CROSSED AXIAL PLANE DISPERSION IN TWO ORGANIC COMPOUNDS. A PECULIAR EXTINCTION PHENOMENON

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In the course of an optical investigation of an acetaldehyde derivative exhibiting crossed axial plane dispersion and certain other attendant phenomena (1), it was found desirable to examine two other crystalline organic compounds, triphenylbismuthine dichloride and ethyl triphenylpyrrolone, both previously described as having the above type of dispersion. The optic axial angles, 2E, of these materials were measured by means of a petrographic microscope at different temperatures, and for several different wavelengths of light.

The optic axial angles of the bismuthine derivative reported by Greenwood (2) in 1923 agree fairly well with those given below. Greenwood's more recent measurements (3), however, are definitely out of line both with his own earlier work and the results obtained in this laboratory.

Optical axial angles of monoclinic ethyl triphenylpyrrolone were determined by Tutton (4) for three wavelengths of light. Unfortunately, he makes no mention of the temperature of his laboratory, a factor which quite appreciably affects the magnitude of the axial angle. The room temperature was carefully noted all through the present research and experiments conducted to show the maximum difference between the temperatures of the room and of the microscope slide adjacent to the crystals under observation. Because of the temperature uncertainty, Tutton's results are not strictly comparable with those of the writer; the two sets of data, however, agree as to order of magnitude.

Some additional light was thrown on a phenomenon associated with crossed axial plane dispersion and described by Greenwood in his earlier paper (2) on triphenylbismuthine dichloride. Greenwood noted that crystals of the bismuthine derivative, when oriented so that the acute bisectrix coincided with the optic axis of the microscope, and illuminated with white light, act as a light filter and transmit a greenish light practically identical with the wavelength producing uniaxiality, although the crystals themselves are colorless in ordinary light. The effect is observed in the extinction position in parallel polarized light. Two Seignette salts, one uniaxial for green and the other for blue light, were also examined and found to behave in the same manner. Greenwood believed that these peculiar properties were due to rotatory polarization. Since all three of the substances discussed in his article belonged to the bisphenoidal class of the orthorhombic system in which rotation of the plane of polarization often occurs, this explanation at first seemed reasonable. The writer, however, recently observed the same peculiar extinction phenomenon in crystals of a polymorph of acetaldehyde 2:4-dinitrophenylhydrazone which belongs to the monoclinic system and probably to the prismatic class, a circumstance which should, on symmetry considerations, exclude the possibility of rotatory polarization. Further inspection of Greenwood's paper showed that it had not been possible to confirm the presence of optical activity in his compounds by the usual test of obtaining extinction of the residual light by rotation of the analyzing nicol. In view of these facts, it appeared unlikely that rotatory polarization was really responsible for the effect. In order to definitely establish the existence of this "extinction color" in a substance which, on theoretical grounds, should not rotate the plane of polarization, it was decided to examine crystals of a suitable compound of known crystallographic symmetry. Tutton's monoclinic ethyl triphenylpyrrolone (prismatic class) (4) was found to have the desired properties. This substance is uniaxial for a wavelength in the greenish yellow and in the present research was found to transmit the same yellow color in the extinction position when illuminated with white light. It is therefore practically certain in view of the symmetry restrictions that rotatory polarization has nothing to do with the effect.

F. E. Wright[1] of the Geophysical Laboratory of the Carnegie Institution of Washington has offered a simple explanation for the above phenomenon. It is essentially as follows: The colors observed at extinction in crystals of the type just described are similar in origin to the residual light which is observed in many sections of uniaxial and of biaxial crystals and normal to an optic axis. Thus a plate of calcite, cut normal to the optic axis and observed between crossed nicols in parallel light, is not perfectly dark, but is perceptibly illuminated. This lack of complete extinction is due in part to internal reflections, but chiefly to the

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[1] Private communication.

fact that the transmitted beam of light is slightly convergent or divergent and not strictly parallel. The axial beam which, in convergent polarized light, emerges at the exact center of the interference figure, is quite dark; but beams which include a small angle with the optic axis and which are also transmitted, are not dark, but are more or less colored. In a biaxial section of a crystal of strong birefringence, and normal to an optic axis, this same effect is observed both in convergent and in parallel polarized light. It is enhanced, in parallel light, if the observer shifts his eye across the exit pupil of the eyepiece, thereby emphasizing the oblique portions of the transmitted beam at the margins of the exit pupil.

