a routine instrument used in the Department of Agricultural Chemistry for pesticide residue analysis.

Aldrin

Aldrin
98 %

Dieldrin

Dieldrin

methanol Dieldrin
98 %

Aldrin
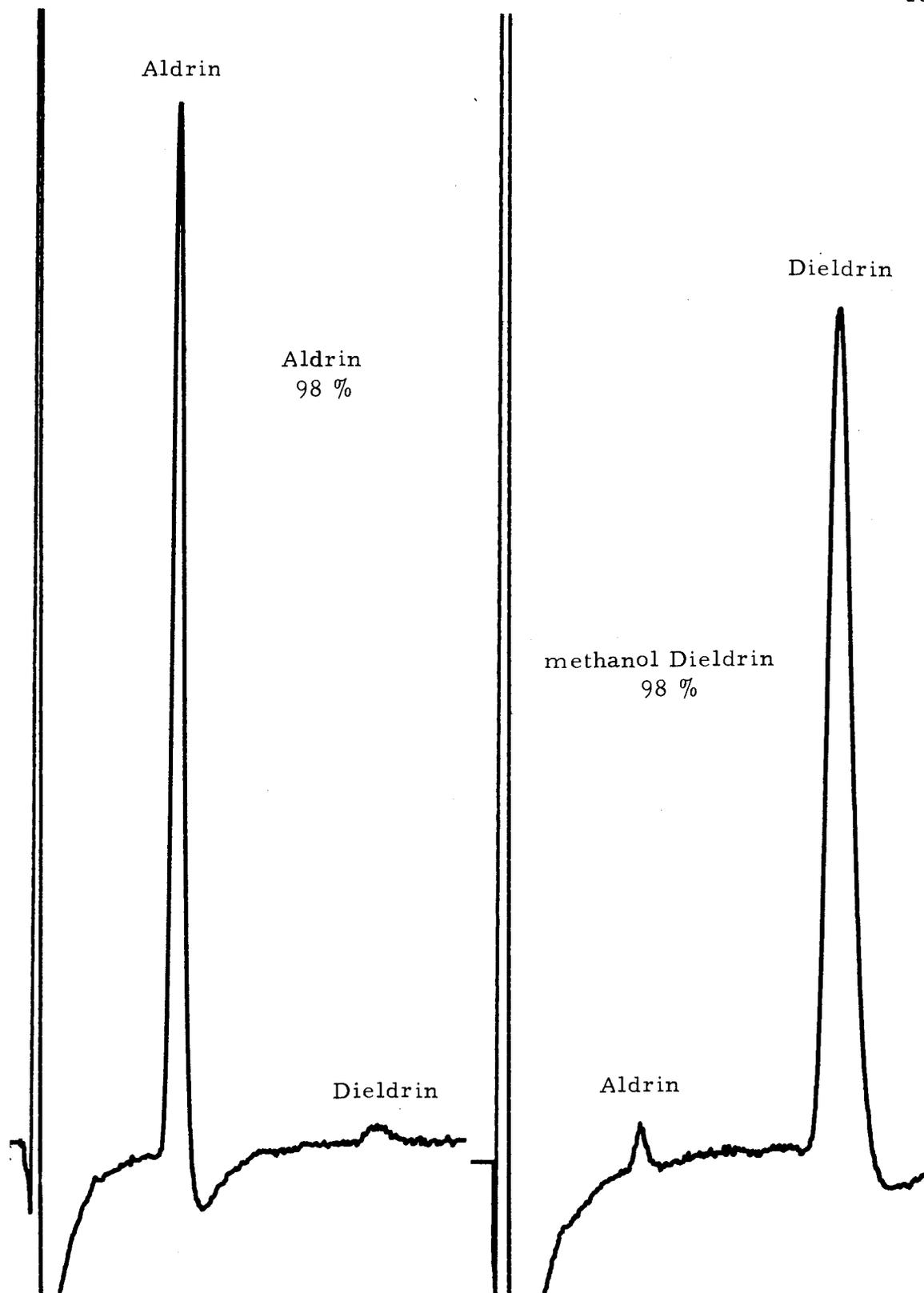
Figure 4.   Gas chromatography for determination of purity -
chromatograms.

