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A FURTHER STUDY OF TRIPHENYLBISMUTHINE DICHLORIDE CRYSTALS

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Some years ago,¹ a crystallographic and optical examination of triphenylbismuthine dichloride was made. It was found that the crystals belong to the orthorhombic system, having an axial ratio of $a:b:c=0.774:1:0.409$, and that they also exhibit the phenomenon of crossed axial dispersion. Furthermore, when examined in parallel polarized light along the b -axis, which is the acute bisectrix, they do not extinguish in the normal manner, but when brought into the extinction position, transmit a green light of the same wave-length for which the interference figure becomes uniaxial. This effect seemed to be due to rotatory polarization which could, of course, only occur in a crystal belonging to the holoaxial class of the orthorhombic system. A certain amount of evidence, based on face development and etching figures, for assigning the crystals to this class was obtained.

Some additional data on the variation of optical properties with wave-length and temperature have now been obtained. An x -ray study, while not elucidating the structure of the crystals, has definitely proved that they belong to the holoaxial class.

CRYSTALLIZATION OF TRIPHENYLBISMUTHINE DICHLORIDE

A stock of very pure triphenylbismuthine dichloride, melting at 141°C , was obtained by repeated recrystallization from acetone of the product prepared by the Eastman Kodak Company according to the methods described in the chemical literature. The crystals used in the investigation were obtained by the slow cooling of a warm acetone solution. Several hundred crops of crystals were examined; they all showed face development of the holoaxial type. Prismatic crystals of the type previously described were usually found. The bipyramidal type of crystals was not obtained, but now and again a variant of the prismatic type occurred. In these particular crystals, which are shown in Fig. 1, the dome (011) is

¹ G. Greenwood, *Mineral. Mag.* (1923), 20, 123; *Zeit. f. Krist.* (1924), 60, 311

absent, and the sphenoid ($\bar{1}\bar{1}1$) has grown quite large. It was found possible to obtain etching figures on the pinacoid (010); etching was done by means of acetone. These etching figures are illustrated in Fig. 2. They show quite distinctly the absence of horizontal and vertical symmetry planes.

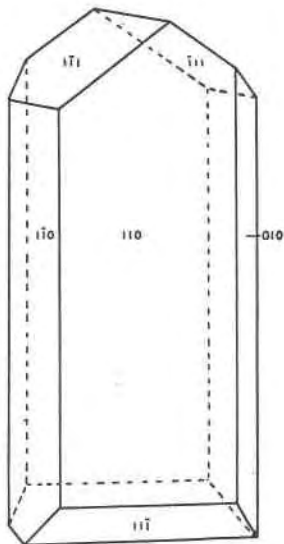


FIG. 1. Crystals of Triphenylbismuthine Dichloride.

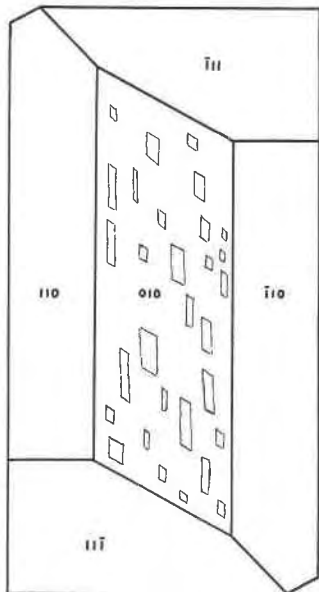


FIG. 2. Etching figures on the (010) face of Triphenylbismuthine Dichloride.

OPTICAL INVESTIGATION

In the previous investigation observations were only made in a few monochromatic lights of wave-lengths easy to obtain. Since a monochromator was now available, it was decided to study more carefully, using the very pure crystals, the variation of optic axial angle with both wave-length and temperature.