In a crystal showing pronounced crossed axial dispersion and uniaxiality for the green or yellow green portion of the spectrum, a section cut normal to the uniaxial optic axis exhibits in convergent polarized light a predominately greenish color near the optic axis. In parallel polarized light the transmitted beam includes, in addition to the waves transmitted along the optic axis, waves whose normals are slightly inclined to the axis with the results that, in this case, the residual extra-axial green light reaches the eye of the observer and colors the section green, or other mid-spectrum hue, at the position of extinction, irrespective of the thickness of the plate.

Besides the five examples cited, F. D. Dodge[2] finds that a modification of lithium acid phthalate is uniaxial for blue and transmits a blue light under the conditions stated above.

EXPERIMENTAL

PREPARATION OF THE CRYSTALLINE MATERIALS: Triphenylbismuthine dichloride was obtained from the Eastman Kodak Company. The original material contained a small amount of a white amorphous solid insoluble in organic solvents but in other respects was practically pure. Crystallizations were made from warm acetone, toluene, benzene-petroleum ether, and chloroform-absolute ethanol. In all cases the first crystallization was followed by a rise in melting point. Additional crystallizations after the first led to a slight lowering of the melting point, probably indicative of a slow spontaneous decomposition of the bismuthine compound.

Crystals resulting from single crystallizations of the Eastman material from acetone and from toluene were employed in a large

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[2] Private communication.

number of optical measurements. Crystals of the lower melting material resulting from five successive crystallizations of the substance from a mixture of chloroform and absolute ethanol were also examined and found to differ only slightly in optic axial angle from the other preparations. Crystallized melts were obtained by rapid fusion of the recrystallized material on a microscope slide under a cover glass. The freshly cooled melt had optical properties practically identical with those of samples crystallized from solvents. This method of examination, however, was not altogether satisfactory because the thin crystalline films of small phase difference produced rather diffuse interference figures. The fused preparations only remained clear for 10 or 15 minutes, after which time a spontaneous decomposition set in, speedily obscuring the crystals by the formation of amorphous grains.

Melting points were determined by the capillary tube method employing Anschutz thermometers calibrated by the U. S. Bureau of Standards. The melting points of several samples of triphenylbismuthine dichloride are recorded below:

Material	*Melting Point, °C., Corr.*
Eastman product	138–139°
1st crystallization, acetone	142–145° (shrinkage at 139°)
1st crystallization, toluene	142–145° (shrinkage at 139°)
5th crystallization, chloroform-absolute ethanol	138–139.5°

The fusion was usually preceded by a considerable shrinkage. The high viscosity of the liquid material impaired the precision of the observations by obscuring to some extent the disappearance of the solid phase.

Ethyl triphenylpyrrolone (1-ethyl-3, 3,5-triphenylpyrrolin-2-one) was prepared by the method of Japp and Klingemann (5), using as starting materials benzil, acetophenone and monoethylamine from the Eastman Kodak Company. α-β-dibenzoylstyrene (M. P. 129.5-130.0° C., corr.) was obtained as an intermediate product. The crude ethyl triphenylpyrrolone was slightly yellow in color and melted at 130.2-130.6° C., corr. The yellow color disappeared in the course of three crystallizations from hot absolute ethanol, but the melting point remained unchanged. Inspection confirmed the fact that the crystals obtained were the monoclinic modification. Japp and Klingemann found a melting point of 129° C. for this modification and 123° for the triclinic form. No triclinic crystals were observed in any of the present preparations and the absence of this form is supported by the sharp melting points obtained.

APPARATUS: The optical data reported in this article were observed with the aid of a carefully calibrated petrographic microscope. The linear ocular micrometer was calibrated for axial angle work by means of an Abbé apertometer and further checked against a condenser apertometer and a standardized cleavage of mica.

For measuring optic axial angles the source of monochromatic light was the mercury arc, isolating the following lines by means of Wratten filters: 4358, 5461, 5780, 6234, and 6908Å. A partial isolation of the bluegreen line at 4916Å was accomplished by combining Wratten filters No. 48 and No. 75. In determining the wave-lengths for which the crystals became uniaxial, a Schmidt and Haentsch monochromator illuminated by a special Osram lamp was employed. This instrument was calibrated by observing the positions of twelve well characterized spectral lines chiefly from the mercury arc spectrum. White light for microscopy was obtained from a tungsten lamp equipped with a Corning "Daylite" filter.

