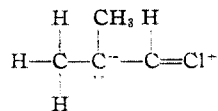H   H
| |
H—C⁻—C=Cl⁺

Because of the similarity in behavior of the chlorides and cyanides, it appeared that replacement of an end hydrogen of vinyl chloride by a methyl group would provide indirect evidence as to the validity of the structure with positive nitrogen suggested as contributing to the structure of crotononitrile. The moment in Table II of isocrotyl chloride, in which both of the end hydrogens of vinyl chloride have been replaced by methyl groups, is again nearly 0.6 higher than that of vinyl chloride, indicating, as in the analogous cases of crotonaldehyde and crotononitrile, considerable contributions from structures such as

H⁺ CH₃ H   H⁺ CH₃ H
| | | |
H—C=C—·—C⁻—Cl   and   H—C=C—·—C   Cl⁻
    | |
    H   H
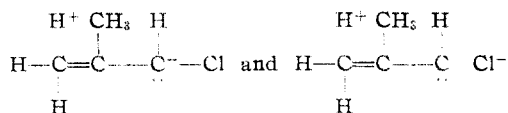
That, at the same time, the contribution from the structure

H   CH₃ H
| | |
H—C—C⁻—C=Cl⁺
    |
    H

is reduced below that from the analogous structure in vinyl chloride is indicated by the fact that electron diffraction shows the shortening of the C—Cl bond by double bond character to be about half as great in isocrotyl chloride[30] as in vinyl chloride.[31] The parallelism observed between the

(30) Beach and Stevenson, THIS JOURNAL, 61, 2643 (1939).
(31) Brockway, Beach and Pauling, ibid., 57, 2693 (1935).

effects for the chlorides and those for the cyanides provides evidence in support of the structures proposed for both.

The theory of hyperconjugation provides a mechanism for the explanation of pronounced differences in moment not readily explicable otherwise and thus receives experimental support from a new type of evidence.

Summary

The dielectric constants of the vapors of formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, crotonaldehyde, diketene, propionitrile, acrylonitrile, crotononitrile and isocrotyl chloride have been measured and used to calculate the dipole moments of the molecules.

The moment of the carbon–oxygen bond in the carbonyl group is recalculated and its inductive effect in aldehydes and ketones is examined.

Close analogies in behavior and in structure are found among unsaturated aldehydes, nitriles and chlorides. Resonance among structures made possible by the presence of a double bond may have a large effect upon the moment of a molecule. Hyperconjugation occurring when a hydrogen adjacent to a double bond is replaced by a methyl group produces a large increase in moment. The variations observed in the moment values are taken as qualitative evidence as to the relative stabilities of various polar structures which are proposed as contributing to the molecular structure.

Optical Crystallographic Studies with the Polarizing Microscope. IV. Axial Dispersion with Change of Sign. Other Dispersion Measurements

BY W. M. D. BRYANT

The optical study of crystals under the microscope using monochromatic polarized light of different wave lengths has been found especially useful for the precise characterization of organic compounds. The various types of dispersion observed in interference figures are sensitive and distinctive optical properties, of frequent occurrence in the aromatic series and among certain classes of aliphatic compounds. The better known types of dispersion of the optic axes and

ellipsoidal axes were exemplified and discussed in the third paper of this series.[1]

The experimental investigation of dispersion in crystals has been continued and in the present

(1) Bryant, THIS JOURNAL, 63, 511 (1941). The term "selective dispersion," employed in paper III to describe the various types of dispersion of the optic axes and indicatrix axes, has been used earlier in quite a different sense, namely, as a synonym for anomalous dispersion, the term applied to simple dispersion in which the usual order of spectral deviation is altered by absorption. Since retention of the earlier usage is desirable, the name "ellipsoidal dispersion" should replace "selective dispersion" in paper III.

paper optical properties of three additional organic substances are given. The hydrocarbon *trans*-stilbene was found to exhibit a rare form of dispersion of the optic axes previously observed to a lesser degree in the mineral danburite.[2] This property is characterized by strong dispersion of the optic axes with 2 V passing through 90° and hence undergoing a change in optical sign. The effect may therefore be fairly accurately described as *axial dispersion with change of sign*. Although stilbene is apparently the first organic example to be studied quantitatively, others have been found quite recently[3] and it is now evident that this criterion is a useful one. The application of Merwin's method[4] in obtaining the dispersion of the individual refractive indices of stilbene offered a good opportunity to test the value of this technique in the organic field.

Benzil exemplifies another rare type of dispersion in which a uniaxial substance becomes isotropic for one wave length of light. Jelley[5,6] has already studied the dispersion of the birefringence using his microspectrograph, but it was felt that measurement of the refractive indices for a number of wave lengths would constitute another useful means of studying this phenomenon. The third substance, thiourea, exhibits crossed axial plane dispersion but differs from examples given in the preceding papers by having its wave length of uniaxiality in the near ultraviolet. Many other compounds with strong axial dispersion in the visible may be expected to show crossed axial plane dispersion at the shorter wave lengths. All three of the above compounds have been the subject of previous crystallographic and optical studies[7] but the very marked dispersion in stilbene and thiourea was apparently overlooked.