The method which was used for measuring the optic axial angle was that suggested by Mallard,² who showed that $D = K \sin E$, where $2D$ is the linear distance between the optic axes measured on a micrometer scale in the eyepiece of the microscope, $2E$ the apparent optic axial angle, and K a constant (the Mallard constant) depending on the lens system of the microscope. A crystal, having the (010) faces developed to a considerable extent, was carefully

² *Bull. Soc. Min. Fr.* (1882), 5, 77.

mounted on a glass slide so that the interference figure was as symmetrical as possible about the axis of the microscope. Any slight error due to lack of coincidence between the acute bisectrix and the microscope axis was eliminated by taking a second reading of D after the section has been rotated through 180° . The constant K was found by calibrating the instrument with a number of mica sections of known optic axial angles. The observations were made at a constant temperature of 23°C and the results are shown in Table I. Those values marked * represent angles in the plane (001); the other values are for angles in the plane (100).

TABLE I
VARIATION OF APPARENT OPTIC AXIAL ANGLE WITH THE WAVE-LENGTH.

Wave-length	2E	Wave-length	2E	Wave-length	2E
4700 Å	*92.6°	5400 Å	9.0°	6100 Å	73.8°
4800	*87.6	5500	30.4	6200	79.4
4900	*76.0	5600	41.4	6300	85.2
5000	*65.2	5700	50.0	6400	90.8
5100	*52.6	5800	59.0	6500	93.0
5200	*41.0	5900	65.2	6600	95.2
5300	*23.6	6000	69.4	6700	98.4
5378	0.				

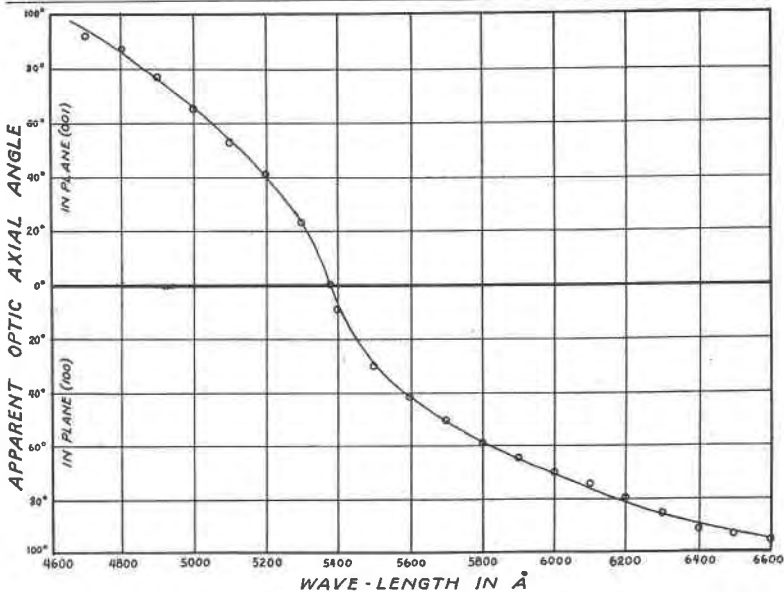
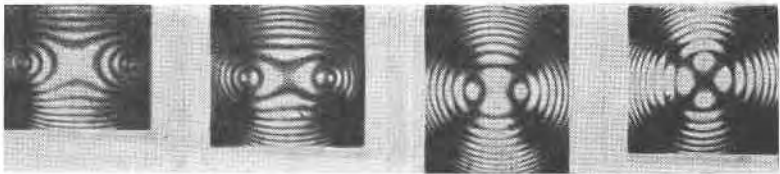
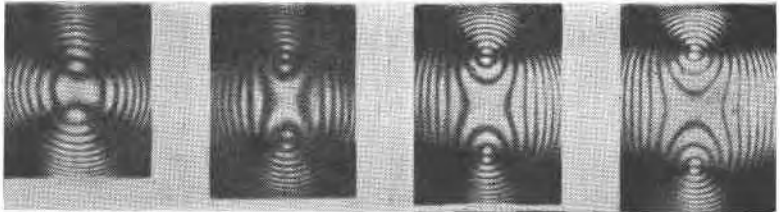


FIG. 3. Variation of apparent optic axial angle with wave-length: temperature constant.

These results are shown graphically in Fig. 3. The curve is similar in shape to that published previously, but because of the purity of the substance and the much larger number of measurements made, it is without doubt a truer representation of the facts.