Temperature measurements were principally those of the room as read from a thermometer placed on the wall near the microscope. The accuracy of these measurements was determined in a series of experiments in which the thermometer readings were compared with those of a No. 30 gauge copper-constantan thermocouple placed on the microscope slide near the crystals under observation. The potentiometer readings, after conversion, were compared with those of a sensitive Bureau of Standards thermometer and found reliable to at least ±0.2° C. The differences between the wall thermometer and the thermocouple readings never exceeded 0.5° C. and were usually less.

INVESTIGATION OF OPTICAL PROPERTIES

TRIPHENYLBISMUTHINE DICHLORIDE: Crystals of this substance in which the acute bisectrix was approximately coincident with the axis of the microscope were selected for measurement of the optic axial angles, their temperature coefficients, and the wavelength of uniaxiality. The individual optic axial angle observations exceeded 360 in number, averaging about 20 observations for each of six wavelengths at three different temperatures. Observations were made in duplicate, the second reading in each case being made after rotating the preparation on the microscope stage through 180°. This procedure was employed to reduce the errors arising from slight departures of the crystals from the correct orientation. Table I contains the average 2E values of the four crystalline preparations examined in this research. These results

TABLE 1.—OPTIC AXIAL ANGLE OF TRIPHENYLBISMUTHINE DICHLORIDE

Wavelength	2E t=20°C.	2E t=25°C.	2E t=30°C.	Axial Plane
		Crystals from Acetone		
4358Å	69.5°	70.3°	70.7°	(001)
4916	38.2	39.8	40.2	(001)
5461	18.2	14.9	12.7	(100)
5780	32.5	31.1	29.9	(100)
6234	43.9	43.0	42.5	(100)
6908	50.5	50.0	49.2	(100)
		Crystals from Toluene		
4358	68.4	69.4	70.4	(001)
4916	39.5	40.3	41.6	(001)
5461	19.2	17.2	14.2	(100)
5780	32.8	32.1	30.4	(100)
6234	44.6	42.9	42.7	(100)
6908	50.9	49.9	49.1	(100)
		Crystals from C_2H_5OH-$CHCl_3$ Mixture		
4358	68.5	69.7		(001)
4916	38.3	40.9		(001)
5461	18.3	15.7		(100)
5780	33.0	31.7		(100)
6234	45.0	43.8		(100)
6908	50.7	50.2		(100)
		Crystals from Melt		
4358		70.3	70.8	(001)
5461		18.5	14.9	(100)
5780		32.4	31.3	(100)
6234		44.8	43.2	(100)
6908		50.8	50.8	(100)
		Average		
4358	69.0±0.5	70.0±0.5	70.5±0.5	(001)
4916	39.0 1.0	40.5 0.5	41.0 1.0	(001)
5461	18.5 0.5	16.5 2.0	14.0 1.0	(100)
5780	33.0 0.5	31.5 1.0	30.5 1.0	(100)
6234	44.5 0.5	44.0 1.0	43.0 0.5	(100)
6908	50.5 0.5	50.5 0.5	49.5 1.0	(100)

are grouped together in a final average at the bottom of the table and the maximum deviation indicated. Since the eyepiece micrometer could be read to the equivalent of ±0.5°, certain real differences in the four preparations become apparent. However, it is believed that these discrepancies represent only slight differences in the purity of the samples.

The approximate temperature coefficient of the optic axial angle could be calculated from the data in Table I. More dependable results were obtained from axial angle measurements on a single crystal over the temperature interval 15-30° C. Values of d(2E)/dt calculated in this way are given below:

Wavelength, Å	4358	4916	5461	5780	6234	6908
d(2E)/dt	+0.1°	+0.25°	−0.55°	−0.25°	−0.25°	−0.15°

It was not feasible to maintain the room temperature at exactly 20, 25 and 30°C. during the optic axial angle experiments. Instead, readings were made when the room was within ±2°C. of the desired temperature, and the small correction applied by means of the above temperature coefficients.