Aldrin

Aldrin & Dieldrin ·
standard
0.080×10^{-9} gms

benzene Dieldrin
97 %

Dieldrin

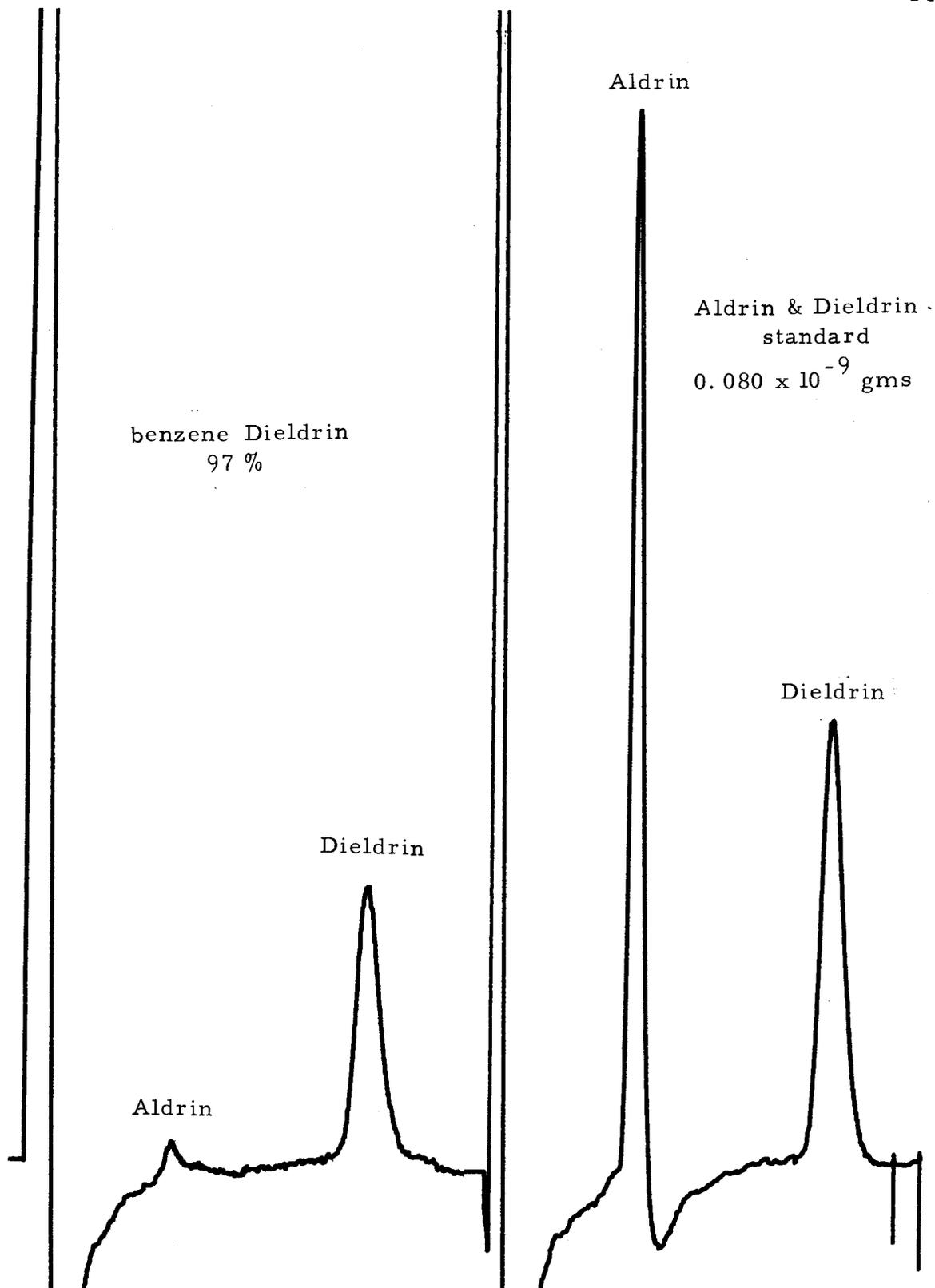Dieldrin

Aldrin

Figure 5.   Gas chromatography for determination of purity -
chromatograms.

METHODS AND RESULTS

Form and Habit

The form of the crystals was determined by direct observation.
The crystals were observed using a low power objective. In the
case of needle-like crystals, it was necessary to embed the tip of
the crystal so that one could view the crystal directly down the
elongated axis. Both compounds tended to form long needles. The
exception was the Dieldrin, recrystallized from benzene or hexane.
These were small, discrete crystals, with clean, sharp terminations
on the ends (see Figure 11).

The crystal form is given in Figure 6. Dieldrin as mentioned
previously can be obtained in two distinct forms. The first form
shall be referred to as the methanol form; since this was the solvent
used for recrystallization. These crystals were very elongated and
generally difficult to observe. They almost always lie on the 130
prism faces and as such provide one with an odd angle of view. The
crystals (methanol form) appear to be orthorhombic since it appears
that three unequal but perpendicular axes are present. The form of
the crystal would further suggest that it belongs to the orthorhombic
bypyrimidal symmetry class, since it has the highest degree of
symmetry to be found in this crystal class.