The variation of optic axial angle with wave-length is also shown by the series of photomicrographs³ of interference figures, which is reproduced as Figs. 4–11. To obtain these photographs a petrographic microscope fitted with a photomicrographic camera was used. By adjusting the position of the eyepiece, in or out of the

FIG. 4. λ 4900Å.FIG. 5. λ 5100Å.FIG. 6. λ 5350Å.FIG. 7. λ 5400Å.FIG. 8. λ 5450Å.FIG. 9. λ 5800Å.FIG. 10. λ 6100Å.FIG. 11. λ 6450Å.

microscope tube, the interference figure was focussed on the ground glass screen of the camera. The illumination was obtained directly from the slit of the monochromator, the source of light being a 100 watt concentrated filament lamp. Even under these conditions each photograph required an exposure of two to three minutes with Wratten *M* plates.

In order to show the effect of temperature on the optic axial angle, it was decided to study the way in which temperature influenced the wave-length of the light in which the crystal was uni-

³ These photographs were made in a hot, badly ventilated, dark room in which the temperature was 27°C. At this temperature the crystals become uniaxial at a wave-length of about 5400 Å.

axial, rather than to keep the wave-length constant and investigate the actual change of angle with temperature. Furthermore the measurement of the wave-length at which the crystal becomes uniaxial is more accurate than the measurement of the optic axial angle itself. The monochromator, which had a direct reading wave-length drum, was accurately adjusted by setting the drum to give correct readings for the lines of a mercury arc. The observations at the lower temperatures were made at the temperature of the room, in certain cases on cold days with the windows open. The higher temperatures were obtained by an electrically heated stage having thermostatic control. The temperatures could be read to 0.1°C on a thermometer which fitted into the heated stage. The wave-length values are the means of six settings of the monochromator, three being made by approaching from the long wave-length side and three from the short. The setting could be made with an accuracy of about 5Å. Table II contains the results.

TABLE II
 VARIATION OF THE WAVE-LENGTH AT WHICH THE CRYSTAL IS
 UNIAXIAL WITH TEMPERATURE.

Temperature	Wave-length at which the crystal is uniaxial	Temperature	Wave-length at which the crystal is uniaxial
7.0°C.	5313Å	28.0°C.	5405Å
11.5	5327	32.0	5415
14.1	5340	36.5	5440
16.0	5351	40.0	5457
19.0	5364	46.0	5483
23.0	5378	47.0	5486
25.0	5392	50.0	5499

These results are plotted in Fig. 12; they give a straight line. It is difficult to say whether the line would remain straight if it could be studied throughout a greater range. L. Brugnatelli⁴ made similar measurements on crystals of saccharine and found that the line showing the variation of wave-length at which the crystal is uniaxial with temperature was slightly curved. His temperature range was about 33°C and his wave-length range was 2600Å; in the case of triphenylbismuthine dichloride the temperature range is 43°C and the wave-length range 200Å.

⁴ *Zeit. f. Krist.* (1898), 29, 54.

