

incipient crystallization. Absolute ethanol and glacial acetic acid were the solvent media used for the condensation reactions.

Summary

1. The authors have reëxamined the condensation reaction described originally by Biginelli, which involves a combination between urea, a β -ketone ester and an aldehyde.

2. We have extended the application of this condensation reaction and find that the change is accelerated by the use of hydrochloric acid.

3. The condensation can be applied in either absolute alcohol or glacial acetic acid solutions.

4. Several new aldehydes have been incorporated in the reaction and several new 2-keto-1,2,3,4-tetrahydropyrimidines have been described.

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

OPTICAL PROPERTIES OF SOME DERIVATIVES OF LOWER ALIPHATIC ALCOHOLS AND ALDEHYDES

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Among physical methods of identifying closely related organic compounds, those of optical crystallography offer great promise both from the standpoint of speed and sensitivity.¹ The members of homologous series of organic compounds, because of their gradual changes in chemical and ordinary physical properties with increasing molecular weight, place great obstacles in the way of the chemist attempting their identification. A number of optical crystallographic properties can be observed by means of the polarizing microscope, many of which are, for all practical purposes, independent physical constants, and greatly increase the possibility of a precise identification of closely related compounds.

The scheme of optical identification employed in this research is one successfully used by Wright,¹ Wherry,² Keenan³ and others,⁴ and depends upon the determination of such properties as refractive index, optic axial angle, extinction angle, optical character, dispersion, together with the orientation of the optical ellipsoid within the crystal. This characteriza-

¹ Wright, *THIS JOURNAL*, **38**, 1647 (1916).

² Wherry, *U. S. Dept. Agr. Bull.*, No. 679 (1918); Wherry and Yanovsky, *THIS JOURNAL*, **40**, 1063 (1918).

³ Keenan, *J. Biol. Chem.*, **62**, 163 (1924); Keenan and Weisberg, *J. Phys. Chem.*, **33**, 791 (1929); Phillips and Keenan, *THIS JOURNAL*, **53**, 1924 (1931).

⁴ Poe and Sellers, *ibid.*, **54**, 249 (1932); Kofler and Mayrhofer, *Mikrochemie*, **10**, 460 (1932); Takahashi and Yaginuma, *J. Soc. Chem. Ind. Japan, Suppl.*, **33**, 370 (1930).

tion is usually carried out upon detached crystals and only rarely with crystals from fused preparations. Chamot and Mason⁵ describe a procedure of obtaining crystals by fusion of substances directly on the microscope slide under a cover glass. Such a procedure naturally gives rise to better plane parallel crystal plates, thus facilitating the determination of the optic axial angle as well as examination with immersion objectives of high numerical aperture. This method has been used together with the others in the present investigation.

More stress is laid upon the optic axial angle in this paper than is usual in the recent literature. This property is a function of differences of the three refractive indices of biaxial crystals. It can be determined independently and is in many cases practically an independent physical property.

The technique outlined above was adopted in characterizing members of two series of aliphatic compounds, the lower saturated alcohols and aldehydes. The alcohols were converted into their 3,5-dinitrobenzoyl esters, and the aldehydes into the corresponding 2,4-dinitrophenylhydrazones. Both series of derivatives crystallize easily from solvents and melt without decomposition, hence are well suited for examination with the polarizing microscope.

Experimental

Materials.—Reagents: *2,4-dinitrophenylhydrazine* was an Eastman Kodak Company product. *3,5-Dinitrobenzoyl chloride* was prepared from the corresponding acid obtained from Eastman, according to Berend and Heymann,⁶ and boiled at 194–196° at 10 mm. pressure. *Methanol* was a J. T. Baker special grade. *Ethanol* (absolute) was obtained from the U. S. Industrial Chemical Co. *n-Propanol* and *isobutanol* were du Pont products of boiling ranges, respectively, 97.1–97.3° and 107.5–107.7°. *Isopropanol*, *normal*, *secondary* and *tertiary butanol* were all obtained from the Eastman Kodak Company. *2-Methyl-butanol-2* was from the Sharples Solvents Corporation. *Formaldehyde* (37%) solution and *acetaldehyde* were Mallinckrodt products. *Propionaldehyde*, *normal* and *isobutyraldehyde* were again Eastman products. All of these substances were of the best grade available.

Preparation of the Derivatives.—The 3,5-dinitrobenzoates of the alcohols were prepared as directed by Reichstein.⁷ The products were recrystallized twice from petroleum ether. The melting points of these derivatives were in satisfactory agreement with the literature as shown in Table I.