a = O. N.
b = Bx$_a$
c = Bx$_o$
orthorhombic

optic plane

a

optic plane

b

section as normally seen

optic plane

a

b

c

010

130

001
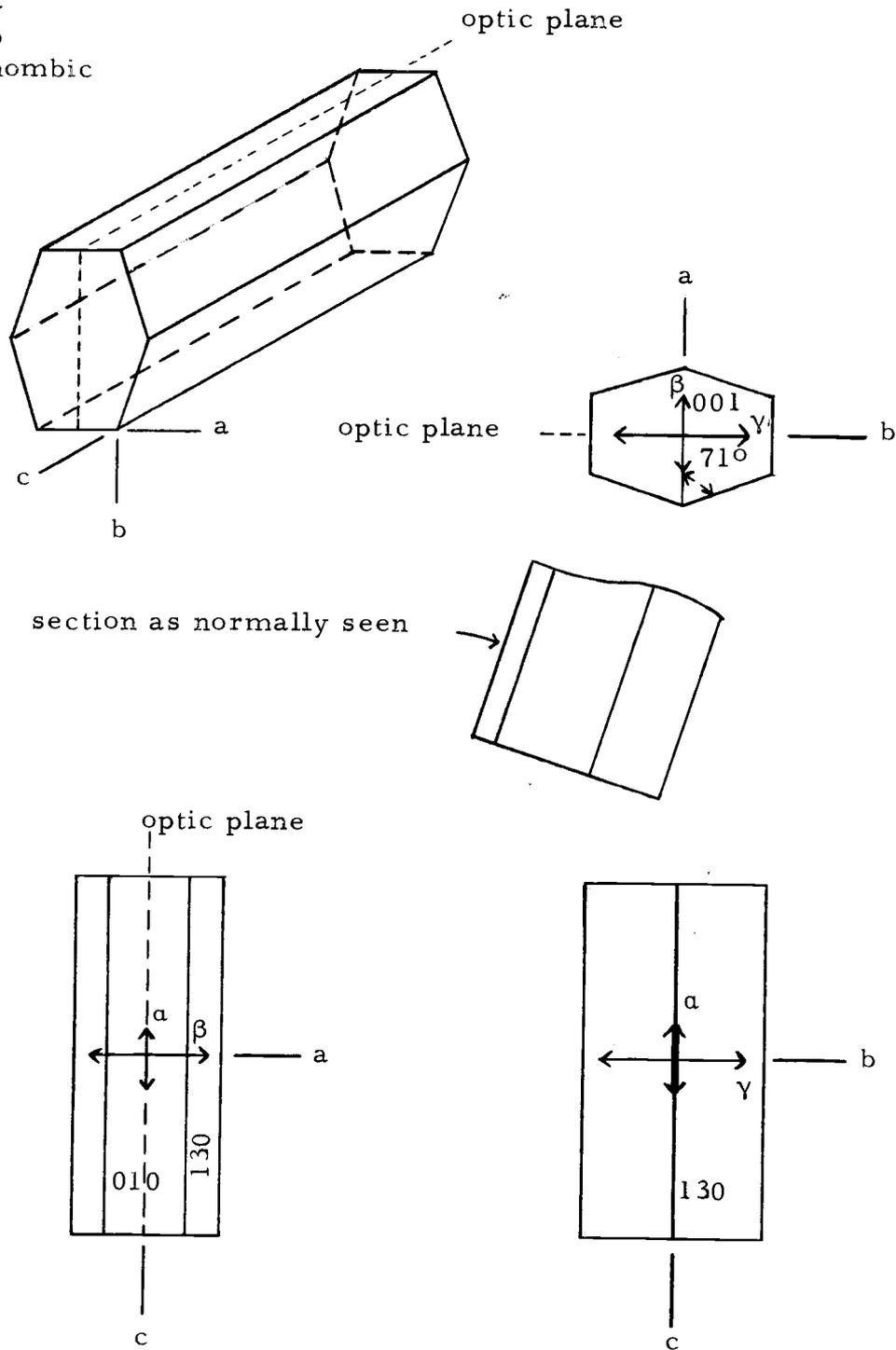
71°

β

γ

a

b

c

a

β

a

b

c

a

γ

130

Figure 6. Crystal structure of methanol Dieldrin.

The second form of Dieldrin, the benzene form, is shown in Figure 7. It appears to be tetragonal or orthorhombic, since it has three perpendicular axes. In the next section it will be shown that this form is tetragonal. Here again it appears that the benzene form is of highest symmetry for its class, and is ditetragonal bypyrimidal.

Aldrin is completely different in structure from Dieldrin. It is a simple monoclinic crystal, as seen in Figure 8. The symmetry is also the highest order of its class, prismatic.

Optical Properties

Using the polarizing microscope, an attempt was made to determine as much as possible about the optical properties of the two compounds. The first property to be investigated was the type of double refraction exhibited; in particular, whether the crystal had one (uniaxial) or two (biaxial) optical axes, and what the associated refractive indices and optic signs were.

The first step was to determine the types of extinction exhibited. All three crystals gave parallel extinction when the long axis was horizontal. The optical vibration directions correspond to the external faces of the crystal. This parallel extinction rules out the possibility of triclinic and rhombohedral (2, p. 264). The benzene Dieldrin, when sliced thinly perpendicular to the long axis,
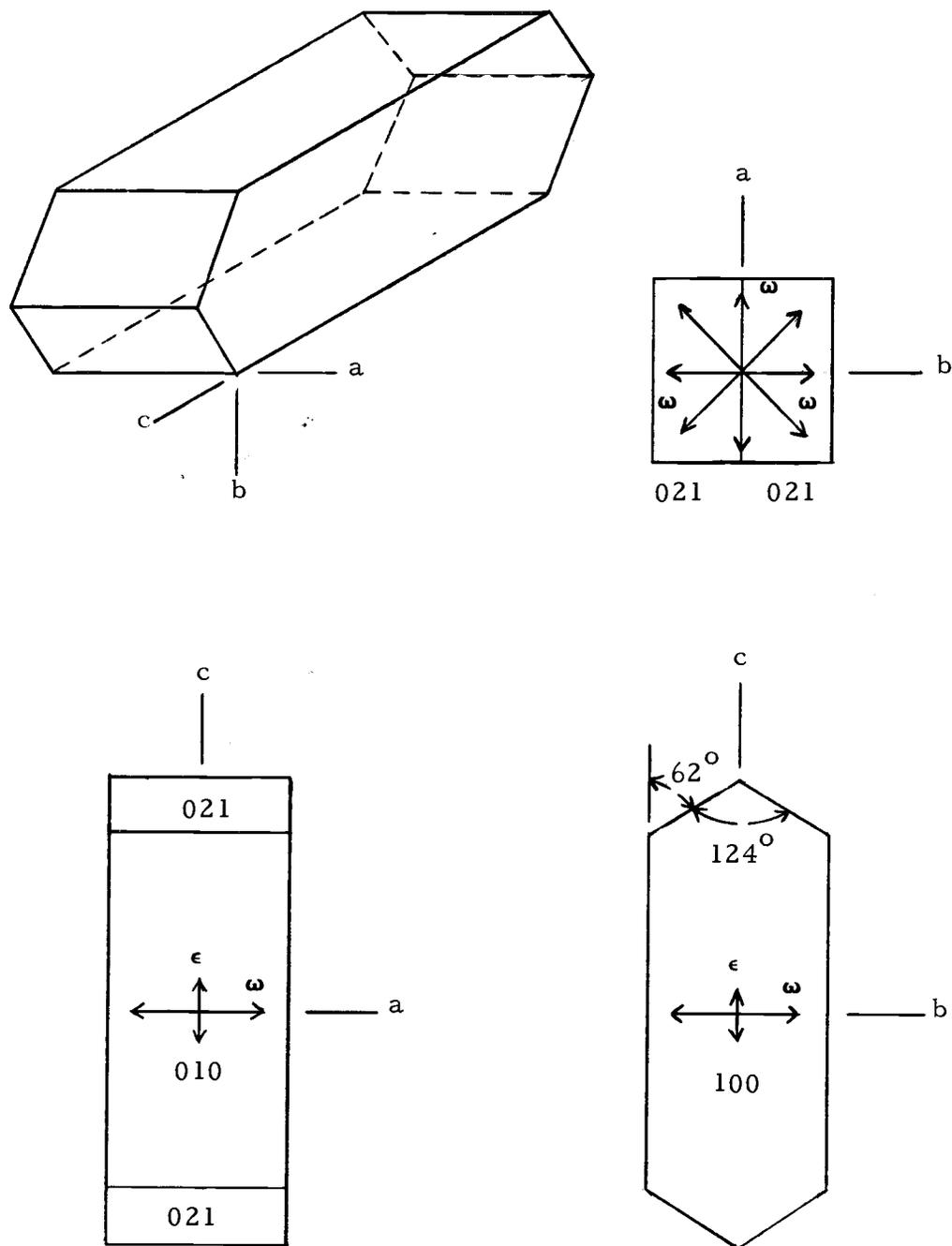
18