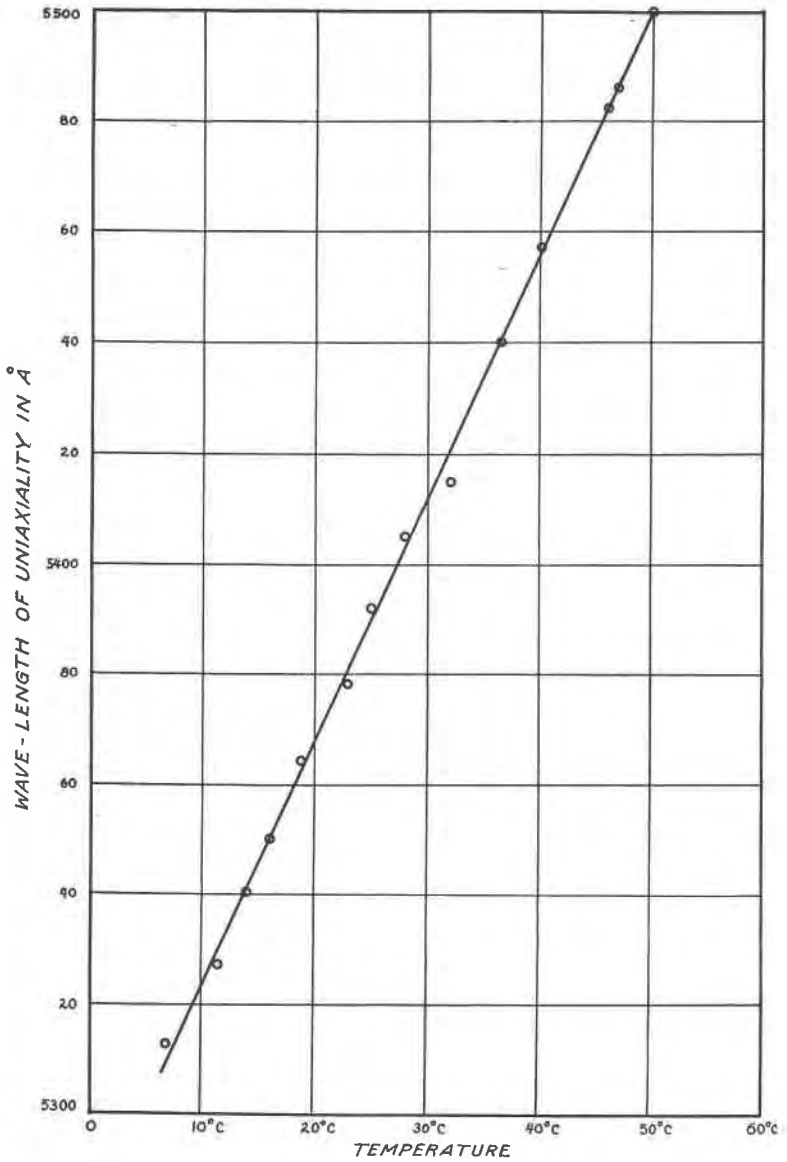


FIG. 12. Variation of Uniaxiality with Temperature.

TABLE III
MEASUREMENTS OF THE SPACE LATTICE AS DERIVED FROM ROTATION PHOTOGRAPHS.

#	Rotation axis [100].	Rotation axis [010].	Rotation axis [001].	Rotation axis [110].	Rotation axis [011].	Rotation axis [101].	Rotation axis [111].
1	μ 5° 5'	μ 3°56'	μ 9°39'	μ 3°53'	μ 3°45'	μ 4°30'	μ 3°48'
2	I 17.39Å	I 22.45Å	I 9.18Å	I 28.50Å	I 24.55Å	I 19.65Å	I 29.10Å
3	μ 10 3	μ 7 56	μ 19 7	μ 7 56	μ 7 20	μ 9 9	μ 7 33
4	I 17.24	I 22.30	I 9.17	I 28.05	I 24.15	I 19.37	I 29.35
5	μ 15 45	μ 12 2	μ 29 59	μ 11 48	μ 11 6	μ 13 46	μ 11 20
6	I 17.35	I 22.18	I 9.24	I 28.30	I 24.05	I 19.45	I 29.47
7	μ 20 54	μ 15 58	μ 22.41	μ 15 46	μ 14 51	μ 18 20	μ 15 9
8	I 17.27	I 22.41	I 9.22	I 28.50	I 24.05	I 19.57	I 29.55
9	μ 26 26	μ 20 6	μ 41 56	μ 19 56	μ 18 31	μ 23 7	μ 19 1
	I 17.26	I 22.45	I 22.45	I 28.32	I 24.20	I 19.61	I 29.70
6	μ 24 24	μ 22.39	μ 24 1	μ 24 1	μ 22 21	μ 28 0	μ 19.68
7	I 22.42	I 22.42	I 28 14	I 28.56	I 26 24	I 33 12	I 19.68
8	μ 33 20	μ 22.45	μ 32 49	μ 28.53	μ 24.25	μ 19.57Å	μ 29.43Å
9	μ 38 7	μ 22.45	μ Mean = 9.20Å	μ Mean = 28.44Å	μ Mean = 24.22Å	μ Mean = 19.57Å	μ Mean = 29.43Å
	I 17.31Å	I 22.39Å	I Mean = 9.20Å	I Mean = 28.44Å	I Mean = 24.22Å	I Mean = 19.57Å	I Mean = 29.43Å
			$\sqrt{I_{100}^2 + I_{010}^2}$ = 28.30Å	$\sqrt{I_{100}^2 + I_{010}^2}$ = 24.20Å	$\sqrt{I_{100}^2 + I_{010}^2}$ = 19.60Å	$\sqrt{I_{100}^2 + I_{010}^2 + I_{001}^2}$ = 29.76Å	