The 2,4-dinitrophenylhydrazones of the aldehydes were prepared by the method of Brady.⁸ The derivatives were crystallized twice from hot aqueous alcohol. The melting points of some of these compounds are

⁵ Chamot and Mason, "Handbook of Chemical Microscopy," John Wiley and Sons, Inc., N. Y., 1930, Vol. I, p. 354.

⁶ Berend and Heymann, *J. prakt. Chem.*, [2]^o **65**, 291 (1902); *ibid.*, **69**, 455 (1904).

⁷ Reichstein, *Helv. Chim. Acta*, **9**, 799 (1926).

⁸ Brady, *J. Chem. Soc.*, p. 756 (1931).

TABLE I
MELTING POINTS OF 3,5-DINITROBENZOYL ESTERS

Derivative	Melting point (observed), °C.	Melting point (literature), °C.
Methanol	108	110 -110.5 ⁷ 107.8 ⁹
Ethanol	93	93 - 94 ⁷ 92.7 ⁹
<i>n</i> -Propanol	74	74 - 75 ⁷ 73.0 ⁹
Isopropanol	123	121 -122 ⁷ 122.1 ⁹
<i>n</i> -Butanol	64	61 - 63 ⁷ 62.5 ⁹
Isobutanol	87	87 - 88 ⁷ 86.5 ⁹
<i>Sec.</i> -butanol	76	75.6 ⁹
<i>Tert.</i> -butanol	142	141.5-142.5 ⁷
2-Methyl-butanol-2	116	117 -118 ⁷

higher than those in the literature, especially in the case of the formaldehyde derivative, for which there are no recent data. These results are given in Table II.

TABLE II
MELTING POINTS OF 2,4-DINITROPHENYLHYDRAZONES

Derivative	Melting point (observed), °C.	Melting point (literature), °C.
Formaldehyde	167	155 ¹¹
Acetaldehyde	167	162 ¹⁰ 147 ¹¹
Propionaldehyde	156	155 ¹⁰
<i>n</i> -Butyraldehyde	123	122 ¹⁰
Isobutyraldehyde	187	182 ¹⁰

Melting Points.—Melting points were determined potentiometrically by means of an electrically heated copper bar similar to that of Dennis and Shelton.¹² The bar was checked by the capillary tube method using calibrated short scale thermometers. The melting points in Tables I and II should be correct to $\pm 0.5^\circ$.

Optical Equipment.—The petrographic microscope used in this investigation was the LCH model of Bausch and Lomb, specially equipped with a 1.40 N. A. immersion condenser. The principal source of light was the green line (5461 Å.) of the mercury arc isolated by means of Corning filters Nos. G-555-Q and G-34-Y. A few observations were made in red light from a Wratten No. 70 filter used in conjunction with an incandescent lamp.

A 7X Huyghenian eyepiece micrometer with a fixed linear scale was used for axial angle determinations. The angular equivalent of the micrometer scale was evaluated empirically with the aid of a Zeiss Abbe apertometer, hence the calibrations are independent of the Mallard relation.¹³ These calibrations were further checked by comparison with a

⁹ Malone and Reid, *THIS JOURNAL*, 51, 3424 (1929).

¹⁰ Brady and Elsmie, *Analyst*, 51, 77 (1926).

¹¹ Purgotti, *Gazz. chim. ital.*, 24, 569 (1894).

¹² Dennis and Shelton, *THIS JOURNAL*, 52, 3128 (1930).

¹³ Wright, "The Methods of Petrographic-Microscopic Research," *Carnegie Bull. No. 158*, p. 148 (1911).

carefully standardized cleavage of muscovite. The two standards agreed within the observational error. In this connection the writer wishes to thank F. E. Wright of the Geophysical Laboratory in Washington both for the mica and for the use of his axial angle apparatus in standardizing the specimen.

Refractive indices were determined by the immersion method and have been reported only where the optical orientation could be verified by interference figures. The immersion liquids used were prepared in intervals of 0.01 in refractive index extending from 1.36 to 1.72. Above 1.72 solutions were prepared only as required. The liquids of low refractive index were standardized by means of the Abbe refractometer. Liquids above 1.60 were determined by the method of minimum deviation using a spectrometer with hollow prisms. The dispersion of the liquids was also determined for sodium and several mercury lines. The following mixtures of liquids were used in the present investigation

$n_D = 1.36-1.40$ glycerol-glycol-water

$n_D = 1.40-1.72$ potassium mercuric iodide-glycerol-water

$n_D = 1.74-1.78$ methylene iodide-sulfur

$n_D = 1.85-2.10$ methylene iodide-arsenic trisulfide

Determination of Optical Properties

The optical characteristics of the fourteen crystalline derivatives of alcohols and aldehydes were determined by the conventional methods in use among petrographers and are given in Tables III and IV.