tetragonal

Figure 7. Crystal structure of benzene Dieldrin.

a = Bx$_a$
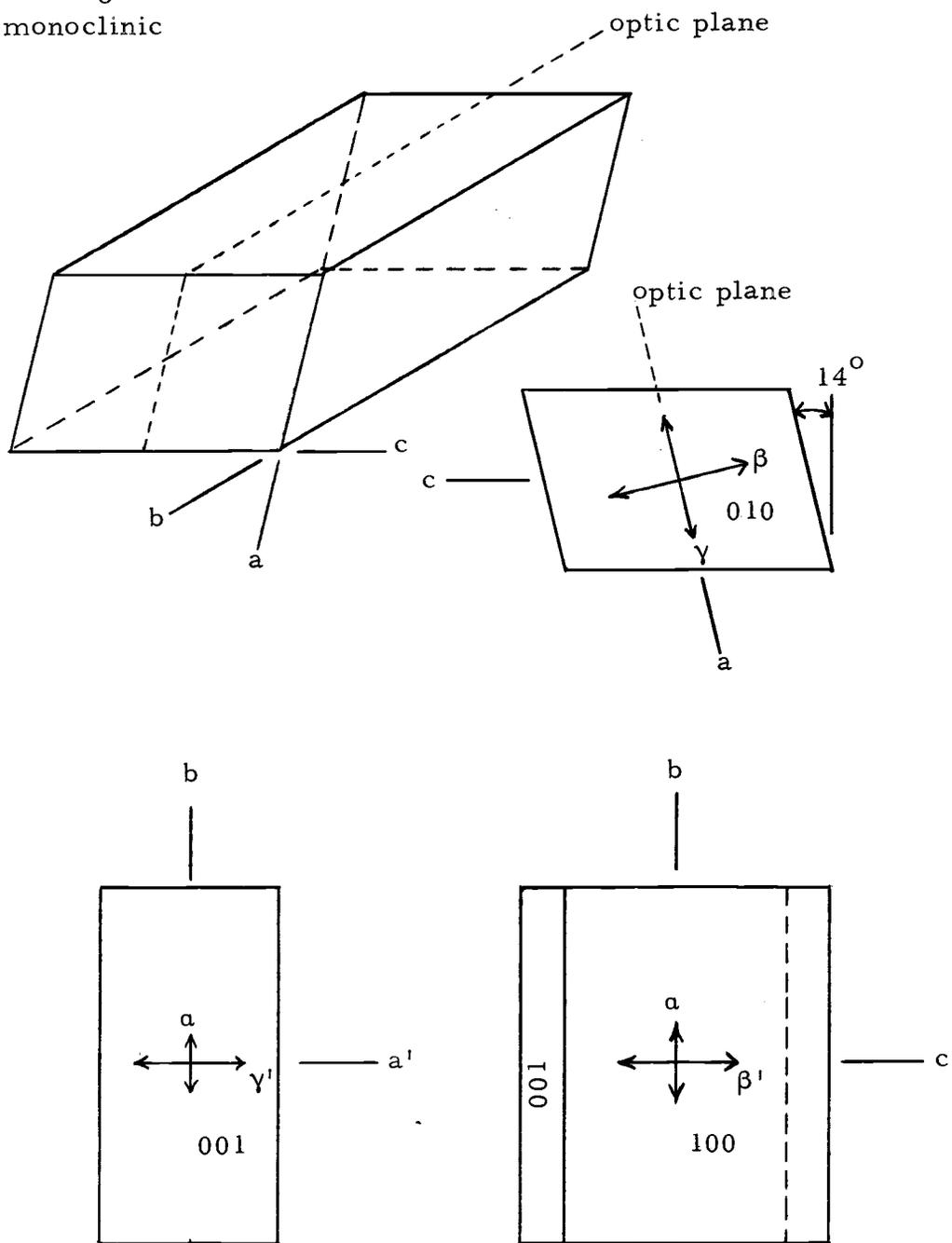b = Bx$_O$
monoclinic

Figure 8.   Crystal structure of Aldrin.

was isotropic, while the methanol Dieldrin was parallel, and the Aldrin parallel to the a axis (obtuse and parallel extinction). This would lead one to believe that the benzene product is tetragonal, since it is four sided. One would also deduce from the above that methanol Dieldrin and Aldrin are either orthorhombic or monoclinic.

Still using parallel light the quartz wedge and first order red plate were used to determine the optic sign of the benzene Dieldrin crystals. The quartz wedge did not give discernable interference colors. The first order red plate, however, gave compensation when the slow ray was parallel to the optic axis; therefore, the sample is optically negative ($\epsilon < \omega$).

Convergent Illumination - Benzene Dieldrin

The next step was to use convergent light to obtain interference figures. The benzene Dieldrin product was the first to be investigated in this manner. The basal section (cut perpendicular to elongation) was first observed. The figure observed was a very weak uniaxial optic axis interference figure which was slightly inclined as shown by Gibb (2, p. 278), the isogyres crossing at the very edge of the field. The isogyres remained parallel to the vibration directions of the polarizer and analyzer, when the stage was rotated. Use of the first order red plate and quartz wedge gave compensation in the quadrants parallel to the slow ray. The crystal is therefore negative

in optic sign ($\epsilon < \omega$).

