[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

# X-Ray Study of Some DDT Analogs

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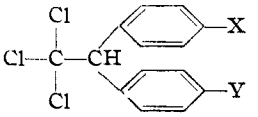
A study has been made of the X-ray crystallography of a number of compounds analogous with DDT. Measurements which include the determination of unit cell size, space group, density, X-ray molecular weight and some data on crystal optics and morphology are recorded in the accompanying table. Single crystal data for DDT have been reported in previous publications.[3,4] Powder diffraction data for DDT and some derivatives have also been reported.[5,6]

Compounds I–VI in Table I have the general structural form



where X and Y are the substituted positions, Table I lists the atom or group of atoms represented by X or Y together with the X-ray and optic data obtained. When X and Y represent chlorine atoms we have DDT itself. Compound VII is the degradation product of DDT in which hydrogen chloride has been split off giving 1,1-dichloro-2,2-bis-(*p*-chlorophenyl)-ethylene. Compound VIII is 1,1-dichloro-2,2-bis-(*p*-chlorophenyl)-ethane (DDD). Compound IX is the naphthalyl derivative, 1,1,1-trichloro-2,2-bis-(naphthalyl)-ethane.

The purpose of this study is to present single crystal X-ray diffraction and optic data which may be useful for the identification and comparison of these compounds from different sources. The particular value of this kind of data is demonstrated in the case of 1,1,1-trichloro-2,2-bis-(*p*-chlorophenyl)-ethane (I) (DDT) and 1,1-dichloro-2,2-bis-(*p*-chlorophenyl)-ethane (VIII) (DDD).

## Experimental

**Source of Materials.**—Purified samples of DDT and analogs were obtained from Prof. G. B. L. Smith and Mr. G. Schneller of the Polytechnic Institute of Brooklyn and from Dr. H. L. Haller of the Bureau of Entomology and Plant Quarantine, Beltsville, Md.

**X-Ray Diffraction Data.**—The X-ray diffraction data were obtained from single crystal oscillation and Weissenberg diagrams. Weissenberg diagrams were taken about as many crystallographic axes as were necessary to give complete data for the determination of space groups and all unit cell dimensions.

**Density Measurements.**—The densities were determined by suspending the crystals in aqueous potassium iodide or $K_2HgI_4$ solutions and adjusting the concentration of the liquid until the solid would neither rise nor fall. At this point the density of the liquid and the solid were the same. The density of the liquid was then determined with a pycnometer.

**Molecular Weight Determination.**—The use of X-ray data to determine chemical molecular weights follows from the relation between crystal density ($d$), the volume ($V$) in cubic ångström units and the mass of the crystal unit cell: mol. wt. $= V \times d/n \times 1.65$, where $n$ is the number of molecules per unit cell.

**Crystal Optics.**—The polarizing microscope was used to obtain the optic data. The crystals were all biaxial. The sign of the birefringence is first recorded followed by the directions of the principal refractive indices with reference to the crystal axes. The interaxial angle (2V) was directly measured by rotating the crystal about the $\beta$ vibration direction using an immersion fluid to reduce refractive effects.

## Discussion

In the course of this X-ray investigation of DDT and analogous compounds, an interesting group isomorphous with DDT (I) was found. These are compounds II–V in Table I. An optic study showed them all to be positive biaxial crystals with the $\beta$ vibration direction along the needle length ($a$-axis). X-Ray data obtained from the Weissenberg diagrams showed them all to be orthorhombic with approximately the same lattice constants. Due to the limitations set by the cell dimensions and due to the fact that the iodine–chlorine molecule (III) cannot have a plane of symmetry, these crystals belong to the space group $P2_1ab$ ($C_{2v}^5$).

We use here a different nomenclature of axes than previously reported by us,[3] by Wild and Brandenberger[4] and by Clark and Cagle.[5] Our symbol for the space group differs, therefore, from the Pbc given before. Most of the crystals reported are orthorhombic. Since the naming of the axes is a matter of convention, we have used that of Buerger[7] in which the orthorhombic axes are chosen as $a<b<c$. This is also consistent with the convention adopted by Bernal and coworkers[8] in their work on sterols. For the mono-

(1) From part of a thesis to be submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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(3) Fankuchen, Schneider and Singer, *Science*, **103**, 25 (1946).

(4) Wild and Brandenberger, *Helv. Chim. Acta*, **28**, 1692 (1945).

(5) Clark and Cagle, *Science*, **101**, 465 (1945).

(6) Andrews, White, Gamor and Peterson, *U. S. Public Health Reports*, **61**, 450 (1946).

(7) M. J. Buerger, "X-Ray Crystallography," John Wiley and Sons, New York, N. Y., 1942.

(8) Bernal, Crowfoot and Fankuchen, *Proc. Roy. Soc.* (London), **A239**, 135 (1940).

