

[CONTRIBUTION FROM THE AMMONIA DEPARTMENT OF E. I. DU PONT DE NEMOURS AND COMPANY, INC.]

Optical Crystallography of Acetaldehyde 2,4-Dinitrophenylhydrazone

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An earlier investigation of the optical properties of several aliphatic 2,4-dinitrophenylhydrazones¹ disclosed the presence of a rare type of dispersion in crystals of the acetaldehyde derivative. It was therefore decided to make a more thorough study of the optical crystallographic properties of this substance.

In the course of the new research it was found that acetaldehyde 2,4-dinitrophenylhydrazone exists in at least two modifications depending upon the conditions of crystallization, and that the newly discovered form also exhibits interesting dispersion phenomena, but of a character quite distinct from that of the other modification.

Optical properties were measured by means of a petrographic microscope, care being taken to substitute quantitative measurements wherever possible for the qualitative data so frequently reported. Approximate geometric measurements were carried out with the same instrument, and although axial ratios could not be determined, there is little doubt that both modifications are monoclinic. Axes in harmony with the apparent symmetry have been provisionally assigned.

Experimental

Preparation of the Derivative.—Acetaldehyde 2,4-dinitrophenylhydrazone was prepared by the method of Brady,² employing an excess of aldehyde to avoid possible contamination of the product by the free base. The reagent was prepared by dissolving 12 g. of Eastman Kodak 2,4-dinitrophenylhydrazine in 90 cc. of concentrated sulfuric acid and diluting to a liter with 95% ethanol. The acetaldehyde also was obtained from the Eastman Kodak Co. The product was submitted to five successive crystallizations from hot 60% ethanol. Single crystallizations of the above purified material were made from absolute ethanol, ethyl acetate, *n*-pentanol, chloroform, benzene, toluene and xylene. All of these solvents yield products free from solvent of crystallization, as shown by the fact that the latter have identical melting points and optical properties, and fuse quietly without evidence of gas evolution when heated upon an object slide. The crystals obtained from the above solvents under normal conditions are presumably the *stable modification*.

The *metastable form* results when fused preparations are allowed to crystallize. It also occurs along with the stable variety where thin films of the solution are allowed to evaporate spontaneously. The conditions most favorable to its formation from solution are not known with certainty.

Slides of the metastable modification obtained by rapid fusion upon a hot plate have reproducible optical properties. The melting point is apparently unchanged by cautious fusion. When the fused material is crystallized from solvents the stable modifica-

(1) Bryant, *THIS JOURNAL*, **54**, 3758 (1932).

(2) Brady, *J. Chem. Soc.*, 756 (1931).

tion is obtained, showing that the former is a true polymorph and not a different chemical compound. No evidence of reversion to the stable modification has been observed in preparations from fusion even after a year at room temperature, the equilibrium between the two forms having been effectively "frozen." Sublimation or prolonged heating at the melting point results in a slight decomposition with attendant changes in optical properties and melting point.

The melting points of several samples of acetaldehyde 2,4-dinitrophenylhydrazone determined by the bar method of Dennis and Shelton³ agreed at 168.5°, *corr.*, a value slightly higher than the one reported earlier¹ (167°), and probably due to the greater purity of the present preparations.

Optical Equipment and Technique.—A Bausch & Lomb LD petrographic microscope was used in the present research. Monochromatic illumination was obtained principally from the mercury arc equipped with suitable Wratten filters. In addition to the usual yellow (5780 Å.), green (5461 Å.) and blue (4358 Å.), the mercury lines at 6234 and 6908 Å. were isolated in moderate purity by means of Wratten filters No. 71A and 70, respectively. These lines, however, were too weak for most purposes so that an incandescent bulb with a No. 70 filter served as the chief source of red radiation. Sodium and thallium flames were used to some extent but the intensity and purity of the latter were not very satisfactory due to the strong absorption of green rays by the derivatives.

Refractive indices were determined by the immersion method using the same series of liquids employed in the earlier work.