With the optic axis horizontal, an attempt was made to observe the uniaxial flash figure, but only very weak isogyres were observed, which were not defined enough for positive identification. It appeared the angular movement required to sweep the flash figure was approximately four degrees, which according to Gibb (2, p. 293), is too short to be an obtuse bisectrix figure. The only confusion would be with an optic normal flash figure.

Convergent Illumination - Methanol Dieldrin

The crystals almost always lie on the 130 face (See Figures 6,11). The interference figure present here was an inclined and extremely diffuse optic normal figure, since we have ruled out uniaxial flash figure by extinction determination. According to Gibb (2, p. 294), the acute bisectrix enters the quadrants where the isogyres leave on clockwise rotation. Using this information and the fact that the extinction is parallel, one finds that the obtuse bisectrix must be parallel to the c axis, the acute bisectrix being in a plane perpendicular to the c axis of the crystal. Since this figure was an inclined optic normal and was obtained while nearly looking down the a axis, it appears at least that the optic normal is coincident with the a axis (see Figure 6). The acute bisectrix would then correspond to the b axis. It might be mentioned here that the crystals were rather thick.

Attempts to produce small crystals failed.

Orientation of the crystals so that the b axis was vertical, produced a slightly inclined acute bisectrix figure, which was fairly diffuse. The line through the eyes was parallel to the c axis of the crystal, reinforcing to assignment of obtuse bisectrix being parallel to the c axis. The b axis appears to be coincident with the acute bisectrix, although slightly inclined figures were the rule when this orientation was tried. This would suggest that maybe the acute bisectrix is a degree or two away from the b axis. With the crystal in this orientation the long axis was turned to 45° and the quartz wedge was used to try to determine the optic sign. The interference colors of the figure were very weak. It appeared that when the optic normal was parallel to the slow ray of the wedge, addition occurred. The crystal appeared to be optically positive in sign.

Convergent Illumination - Aldrin

The case of Aldrin was similarly investigated. The crystal normally lies on the ortho pinacoid face with the a axis oriented nearly vertical. This orientation when viewed under convergent light gave an inclined acute bisectrix interference figure. The eyes were outside of the field of view. The position of the isogyres and colored arcs would put the eyes in parallel with the b axis. Orientation of the crystal so that the a axis was more vertical centered

the figure and brought the eyes just into view. The acute bisectrix appears to coincide with the a axis. Using the quartz wedge, compensation was observed when the obtuse bisectrix was parallel to the slow ray, therefore, Aldrin appears to be optically positive.

Observation of a basal section cut perpendicular to the b axis should give one an obtuse bisectrix figure. This figure was indeed the case as one would assume from acute bisectrix and eye positions. A fairly defined figure was obtained which gave a flash with approximately 20° of rotation, which should distinguish this figure. Using the rule that the acute bisectrix turns into the quadrants that the isogyres leave on clockwise rotation, plus the fact that this section gives extinction parallel to the a axis, defines the a axis to indeed be the acute bisectrix. Addition was observed, using the quartz wedge, when the slow ray was parallel to the BXA; therefore, the optic sign again was determined to be positive. Attempts to observe the optic normal figure for Aldrin were unsuccessful, probably due to the crystal being too thick.

Due to the diffuse nature of the acute bisectrix figures for methanol Dieldrin and Aldrin, determination of the optic axial angle was difficult. The isogyres were not defined enough to allow accurate measurement of their angle when the crystal was at 45 degrees. It appeared that the axial angle for the methanol Dieldrin was approximately 25 degrees, and for Aldrin, approximately 10 degrees.

Observation of axial dispersion was attempted, but no dispersion was observed.

<div align="center">Refractive Indices</div>

The measurement of refractive indices was done using the Becke line method, or central illumination method. This method was used for all determinations. Both compounds were quite soluble in the immersion oils used (Shillaber's). Thus, fast orientation and determination was a necessity.

The benzene Dieldrin crystals were measured first. The crystals were small and were easily oriented. The results were as follows using monochromatic light (yellow filter).

$$\epsilon = 1.613 \ (\pm 0.002)$$
$$\omega = 1.639 \ (\pm 0.002)$$

The indices for methanol Dieldrin and Aldrin were not obtained. The general shape and difficulty of orientation combined to defeat attempts made. The Becke test works best with particles having thin edges. The crystals would turn into rounded particles before orientation of an axis was obtained and focus on an edge made. The solution near the crystal would by this time contain dissolved compound, which would reduce to difference between the index of the crystal and the liquid. The author feels that any further work would

best be done by using the oblique illumination method, and having

the crystal oriented prior to immersion.

Fusion Data

The manner in which these compounds behave when heated was

investigated. The Kofler hot stage was used in conjunction with an

ordinary microscope. The melting points found are shown in the

following table along with the published value (4).

Compound	Melting Points MP Found (^{o}C)	MP Published ^{o}C
Aldrin	104-106	104-104.5
Dieldrin benzene	174-177	175-176
Methanol	179-182	

These values were determined by heating at a rate of less than

four degrees per minute on the stage. They are corrected readings

taken from a calibration curve.

The compounds both condense onto the cover glass as a liquid.

The Aldrin fogs the glass at approximately 90° C, the methanol

Dieldrin at 150-155° C, and the benzene Dieldrin at 135-140° C.

All three, when cooled, formed a glass with some crystals present.

When heated again to the melting point, the condensation on the cover glass was much less than the first heating. The melting point range was the same as for the first heating. The author believes that condensed liquid on the cover glass was water released from the crystal structure. No evidence of phase change or other temperature phenomenon were observed.