All refractive index measurements were carried out at $25 \pm 3^\circ$ using liquids standardized at 25° . In the alkyl dinitrobenzoate series the refractive index γ is not reported. This is because of the thin plate-like character of the crystals which makes the determination of the edgewise γ index extremely difficult. Likewise the optical data for formaldehyde 2,4-dinitrophenylhydrazone are extremely meager due to the peculiar habit of the crystals.

"Hydrazone" crystals presenting the β - γ index plane were obtained by sublimation from a cover glass, followed by cautious fusion upon the slide. Tabular forms of the desired orientation result from the crystallization of the minute fused droplets.

The third decimal place of the refractive index has been approximated by proportional mixing of adjacent immersion liquids. In the ester series the refractive indices should be correct to ± 0.003 . In the case of the "hydrazones" the error should not exceed ± 0.005 , but is probably greater than in the preceding series, due in part to the extremely strong double refraction which magnifies errors of optical orientation and to the instability of the more highly refracting solutions. Work is now under way to improve the precision of the measurements and to supply the missing refractive indices.

TABLE III
OPTICAL PROPERTIES OF 3,5-DINITROBENZOYL ESTERS

Derivative	Methanol	Ethanol	<i>n</i> -Propanol	Isopropanol	<i>n</i> -Butanol	Isobutanol	<i>Sec.</i> -butanol	<i>Tert.</i> -butanol	2-Methyl-butanol-2
Habit	Elongated plates	Prismatic needles	Elongated plates	Prismatic needles	Plates, needles	Plates, needles	Elongated plates	Elongated plates	Elongated plates
Probable crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic
Elongation	Elongation inclined 45° from β	Elongation = β	Elongation inclined 35° from α	Elongation = β	Elongation = β	Elongation = β	Elongation = β	Elongation = β	Elongation = β
Refractive indices	α 1.382	1.560	1.486		1.488	1.558	1.486	1.484	1.491
$\lambda = 5461 \text{ \AA.}$ at $25 \pm 3^\circ$	β 1.780	1.576	1.603	1.609	1.621	1.558	1.578	1.585	1.588
Precision	± 0.003								
Birefringence	Very strong	Medium	Strong	Strong	Strong	Medium	Strong	Strong	Strong
Optical character	Negative	Positive	Negative	Negative	Negative	Positive	Negative	Negative	Negative
Optic axial angle, $2E$	$74 \pm 5^\circ$ (Calcd.) ^b	$74 \pm 2^\circ$ (Calcd.) ^b	Large	$126 \pm 3^\circ$ (Calcd.) ^b	$107 \pm 4^\circ$ (Calcd.) ^b	$15 \pm 2^\circ$ ^a	$126 \pm 6^\circ$ (Calcd.) ^b	Large	Large
$\lambda = 5461 \text{ \AA.}$									
$2V$	40°	45°		67°	59°	10°	70°		
Remarks	Extinction inclined	Extinction parallel	Extinction inclined	Extinction parallel	Extinction parallel	Extinction parallel	Extinction parallel	Extinction parallel	Extinction parallel

^a Microscope system calibrated directly with aid of the angle scale of the Abbe apertometer.

^b Calibration as in (a), but using the numerical aperture scale of the apertometer, and converting the readings to $2E$ by means of the relation $\sin E = N. A.$

TABLE IV
OPTICAL PROPERTIES OF 2,4-DINITROPHENYLHYDRAZONES

Derivative		Formaldehyde	Acetaldehyde	Propionaldehyde	<i>n</i> -Butyraldehyde	Isobutyraldehyde	
Habit		Elongated prisms	Elongated prisms and tablets	Prisms	Elongated prisms	Elongated prisms	
Probable crystal system		Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic	
Optical orientation			$b = \beta$ $b = \gamma$ (red)	$b = \gamma$	$c = \alpha$	$c = \alpha$	
Refractive indices for	α		1.412 1.410 (red)	1.426	1.426	1.426	
	$\lambda = 5461 \text{ \AA. at } 25 \pm 3^\circ$	β	2.078 1.938 (red)	1.917	1.869	1.906	
	Precision ± 0.005	γ	2.078 1.948 (red)	1.959	1.965	2.002	
Birefringence		Very strong	0.666 0.538 (red)	0.533	0.539	0.576	
Optical character		Negative	Negative	Negative	Negative	Negative	
Optic	$\left\{ \begin{array}{l} 2E_{6401}^a \\ 2E_{6800}^a \\ 2V_{6461} \end{array} \right.$	Large	I	II			
Axial			$16 \pm 2^\circ$	$5 \pm 2^\circ$	$44 \pm 1^\circ$	$80 \pm 1^\circ$	$78 \pm 1^\circ$
Angle			$42.5 \pm 1^\circ$	$45 \pm 1^\circ$	$58 \pm 1^\circ$	$88 \pm 1^\circ$	$87 \pm 1^\circ$
Remarks		Extinction oblique in prisms from alcohol	Crossing of axial planes between 5461 and 5780 \AA. Elongation inclined 51-56° from α in prisms from alcohol	Elongation inclined 54° from α in prisms from alcohol	Extinction parallel or symmetrical	Extinction parallel or symmetrical	