Calibration of the microscope system for axial angle measurements was accomplished by means of the angle scale of the Abbé apertometer. These calibrations were in essential agreement both with a standardized cleavage of mica and the condenser apertometer supplied with the microscope.

Literature references and additional details regarding the methods employed are given in the earlier article.

Optical Crystallographic Data

Stable Modification.—The substance crystallizes from absolute ethanol, ethyl acetate, *n*-pentanol, chloroform, benzene, toluene and xylene in bright yellow rectangular plates belonging to the monoclinic system, and probably to the prismatic class. The principal form is the basal pinacoid upon which face the crystal usually lies. Other forms identified are the clinodome, prism and ortho pinacoid. Crystals from 60% ethanol are in needles with the clinodome most common. Both types are usually elongated along the clinaxis.

β coincides with crystallographic b and α is inclined slightly from a in the symmetry plane 010. Extinction is parallel on 001 as required for monoclinic crystals. An extinction angle, $\alpha \wedge a = 4 \pm 1^\circ$ on the clinodome, is common in crystals from 60% ethanol.

The optic axial plane coincides with the symmetry plane 010, and the obtuse bisectrix emerges from the 001 face at a slight angle from the normal, as shown by interference figures. The optical character is negative.

Fragments show interference figures with one visible melatope, and occasionally a complete acute bisectrix figure. $2E = 80.5 \pm 1^\circ$ (5461 Å.),

(3) Dennis and Shelton, *THIS JOURNAL*, **52**, 3128 (1930).

$85.5 \pm 1^\circ$ (ca. 6800 Å.); $2V = 38 \pm 0.5^\circ$ (5461 Å.); and $42.5 \pm 0.5^\circ$ (ca. 6800 Å.).

Conoscopic observations in white light show strong inclined dispersion with colors reversed and fainter about one isogyre. On passing from green to red monochromatic light, one melatope (the one with the weaker color margins) remains sensibly stationary while the other moves away from the acute bisectrix. The inclined dispersion of the bisectrices amounts to about 2.5° . This type of dispersion definitely identifies crystallographic b with β in monoclinic crystals.

Refractive indices were measured at $25 \pm 3^\circ$ for the same two wave lengths. The results are as follows. For the green line at 5461 Å., $\alpha = 1.560$, $\beta = 1.969$, $\gamma = 2.040$, $\gamma - \alpha = 0.480$; for the red band near 6800 Å., $\alpha = 1.540$, $\beta = 1.866$, $\gamma = 1.938$, $\gamma - \alpha = 0.398$; all ± 0.005 .

The crystals are pleochroic. On the 001 face the transmitted color is greenish-yellow along α , and orange-yellow parallel to β . Absorption is practically complete for wave lengths shorter than the blue-green.

Metastable Modification.—This polymorph is obtained in orange-yellow monoclinic crystals either from fusion or along with the stable variety when the xylene solution is evaporated in thin layers (as upon a microscope object slide). The crystals from fusion or sublimation are mostly lozenge shaped and tabular with plane terminal angles of $40 \pm 1^\circ$. The basal pinacoid is usually the best developed form although the prism is present, and also possibly the pyramid. Crystals from xylene show the same forms but, in addition, the ortho pinacoid which gives them a coffin-like appearance. The tabular crystals described above are elongated parallel to the clinoaxis and always lie upon the 001 face. Some of the crystals from xylene, however, are of rhomboidal outline, elongated along the vertical axis and lying upon a prism face.

Since the metastable variety exhibits crossed axial plane dispersion, the optical orientation is not the same for all wave lengths. b coincides with γ for red, but with β for the green thallium line (5351 Å.). α is inclined strongly with respect to the c -axis. Extinction is symmetrical on (001). On prism faces, $\alpha \wedge c = 41 \pm 1^\circ$.

The plane of the optic axes coincides with the symmetry plane (010) for green (5351 Å.) but is at right angles to the latter for red. The acute bisectrix emerges practically normal to (001). The optical character is negative.