TABLE I

| | X | Y | $a$ | $b$ | $c$ | $\beta$ | Space group | $n$ |
|---|---|---|---|---|---|---|---|---|
| I[a] | —Cl | —Cl(DDT) | 7.85 | 9.96 | 19.14 | 90° | $P2_1ab$ ($C_{2v}^5$) | 4 |
| II[a] | —Cl | —Br | 7.85 | 9.93 | 19.38 | 90° | $P2_1ab$ ($C_{2v}^5$) | 4 |
| III[a] | —Cl | —I | 7.97 | 9.87 | 19.83 | 90° | $P2_1ab$ ($C_{2v}^5$) | 4 |
| IV[a] | —Br | —Br | 7.93 | 9.93 | 19.68 | 90° | $P2_1ab$ ($C_{2v}^5$) | 4 |
| V[a] | —I | —I | 8.02 | 9.80 | 20.22 | 90° | $P2_1ab$ ($C_{2v}^5$) | 4 |
| VI[a] | $-OC_2H_5$ | $-OC_2H_5$ | 7.90 | 9.93 | 25.51 | 115° | $P2_1/a$ ($C_{2h}^5$) | 4 |
| VII[a] | —Cl | —Cl unsat. cpd. | 9.22 | 35.46 | 9.41 | 115° | $P2_1/c$ ($C_{2h}^5$) | 8 |
| VIII[b] | —Cl | —Cl (DDD) | 19.30 | 7.66 | 20.19 | 106° | $A2/a$ ($C_{2h}^6$) | 8 |
| IX[a] | Naphthalyl derivative | | 13.99 | 14.25 | 17.81 | 90° | $Pcab$ ($D_{2h}^{15}$) | 8 |

TABLE I (*Continued*)

| $d^{20}_4$ | Mol. wt., X-Ray | Mol. wt., Calcd. | Optics Sign | $\alpha$ | $\beta$ | $\gamma$ | $2V$ | Morphology[c] | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 1.556 | 353 | 354.5 | + | $b$ | $a$ | $c$ | 30° | Long needles | [100] | {001} |
| 1.729 | 396 | 398.9 | + | $b$ | $a$ | $c$ | 40° | Laths | [100] | {001} |
| 1.868 | 442 | 445.9 | + | $b$ | $a$ | $c$ | 55° | Prisms | [100] | {001} |
| 1.887 | 443 | 443.4 | + | $b$ | $a$ | $c$ | 40° | Laths | [100] | {001} |
| >2.27 | | 537.4 | + | $b$ | $a$ | $c$ | 54° | Prisms | [100] | {001} |
| 1.366 | 375 | 373.7 | + | | $b$ | 65°[d] | 25° | Plates | | {001} |
| 1.506 | 318 | 318.0 | − | | $b$ | | 25° | Prisms | [100] | {010} |
| 1.476 | 321 | 320.1 | + | $b$ | | | 65° | Long tab. | [010] | {001} |
| 1.433 | 385 | 385.7 | + | $c$ | $b$ | $a$ | 15° | Plates | | {001} |

[a] From Prof. Smith and Mr. Schneller. [b] From Dr. Haller. [c] The crystals are classified first according to habit, *e. g.* as plates, prisms, needles, etc. This is followed by a zone symbol to show direction of elongation, if any, *e. g.* [010], and then a form symbol, *e. g.* {001}, to indicate the dominating face. [d] From {001}.

clinic case, $b$ is of course chosen as the orthogonal axis and $a$ has been chosen as the smaller of the two remaining cell dimensions.

The series of isomorphous crystals should lend itself very well to a detailed structure analysis and work along these lines is now in progress. Patterson diagrams and preliminary Fourier projections have located the iodine atoms in the iodine–chlorine compound (III). It now seems that the parameters reported by Wild and Brandenberger[4] for the chlorine atoms in DDT will require some correction.

All halogen compounds so far tested with substitutions in the $p,p'$ positions do not affect the crystal structure at all. Substitution in these positions by any other group has resulted in entirely different structures in the compounds so far studied.

The utility of X-ray methods in analysis was demonstrated in one interesting case during this work. A sample was submitted to us as DDT. An oscillation diagram showed the needle axis to be orthogonal and its period to be very close to that for DDT. However, a Weissenberg diagram taken about the needle axis showed the material to be monoclinic. The molecular weight of the compound calculated from the X-ray data and a density measurement showed it to differ from DDT by the weight of one chlorine atom. Comparison of the Weissenberg diagrams with those for the two possible compounds available to us, showed them to be identical with compound VIII (DDD).

## Summary

An X-ray study has been made of a number of crystalline compounds analogous with DDT. The single crystal data obtained have been tabulated giving cell dimensions, space groups, densities and molecular weights calculated from this data. Some optic data are also given.

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