^a Microscope calibrated directly with aid of the angle scale of the Abbe apertometer.

The apparent optic axial angle in air, $2E$, was measured directly from interference figures of which both melatopes were visible, using an eyepiece micrometer calibrated with the angle scale of the Abbe apertometer. Where the angular field of a dry objective did not include both melatopes, or the crystal grains were too small to produce clear interference figures in the ordinary manner, a homogeneous oil immersion objective was used. In this case the ocular micrometer was calibrated by means of the numerical aperture scale of the apertometer and $2E$ calculated from the relation, $N. A. = \sin E$. If the optic axial angle in air is very large, the angle in oil, $2H$, may be calculated, using the expression, $\sin H = N. A./n$, where n is the refractive index of the immersion oil. Rough estimates were obtained by other methods¹⁴ where suitable interference figures were lacking. The estimated precision of the observations varies, becoming less for greater angles. Other factors¹⁵ may affect the results to some extent but need not be considered here. For the sake of completeness the axial angle measurements have been reduced to the true angle $2V$ by means of the intermediate index β .

The 2,4-dinitrophenylhydrazones exhibit strong dispersion of the optic axes, and in one instance a crossing of the axial planes. The optic axial angles of these substances have therefore been reported for both the green mercury line at 5461 Å. and a narrow band in the red (6500–7000 Å.). They are practically opaque to the blue and violet mercury lines.

The crossed axial plane dispersion of the acetaldehyde derivative is particularly valuable for identification because of the comparative rarity of this phenomenon. Two samples of the derivative have been prepared which show slightly different axial angles, the difference being more marked in the green. Both preparations have the same melting point with no noticeable depression on mixing. It was further ascertained that the difference is not caused by either decomposition during fusion or a noticeable temperature coefficient. There is some indication of slight contamination since such an effect would increase $2E$ for green. Additional experiments are being carried out to clear up this uncertainty.

The probable crystal systems to which the two series of crystalline compounds belong were deduced from elementary symmetry considerations. In the less certain cases, optical properties are referred to the elongation of the crystal.

Metastable Modifications.—Very little interference has been encountered from metastable forms resulting from the crystallization of fused preparations. A negative uniaxial tabular form of both the normal and isobutyraldehyde "hydrazone" has been observed on rare occasions. Isobutyl 3,5-dinitrobenzoate sometimes remains for several hours as a negative modification optically isomorphous with the other butyl esters.

¹⁴ Wright, Carnegie Bull. No. 158, p. 152; *Am. J. Sci.*, [4] 20, 285 (1905).

¹⁵ Wright, *J. Opt. Soc. Am.*, 7, 779 (1923).

Conclusions.—The results of the present investigation indicate that optical methods of identification are entirely feasible for differentiating between closely related substances, particularly when used in conjunction with the melting point. In the aldehyde series gratifying differences in refractive index and optic axial angle were observed. On the other hand, the differences in properties between the adjacent and isomeric alcohol derivatives were not as great as had been hoped, yet taken collectively there is little doubt that identification could be satisfactorily accomplished.

It seems likely that reagents could be selected which would yield compounds exhibiting greater variations in optical properties. Such a property might be encouraged by increasing the structural asymmetry of the reacting molecule. However, it is reasonable to believe that, ascending in an homologous series, the differences in physical properties would continually become less, and a point be reached where the ordinary precision of optical measurement would not be sufficient to distinguish between isomers. Such an effect might to some extent be offset by increasing the precision of the work.

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Summary

1. Optical properties of fourteen crystalline organic compounds have been determined. The compounds investigated include the 3,5-dinitrobenzoates of nine alcohols, and the 2,4-dinitrophenylhydrazones of five aldehydes, all of the saturated aliphatic series.

2. Acetaldehyde 2,4-dinitrophenylhydrazone is reported as a new example of crossed axial plane dispersion in crystals.

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