A more careful study of the crossed axial plane dispersion observed in this modification of acetaldehyde 2,4-dinitrophenylhydrazone has been carried out. The optic axial angle in air was measured for several wave lengths of monochromatic light. The values of $2E$ given in Table I (see Fig. 1 also) are the averages of at least six observations for each wave length.

TABLE I

VARIATION OF OPTIC AXIAL ANGLE WITH WAVE LENGTH IN ACETALDEHYDE 2,4-DINITRO-PHENYLHYDRAZONE (METASTABLE FORM)

Source of light	2E	Plane of optic axes	Source of light	2E	Plants of optic axes
Hg 6908 Å.	45.0°	⊥ to (010)	Hg 5780	32.0	⊥ to (010)
Hg 6234	41.5	⊥ to (010)	Hg 5461	8.0	⊥ to (010)
Na 5893	35.0	⊥ to (010)	Tl 5351	23 ca.	(010)

The observations made in green thallium light (5351 Å.) are only approximate. The purity and intensity of the light available were not sufficient to produce well-defined interference figures. The optic axial angle for the 5461 Å. mercury line was readily reproducible in any given crystal, but

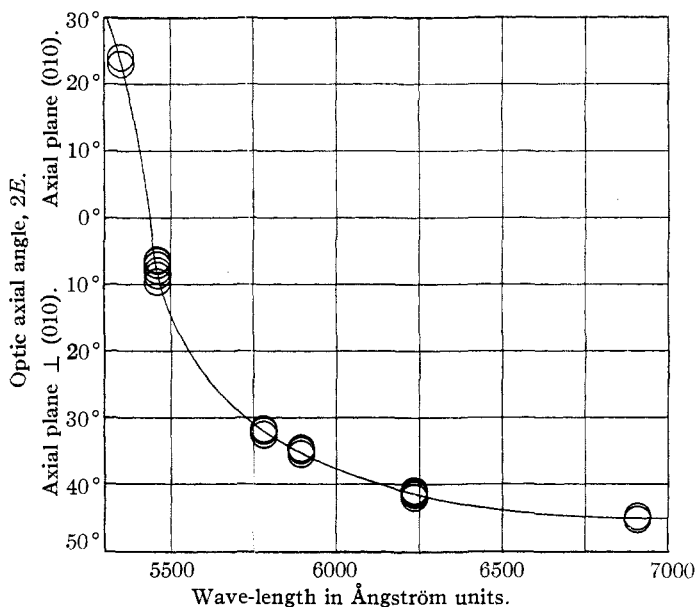


Fig. 1.—Optic axial angle of acetaldehyde 2,4-dinitrophenylhydrazone for light of different wave lengths.

showed a maximum variation of $\pm 2^\circ$ on passing from one crystal to another, a condition probably caused by slight contamination resulting from local decomposition in the fusion process (see curve in Fig. 1). With the above exceptions the precision of the observations in Table I should be about $\pm 0.5^\circ$. These measurements were executed at 25–27°. No change of optic axial angle with temperature was observed over the range 17–27°, even for the sensitive 5461 line. The substance becomes uniaxial for a wave length near 5440 Å.

Because of the difficulty experienced in earlier experiments of obtaining reproducible optic axial angles from different batches of crystals, it was decided to measure the change of this property with wave length in samples

contaminated up to 40% with known amounts of the corresponding propionaldehyde derivative.¹ This was done in order to discover whether or not contamination could account for the discrepancies.⁴ Table II (Fig. 2) shows how increasing amounts of the propionaldehyde compound displace the wave length of uniaxiality toward the red end of the spectrum. Where two axial angle values are given for the same conditions, two separate fused preparations were observed in order to form an idea of the reproducibility of optical properties in fused mixtures of this type.