The above measurements of 2E, while not at the same temperatures as Greenwood's results, can be made comparable by extrapolation. This has been done in figure 1. Greenwood's 1923 results (2) in most cases show good agreement with the extrapolated values, the maximum difference amounting to about 5°. This difference may partly be due to the crude character of the temperature coefficients employed. Greenwood includes among his results at 17°C. a uniaxiality value by Barker (temperature unspecified) which agrees poorly with both his own and the present extrapolated data. When this result is excluded from consideration the agreement with the present experiments is much improved. Greenwood's more recent optic axial angle determinations (3), which are supposed to supersede his earlier results, are of a different order of magnitude, as is shown in figure 1. The discrepancy between these later results on one hand and his 1923 data and the present results on the other is negligible at uniaxiality but rapidly becomes greater with increasing optic axial angle, the 1931 results being numerically greater by a factor of about two. Such a divergence is scarcely to be accounted for by differences in the purity of the crystalline material, since contamination would affect the small angles to a greater extent than it would the large. Differences in temperature, wavelength, and composition all tend to produce the most marked changes in angle when 2E is near zero. About the only reasonable explanation of this major discrepancy lies in the possibility that Greenwood's later results are erroneous.

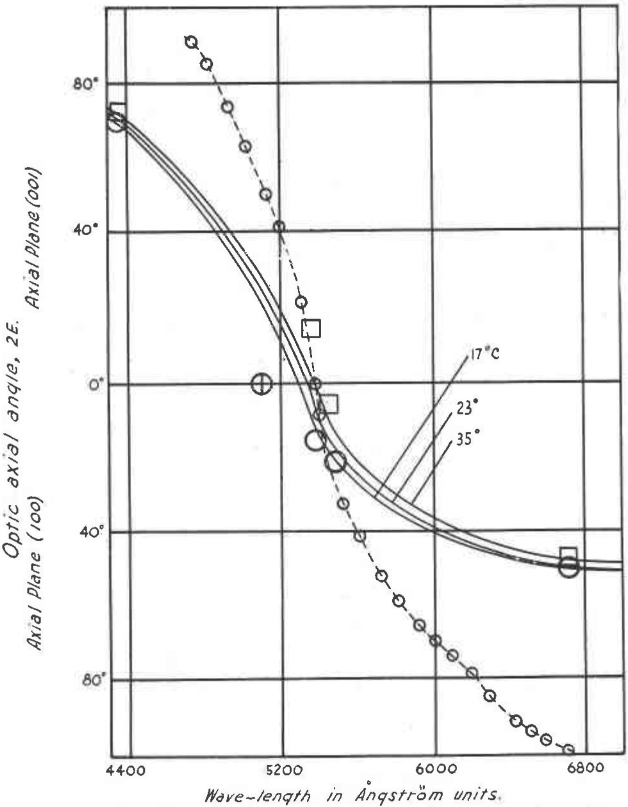

Fig. 1.- Optic Axial Angle of Triphenylbismuthine Dichloride.
○ Greenwood (1923) 17°C.; □ 35° C.; ○ Greenwood (1931) 23°C.;
⊕ Barker (1923), —— Bryant (1933), 17°, 23°, 35°C. *(Interpolated)*

The wavelengths for which the crystals became uniaxial were determined under the microscope with the aid of a calibrated monochromator. The following results are the averages of observations on about twenty different crystals obtained from the samples employed above:

t°C.	20°	25°	30°
Wavelength of Uniaxiality, Å (present research)	5330±20	5370±20	5385±20
Wavelength of Uniaxiality (Greenwood, 1931)	5368	5392	5410

The reproducibility of this property for any given crystal was about ±5Å. The agreement between different crystals, however, was less satisfactory and did not justify separate treatment of the four samples. Results from Greenwood's later paper are included for purposes of comparison.

The crystals of triphenylbismuthine dichloride used for optic axial angle measurements were correctly oriented for observation of the color phenomenon that is seen in the extinction position under crossed nicols. As stated earlier, this phenomenon is characterized by the ability of the crystal, when illuminated by white light, to selectively transmit a radiation approximately identical in color with that for which the crystal becomes uniaxial. In the position of maximum illumination the crystals transmit a light rich in wavelengths somewhat removed from that of uniaxiality. In the present case the light transmitted at extinction was from the middle green, while at maximum illumination a lavender pink light was transmitted. These colors, unlike those arising from phase difference in ordinary doubly refracting materials, did not vary with the thickness of the preparation. Crystals varying from 0.05 to 2 mm. in thickness were examined in this laboratory and no discernible change in the color of the transmitted light was noted for either of the two positions provided the orientation remained correct. The same effect was also previously observed in similarly oriented crystals of the metastable acetaldehyde 2:4-dinitrophenylhydrazone (1), with the exception that only the extinction color could be observed because of the strong orange color of the crystals themselves.