X-RAY DIFFRACTION

Powder Diffraction

X-ray diffraction was next used to try to elucidate the inner structure of the crystal. An attempt was made to use X-ray powder diffraction and rotating crystal methods. The attainment of X-ray powder diffraction patterns was first undertaken. It was quickly found that these compounds do not reflect X-rays very well. It was necessary to expose the film for long lengths of time to get lines, and then they were barely visible above a dark background. When the patterns were measured, even the duplicates were not consistent. There were several persistent lines which were in all the patterns (Aldrin and Dieldrin). It appears these lines are due to the oscillating wedge, and not to the sample. The lines that were not the same between all samples were faint and not even reproducible between duplicate runs of the same sample.

Rotating Crystal Method

This method was successful. The author was able to obtain good results with two of the crystal types (methanol Dieldrin and Aldrin). The source of radiation was the General Electric XRD-1 X-ray diffraction instrument fitted with a coolidge tube having a cobalt target. At the auxilliary beam window was installed a Unicam

(s-25) single crystal goniometer. Probably the most difficult part of this determination was getting the goniometer aligned with the X-ray beam from the XRD-1. This was accomplished after several hours of semi-trial and error adjustments were made. It seems the beam comes out of the XRD-1 at an odd angle. The instrument was aligned so that the collimated X-ray beam was incident on the axis of rotation of the goniometer and coincident with the horizontal cross hair of the observation telescope. This was to facilitate the insertion and alignment of each crystal on the axis and in the beam.

The crystals were attached to the top of the goniometer head with a small amount of beeswax. The crystal was then aligned using the adjustments of the goniometer head. The alignment was made so that one of the principle axes of the crystal was parallel and coincident with the axis of rotation of the goniometer. The crystal was adjusted to the center of rotation and then adjusted vertically so that the X-ray beam impinged upon the center of the crystal. The crystal is rotating upon one of its principal axes.

The film used to record the patterns was Kodak medical X-ray film with no screen. The crystal was rotated continuously during exposure at 1 r.p.m., the exposure being about four hours. The tube current meter reading was about eight milliamperes during the irradiations. No attempt was made to filter the beta radiation since this would only increase the exposure time required. The beta

radiation did not lead to confusion, and in fact, could be used for

supplementary measurements.

The films were developed for two minutes in Kodak X-ray

developer and then stopped using acetic acid. The films were then

fixed in Kodak X-ray fixer, washed and air dried. The measure-

ments of distance on the film were made using a pair of dividers

and a scale. These were made with an accuracy of approximately

0.2 mm. Duplicate films were run for each orientation of each

compound, the duplicates being made with different crystals.

Patterns were not obtained for benzene Dieldrin due to the small

size of the crystals. They were very hard to mount in the wax

without crushing them or burying them in the wax. They were not

large enough to give intense enough reflections.

The crystals were aligned according to the location of the axes

shown in Figures 6 and 8. An example of a pattern obtained is

shown in Figure 9, along with a diagram showing the general geo-

metry of the system. A diagram showing the geometrical details

upon which the following unit cell spacing calculations are based

will be found as Figure 10. The following treatment is due to

Buerger (1, p. 95).

The angle v for the first layer is given by:

$$\text{Sin } v_1 = \frac{\lambda}{t} \tag{1}$$
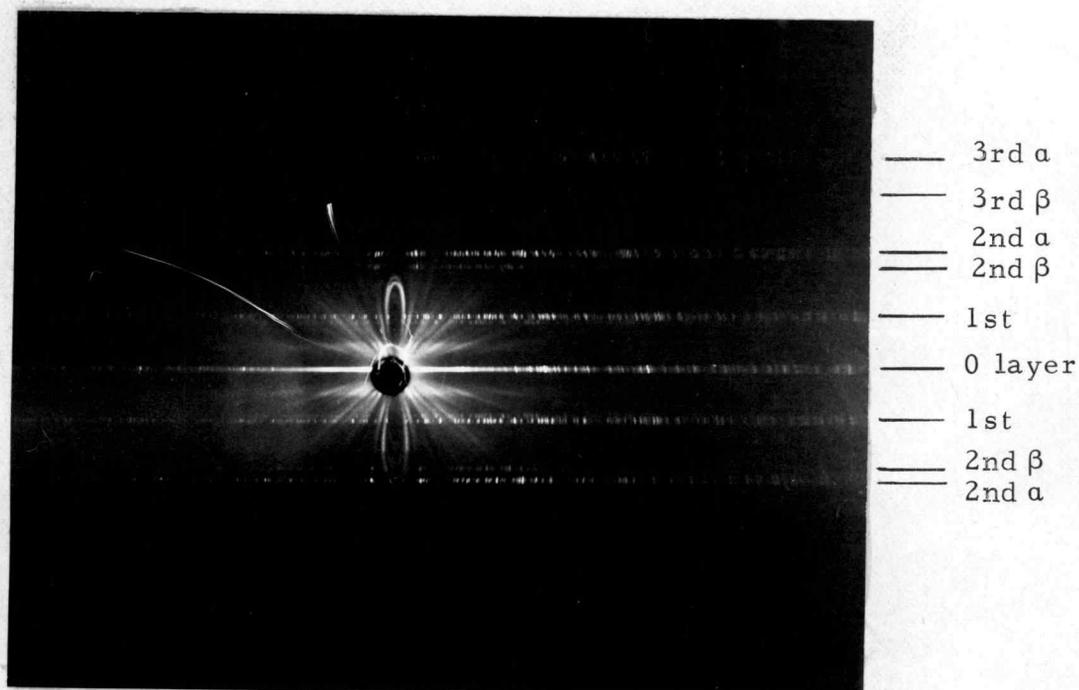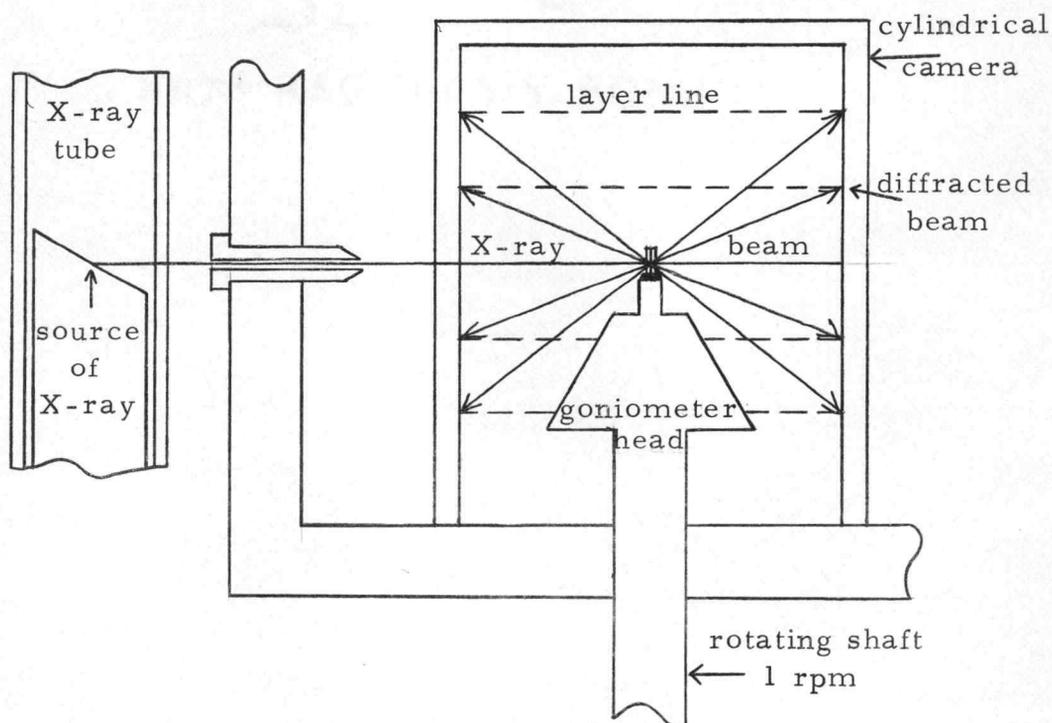
Pattern for C axis Methanol Dieldrin