TABLE II

VARIATION OF OPTIC AXIAL ANGLE WITH COMPOSITION IN FUSED MIXTURES OF ACETALDEHYDE AND PROPIONALDEHYDE 2,4-DINITROPHENYLHYDRAZONES

Wt. per cent. propionaldehyde derivative	Optic axial angle, $2E$		
	5461 Å.	5780 Å.	ca. 6800 Å.
0	8.0°	32.0°	45.0°
5	17.5 19.0 (010) ^a	24.5 26.0	40.5 41.0
10	29.5 31.0 (010)	11.0	35.5 36.0
15	36.5 (010)	13.0 (010)	31.5
20	39.0 39.5 (010)	18.5 (010)	29.0 30.0
30	40.5 41.5 (010)	22.5 23.5 (010)	25.0 26.5
40	43.0 43.5 (010)	25.0 26.5 (010)	21.5 23.0

^a Where the designation (010) appears, the optic axial plane coincides with the symmetry plane. In all other cases the optic axial plane is at right angles to the symmetry plane.

The fused mixtures were prepared by weight and their compositions should be correct to $\pm 1\%$. It is apparent from Table II that as little as 1% of contamination can produce a change of 5° in $2E$. This probably accounts for the lack of constancy in the earlier results.¹

Refractive indices for the green mercury line (5461 Å.) are $\alpha = 1.412$, $\beta = 2.078$, $\gamma = 2.078$, $\gamma - \alpha = 0.666$; for the red (ca. 6800 Å.), $\alpha = 1.410$, $\beta = 1.938$, $\gamma = 1.96 \pm 0.01$, $\gamma - \alpha = 0.45 \pm 0.01$. The precision is ± 0.005 except where noted. The true optic axial angle has been calculated from β and $2E$: $2V = 4 \pm 1^\circ$ (5461 Å.), $2V = 23 \pm 0.5^\circ$ (ca. 6800 Å.).

Pleochroism similar to that of the stable form has been observed. On the prism face the color is greenish-yellow along α and orange-yellow at right angles to α . Pleochroism on the 001 face is very slight. All orientations absorb strongly in the blue and violet.

In parallel or gently convergent white light with crossed nicols, the 001 face transmits a peculiar green light in the positions of extinction. The

(4) The exact nature of these fused mixtures has not yet been determined. They might be explained either by solid solution or complex compound formation, although the former explanation appears more likely in view of the continuous character of the $2E$ vs. composition curves. $2E$ can be measured only in certain properly oriented crystals in melts; consequently it is not definitely certain that a single phase was present in all of the mixtures, although there is some evidence to this effect. Single crystals with optical properties in harmony with those of the melts were obtained by cautious sublimation. Twinning (probably of the penetration type) was more common in the mixtures than in the pure substances.

green color is not observed in orientations appreciably removed from the above. A similar phenomenon has been reported by Greenwood⁵ for triphenylbismuthine dichloride. He attributes the effect to rotatory polarization. When 20 to 30% of propionaldehyde derivative is fused with the acetaldehyde 2,4-dinitrophenylhydrazone, the resulting crystals show a similar green color in the position of maximum illumination rather than at extinction. Within the limits of 2 to 15 microns no definite change in color with thickness occurs.