MONOCLINIC ETHYL TRIPHENYLPYRROLONE: Optical properties of this compound were investigated as in the previous case. The acute bisectrix emerges at an appreciable angle from the normal to the orthopinacoid. Well centered acute bisectrix interference figures could not be obtained from any naturally occurring faces. However, by carefully crushing large crystals of the pyrrolone, occasional fragments of the desired orientation were obtained. In spite of this difficulty the optical properties of various batches of crystals exhibited a constancy that was generally within the error of the determinations.

Optic axial angles at 25 and 30°C. are given in Table 2. These data are the averages of about 120 single observations. A separate investigation over the range 20 to 32.5°C. led to the following approximate temperature coefficients:

Table 2.—Optic Axial Angle of Monoclinic Ethyl Triphenylpyrrolone

Wavelength	2E $t=25°$C.	2E $t=30°$C.	Axial Plane
4358	73.0±1.0°	72.0±2.0°	(010)
4916	45.0 0.5	42.5 0.5	(010)
5461	22.5 0.5	21.0 1.0	(010)
5780	8.0 1.0	10.5 0.5	⊥ to (010)
6234	24.5 0.5	25.5 1.0	⊥ to (010)
6908	31.0 0.5	31.5 0.5	⊥ to (010)

Wavelength, Å	4358	4916	5461	5780	6234	6908
$d(2E)/dt$	−0.2°	−0.3°	−0.4°	+0.55°	+0.25°	+0.2°

Figure 2 shows the agreement between the present optic axial angle data and those of Tutton (4). The temperature of Tutton's experiments is not stated so that an exact comparison is not possible. Inspection of figure 2 suggests that his observations were not all carried out at a single temperature.

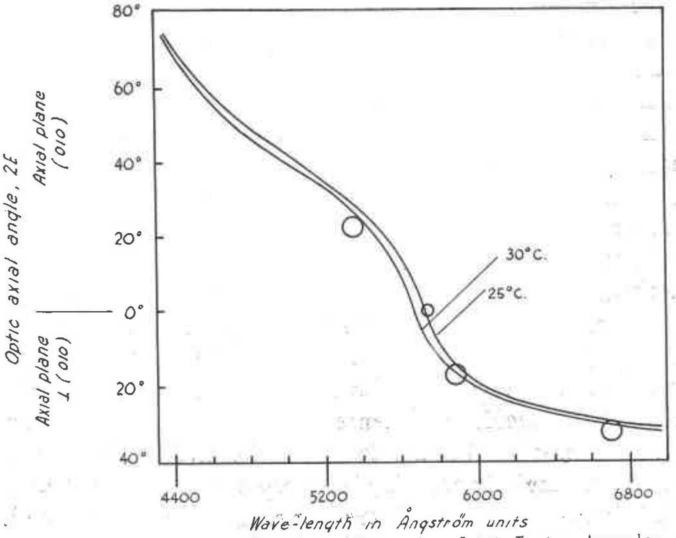

Fig 2 Optic Axial Angle of Monoclinic Ethyl Triphenylpyrrolone
○ Tutton (1890), ○ Tutton (1920), — Bryant (1933), 25+30°C

The wavelength of uniaxiality was determined at 20, 25 and 30°C. The reproducibility was good throughout and it is believed that the results are correct to ±10 Ångstrom units. They are tabulated below:

t°C.	20°	25°	30°
Wavelength of Uniaxiality, Å	5790	5740	5680

The wavelength of uniaxiality is shifted toward the blue end of the spectrum at the rate of about 12Å for a rise in temperature of 1°C. Tutton determined the wavelength of uniaxiality of this substance as recently as 1920 (6) and obtained a value of 0.000575 mm., temperature unspecified. Assuming Tutton's preparations to be identical with those described above, his measurement would correspond to a temperature of 24°C.

The light transmitted at extinction along the direction of the acute bisectrix under the conditions specified earlier, was of a slightly greenish yellow color corresponding to that of uniaxiality. At maximum illumination a pale lavender color was observed. As in the case of the bismuthine compound, the thickness of the crystal fragment did not affect the color of the light transmitted.

SUMMARY

1. The optic axial angle 2E, its approximate temperature coefficient, and the wavelength of uniaxiality of two organic compounds, triphenylbismuthine dichloride and monoclinic ethyl triphenylpyrrolone, have been determined.

2. A peculiar extinction phenomenon described by Greenwood has been further investigated. Evidence is presented to show that this phenomenon is not dependent upon rotatory polarization as was formerly believed.

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