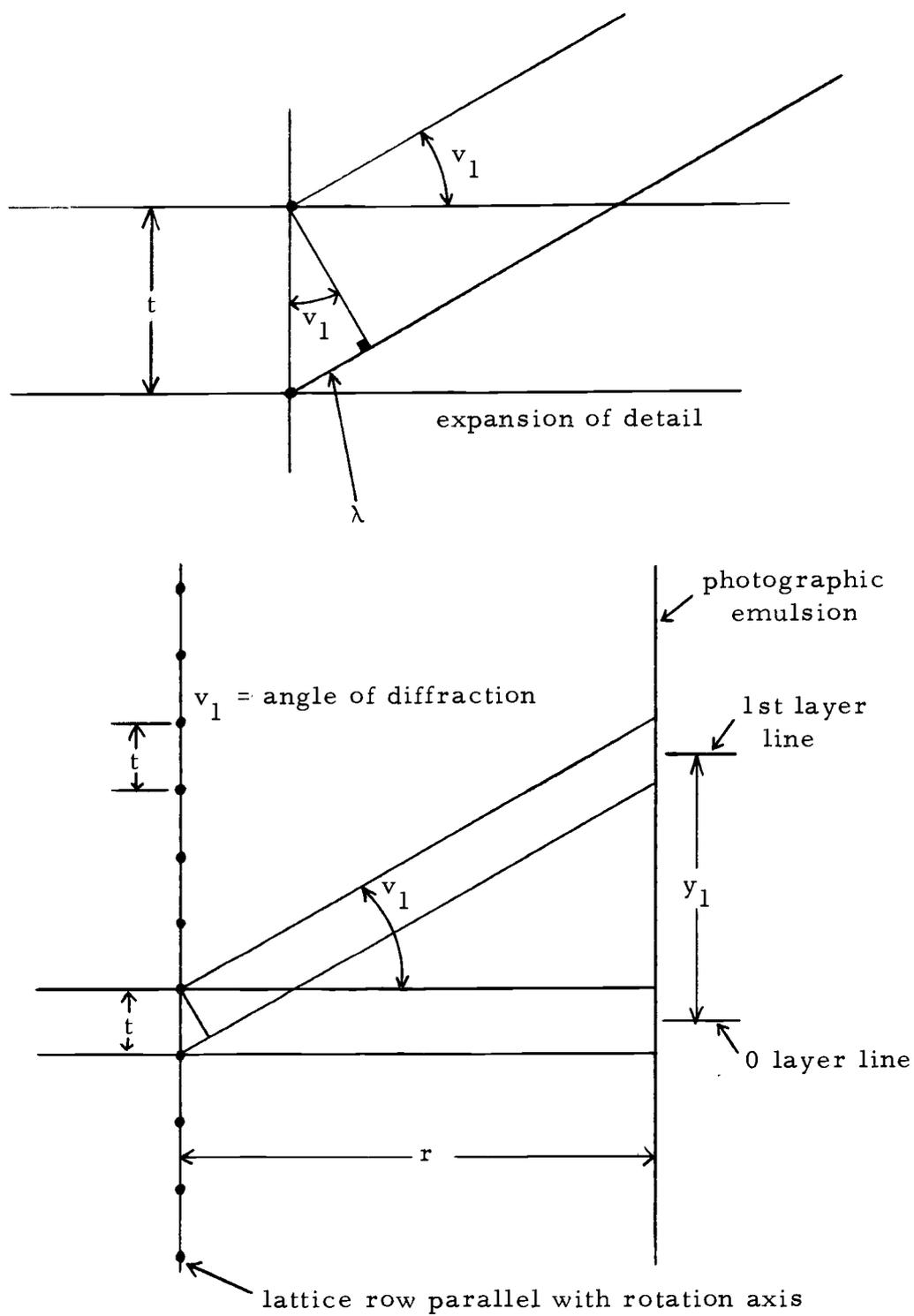Figure 9. Rotating crystal diffraction pattern and geometry of apparatus.