X-RAY INVESTIGATION

The x -ray study was made by means of rotation and oscillation photographs. The source of the x -rays was a Hadding-Siegbahn tube, which was operated at about 35,000 volts with a tube current of about 25 milliamperes. Photographs were made using the $K\alpha$ radiation from copper and iron anticathodes. Two cylindrical cameras of diameters 57.4 mm. and 114.8 mm. were used.

MEASUREMENT OF IDENTITY PERIODS. Rotation Photographs were made by rotating about the directions [100], [010], [001], [110], [011], [101] and [111]. The values of the identity periods I in these directions were obtained by using the formula:—

$$I = n\lambda / \sin\mu.$$

The angles μ are obtained from measurement of the distances between the "layer lines." The results obtained are shown in Table III. The unit cell has the dimensions

$$I_{100} = 17.31\text{\AA}; I_{010} = 22.39\text{\AA}; I_{001} = 9.20\text{\AA}.$$

These values give an axial ratio:—

$$a:b:c = 0.7743:1:0.4115.$$

The crystallographic axial ratio, which depends on the arbitrary choice of the parametral (111) face, is thus confirmed.

The measurements of the identity periods in the diagonal directions and their comparison with the calculated lengths of the diagonals of the above unit cell show that neither the faces, nor the cell itself, are centered. The space lattice on which the structure is based is therefore the simple orthorhombic lattice Γ_v .

DETERMINATION OF THE SPECIFIC GRAVITY AND THE NUMBER OF MOLECULES IN THE UNIT CELL. An accurate determination of the specific gravity of triphenylbismuthine dichloride, made by means of the pycnometer, gave the following result:—

Sp. gr. of triphenylbismuthine dichloride at $20^\circ/4^\circ = 1.908 = \rho$.
The number of molecules in the unit cell is given by:—

$$N = V / M m_H.$$

where V is the volume of the cell, M the molecular weight of the substance, and m_H the mass of the hydrogen atom. Substituting the appropriate values we get

$$N = \frac{1.908 \times 17.31 \times 22.39 \times 9.20 \times (10^{-8})^3}{511.1 \times 1.65 \times 10^{-24}} = 8.07.$$

There are therefore 8 molecules in the unit cell.

ACCURATE VALUES FOR THE IDENTITY PERIODS OBTAINED FROM THE CONCEPTION OF TOPIC AXES. The measurements of identity periods obtained from rotating crystal photographs are not very accurate; it is usually necessary to carry out more precise measurements. An increase in the accuracy of measurement of rotation photographs has been obtained by G. Hoffmann and H. Mark,⁵ who used a narrow horizontal slit, which makes the "layer lines" become very thin and narrow. Accurate measurements can also be obtained by measuring one of the pinacoid spacings by means of an *x*-ray spectrometer. In this investigation an *x*-ray spectrometer was not available. Owing to the closeness of the lines on the rotation photographs very accurate measurements were not obtainable, even by means of the narrow horizontal slit. The conception of topic axes has been familiar to crystallographers for many years. These axes are obtained by considering a volume equal to the molecular volume, associated with a cell, the edges of which stand to one another in the same ratio as the axial ratio. The standard formula for topic axes may easily be applied to calculate the dimensions of the unit cell, by substituting for the molecular volume *V* the volume *V'* of unit cell. If there be *N* molecules of molecular weight *M* in the cell, then the mass of a unit cell is *NMm_H* and its volume *V'* is *NMm_H/P*. Substituting the values for triphenylbismuthine dichloride we have:

$$V' = \frac{8 \times 511.1 \times 1.65 \times 10^{-24}}{1.908} = 3.530 \times 10^{-21} \text{ ccs.}$$

Knowing the true axial ratios, for which accurate values can be obtained from the ordinary crystallographic axial ratios, and the approximate dimensions of the unit cell got from the rotation photographs, accurate values for $I_{100} = \chi'$, $I_{010} = \psi'$ and $I_{001} = \omega'$ can be calculated.