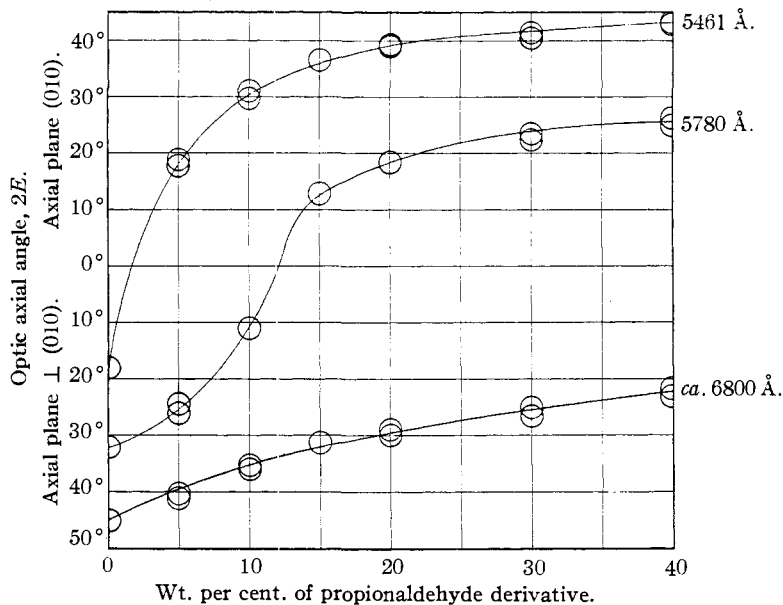


Fig. 2.—Optic axial angle in mixtures of acetaldehyde and propionaldehyde 2,4-dinitrophenylhydrazones.

Discussion of Dispersion Results

The stable modification is a fine example of inclined dispersion of the bisectrices. According to Tutton,⁶ this type of dispersion is seldom very pronounced, "rarely exceeding a degree and generally only a few minutes." It will be recalled that a value of approximately 2.5° at room temperature was obtained in this research.

The chief features of the crossed axial plane dispersion present in the metastable form are in harmony with Tutton's experimental generalizations on this subject.⁷ The substance clearly belongs to Tutton's second class in which the optic axial angle is more sensitive to changes of wave length

(5) Greenwood, *Z. Krist.*, **60**, 311 (1924); *Am. Mineral.*, **16**, 473 (1931).

(6) Tutton, "Crystallography and Practical Crystal Measurement," The Macmillan Co., London, 1922, Vol. II, p. 1049.

(7) Tutton, Ref. 6, Vol. II, Chapt. 49.

than temperature. Likewise, the β and γ refractive indices are relatively close together in magnitude. The extremely high birefringence is somewhat at variance with his condition requiring weak double refraction in order to produce "wide separation of the optic axes in the two planes for the two ends of the spectrum." The crossed axial plane dispersion of the metastable modification is slightly less than in Brookite⁶ but much greater than that of saccharine,⁶ the lactone or anhydride of saccharic acid, although both of these substances have a considerably smaller birefringence. The occurrence of this type of dispersion in the present case is probably explained by the dispersions of the β and γ refractive indices which are probably sufficiently great to compensate for the wide separation of α and γ .

Summary

1. Optical crystallographic data for two crystalline modifications of acetaldehyde 2,4-dinitrophenylhydrazone have been determined.

2. The stable form has been found to exhibit strong inclined dispersion of the bisectrices amounting to about 2.5° at room temperature.

3. The crossed axial plane dispersion of the metastable modification has been studied in greater detail. The wave length of uniaxiality was found to be near 5440 \AA .

4. Contamination with small amounts of the corresponding propion-aldehyde derivative was found to have a marked effect upon the magnitude of the optic axial angle.

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A Study of the Isotopes of Cobalt by the Magneto-optic Method

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As a reference substance for setting the fixed trolley of a newly installed magneto-optic apparatus, so that all subsequent readings would correspond to those recorded by Dr. Fred Allison¹ and his co-workers in their numerous publications, cobalt chloride seemed to be an ideal salt to use. Cobalt has been reported by both Aston² and Allison and Murphy to have only one atomic mass. The latter authors, using the magneto-optic apparatus, reported a single point of minimum light transmission for cobalt chloride at 20.15 on their scale. Nickel, which is always present in cobalt salts, was reported to show minima at 20.30 and 20.40, when present as the chloride. By using a solution of cobalt chloride containing about one part

(1) Allison and Murphy, *THIS JOURNAL*, **52**, 3796 (1930); Allison, *J. Chem. Education*, **10**, 71 (1933); Allison and co-workers in numerous articles in *Phys. Rev.* since 1927.

(2) Aston, *Nature*, **112**, 449 (1923); *Phil. Mag.*, **47**, 385 (1924).