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Figure 10.   Geometry of diffraction and nomenclature.

Similarly, for the nth layer:

$$\sin v_n = \frac{n\lambda}{t} \tag{2}$$

The first layer recorded at a height on the film of y_1 given by:

$$\tan v_1 = \frac{y_1}{r} \tag{3}$$

where r is the radius of the cylindrical camera. The nth layer line similarly records at a height of y_n, given by:

$$\tan v_n = \frac{y_n}{r} \tag{4}$$

Eliminating v_1 and v_n from their respective equations, the following relations result for the first layer and nth layer, respectively.

$$t = \frac{\lambda}{\sin \tan^{-1}(y_1/r)} \tag{5}$$

$$t = \frac{n\lambda}{\sin \tan^{-1}(y_n/r)} \tag{6}$$

The data for this investigation was treated via equations (5) and (6) to obtain values of t (unit cell dimension along axis of rotation). For this investigation, the following were true:

$$r = 30.0 \text{ m.m.}$$
$$\lambda = 1.789 \text{ } \overset{o}{A}$$

The results are tabulated in the following table.

Unit Cell Dimension Determination

Axis Measured	Film Distance mm				Cell Dimension, $\overset{o}{A}$			
	1	2	3	4	1	2	3	4
Methanol Dieldrin								
a axis	3.9	8.0	12.4		13.7	13.9	14.1	
	3.9	8.0	12.6		13.7	13.9	13.9	
	3.9	8.0	----		13.7	13.9	----	
b axis	1.5	3.0	4.3		35.8	35.8	23.4	
	1.5	---	4.3		35.8	----	23.4	
c axis	6.8	15.0	26.8		8.09	8.04	8.05	
	6.8	15.0	26.8		8.09	8.04	8.05	
Aldrin								
a axis	4.0	8.05	12.6		13.4	13.9	13.9	
	4.0	8.1	12.8		13.4	13.7	13.6	
b axis	3.85	7.65	12.1	17.4	13.9	14.5	14.4	14.3
c axis	3.7	7.5	11.7		14.5	14.8	14.8	
	3.75	7.5	11.8		14.3	14.8	14.6	

The average values in a, b, c order were as follows:

Dieldrin   13.9,   35.8,   8.05 $\overset{o}{A}$

Aldrin   13.6,   14.3,   14.7 $\overset{o}{A}$

Using the density of Dieldrin, one finds 11.1 molecules per unit cell.

MICROPHOTOGRAPHY

Photographs of the crystals were taken through the microscope. A 35 mm single lens reflex camera mounted on a tripod with no lens was used, with a bellows unit being used to remove unwanted light. The author was able to quite satisfactorily use the camera's built-in meter to judge the exposure. A few examples are given as Figure 11. A photo of a benzene Dieldrin crystal showing good crystal form is shown, with another photo showing methanol Dieldrin as it is normally seen, lying on the 130 face. This is a broken section of a longer crystal. The three colored pictures illustrate the determination of the optic sign of benzene Dieldrin. Attempts to photograph the interference figures were not successful, mainly due to weak, diffuse isogyres.
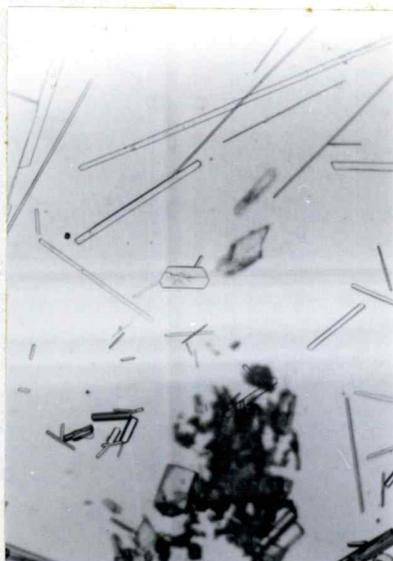
Benzene Dieldrin

Methanol Dieldrin lying on
130 face and end view of
cleaved section
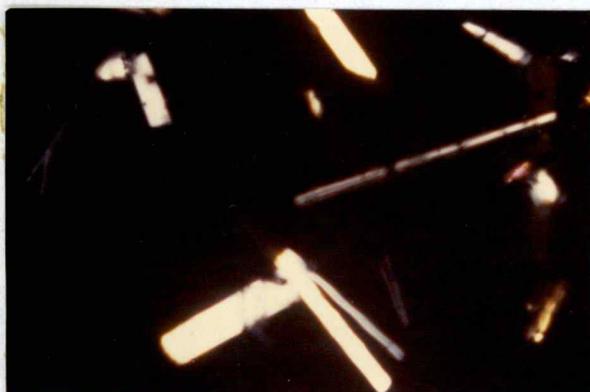
Benzene Dieldrin under
crossed polars

Benzene Dieldrin with first order
red compensator

Benzene Dieldrin with first
order red compensator
crystals rotated 90°

Figure 11.   Microphotographs.

SUMMARY

The two compounds were investigated as set forth and the following information was obtained.

Dieldrin crystallizes into two forms, depending presumably upon the polarity of the solvent used. One form (benzene) is tetragonal, and was found to be uniaxial negative in character. The other was orthorhombic and biaxial positive.

Aldrin crystallizes in the monoclinic system and is also biaxial positive. Both Aldrin and Dieldrin have rather large unit cells.

The author had considerable difficulty in obtaining the proper sized crystals for analysis. Nevertheless, it was demonstrated that the commercial and rather crude product could be recrystallized a few times using ordinary techniques, and the crystals obtained could be used to provide a fairly specific identification.

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