These calculations give:

$$\begin{aligned} I_{100} = \chi' &= \sqrt[3]{a^2 V' / c} = 17.30 \text{ \AA} \\ I_{010} = \psi' &= \sqrt[3]{V' / ac} = 22.36 \text{ \AA} \\ I_{001} = \omega' &= \sqrt[3]{c^2 V' / a} = 9.14 \text{ \AA} \end{aligned}$$

DETERMINATION OF THE SPACE GROUP. The spots on the rotation photographs are so numerous that in most cases the "layer-lines" appear as continuous lines; it is therefore impossible to obtain the indices of individual reflecting planes from such photographs.

⁵ *Zeit. f. phys. Chem.* (1924), **111**, 321.

Several oscillation photographs, having an oscillation range of 25° , were made; it was possible to obtain from these photographs the indices of a large number of reflecting planes. Photographs were obtained by oscillation of the face (001) about [110], face (100) about [001] and face (110) about [001]. That these photographs show less spots is due to the fact that only a restricted number of planes come into the reflecting position. It is comparatively easy, by means of the method based on the polar lattice and described by J. D. Bernall,⁶ to find which planes are capable of reflecting. The index of the spot is then easily found by comparing the square of the sine of the measured glancing angle with the squares of the sines of glancing angles of the possible reflecting planes for the particular "layer line." These experimentally found reflecting planes are then examined for missing odd-order spectra, caused by the halving of the planes apparent and dependent on the symmetry of the structure. The following results were found:—

1. Pyramids of the type (hkl) . All kinds present, including planes for which $(h+k)$, $(k+l)$, $(l+h)$ or $(h+k+l)$ are odd.
2. Prisms of the type (hko) . All kinds present, including planes for which h , k , or $(h+k)$ are odd.
3. Pinacoids of the type (hoo) . Odd orders of reflection occur for the planes (010) and (001), whilst only even orders occur from (100).

The presence of odd order reflections from the various kinds of pyramid faces is merely the result of the underlying space lattice being Γ_v . The space group must therefore, using the notation of Schoenflies, be one of the following:—

$$C_{2v}^1 \text{ to } C_{2v}^{10}, V^1 \text{ to } V^4, V_h^1 \text{ to } V_h^{16}.$$

One should note that in the orthorhombic system the three axial directions are interchangeable and prisms of the type (hko) therefore include (hol) and (okl) . The fact that odd order reflections occur from all the kinds of these prisms excludes many of the above space groups. Reference to space group tables⁷ shows that the space group is therefore either:—

$$C_{2v}^1, V^1, V^2, V^3, V^4 \text{ or } V_h^1.$$

The space groups C_{2v}^1 , V^1 and V_h^1 require odd order reflections from all faces; V^2 requires only even orders from one pinacoid; V^3

⁶ *Proc. Roy. Soc.* (1926), **113A**, 117.

⁷ H. Mark. *Die Verwendung der Röntgenstrahlen in Chemie und Technik.*, p. 387.

requires only even orders from two pinacoids; V^4 requires only even orders from the three pinacoids. The occurrence of only even orders from the pinacoid (100) therefore places the structure in the space group V^2 .

The symmetry of this space group V^2 is holoaxial. X-ray evidence is therefore in favor of holoaxial symmetry for the crystals of triphenylbismuthine dichloride.

To bring the crystallographic axes into coincidence with those of the space group, in its usual orientation, a and c must be interchanged. There is also the possibility of interchanging b and the new a axis; no information, however, can be obtained from space group data regarding the relative position of these two axes.

Very little information as to the actual arrangement of the atoms can be obtained from space group considerations. Reference to the tables shows that the most general position in the space group V^2 consists of four equivalent points. Now triphenylbismuthine dichloride contains eight molecules in the unit cell, and it is therefore evident that various atoms of the same chemical element cannot be crystallographically equivalent.

In conclusion I wish to express my gratitude to Dr. Harold L. Alling for the loan of microscopic apparatus and for help in photographing the interference figures. Without his help this part of the investigation could not have been carried out.