Materials.—*trans*-Stilbene (m. p. 124.9°), benzil (m. p. 95.0°), and thiourea (m. p. 182.4°) from Eastman Kodak Co. were sharp melting and uniform in appearance and so were used without further purification. Melting points were measured on a calibrated Dennis melting point bar.

Optical Equipment and Technique.—The apparatus and technique employed were identical with those of paper III[1] except in the following details. The Ahrens type polarizer

of the regular LD petrographic microscope of Bausch and Lomb was found to absorb a large fraction of the 3650 Å. mercury radiation due to the aging of linseed oil films used in cementing the prism components. The prism was recemented by the manufacturers using a colorless resin. The ultraviolet cut-off of the recemented unit was near 3000 Å. and the photographic exposure time at 3650 Å. was reduced appreciably. The absorption of ultraviolet radiation in various parts of the optical system was checked by means of photocells. For oil immersion contacts, Shillaber's grade A immersion oil[8] was preferred since its ultraviolet absorption is less than that of either cedar or sandalwood oils and it is non-drying. Defender X-F panchromatic film was used for most of the photography. As previously, the lens system of the microscope was calibrated for optic axial angle measurements by means of an Abbe apertometer.[9]

Valuable qualitative information regarding the dispersion of the principal birefringences was obtained by noting the increase or decrease in phase difference through the spectrum as shown by the motion of the isochromatic curves between an optic axis and a bisectrix in the corresponding interference figures, on rotating the wave length drum of the monochromator. Ordinarily the phase difference and birefringence decrease with increasing wave length. Sometimes, however, the birefringence increases or passes through a maximum or minimum and this effect is reflected in the motion of the isochromatic curves.

Refractive indices were determined by the immersion method, care being taken to use index liquids saturated with the crystalline material in all cases where the crystal edges were rounded by the untreated liquid.[10] K_2HgI_4–H_2O–glycerol solutions were used with benzil to avoid solubility. Thiourea was attacked chemically by both methylene iodide and phenyldiiodoarsine,[11] mixtures of which would logically have been used to determine β and γ. β and γ were obtained with the aid of an Emmons model universal stage, using the α index of the crystal and an immersion oil composed of α-iodonaphthalene saturated with iodoform. The following glass color filters were found superior to those previously employed for the isolation of various mercury lines. The combinations Jena OG2 (4 mm.) and VG9 (2 mm.) or Corning 349 (2 × s. t.) and 401 (1/2 s. t.) are more efficient than Corning 348 and 430 for isolation of the 5780 Å. yellow lines. Jena RG8 (2 mm.) is preferable to Wratten 70 for the 6908 Å. line.

Merwin's Dispersion Method.—The dispersions of the principal refractive indices were determined by immersion using monochromatic light from a calibrated monochromator. The match between the crystal and a suitable immersion liquid was obtained by continuously varying the wave length of light employed. With a complete dispersion curve available for each liquid, three or four determinations at widely separated wave lengths are sufficient

(2) Brush and Dana, *Am. J. Sci.*, **20**, 111 (1880); also Johannsen, "Manual of Petrographic Methods," McGraw-Hill Book Co., Inc., New York, N. Y., 1918, p. 105.

(3) Paper V, Mitchell and Bryant, THIS JOURNAL, **65**, Feb. (1943).

(4) Posnjak and Merwin, *ibid.*, **44**, 1970 (1922).

(5) Jelley, *Phot. J.*, **74**, 514 (1934).

(6) *Ind. Eng. Chem., Anal. Ed.*, **13**, 196 (1941).

(7) Groth, "Chemische Krystallographie," Vol. III, W. Engelmann, Leipzig, 1910, p. 555; Vol. V, 1919, pp. 192, 200.

(8) Supplied by R. P. Cargille, 118 Liberty Street, New York, N. Y.

(9) Bryant, THIS JOURNAL, **60**, 1394 (1938), Paper I.

(10) The author is grateful to Dr. E. E. Jelley of the Eastman Kodak Co. for this suggestion. The liquids must be re-standardized after saturation. Generally only a few tenths ml. of solution need be prepared.

(11) Anderson and Payne, *Nature*, **133**, 66 (1934).

to fix the dispersion curve of a particular crystal refractive index.[12]

Dispersion and Other Optical Data

trans-Stilbene.—The dispersion of the optic axes in this compound is very strong. The optic axial angle 2 H having γ as its bisectrix changes in the following manner with the wave length of light: 2 H = ~112° (4047); 98 ± 2° (4358); 77° (4916), 65° (5461), 59° (5780), 51.5° (6234), 45.5° (6908) ± 1°. The angle with α as bisectrix varies as follows: 2 H = 71 ± 1° (3650); ~109° (4047). Figure 1 shows the curves derived from the two sets of data. The
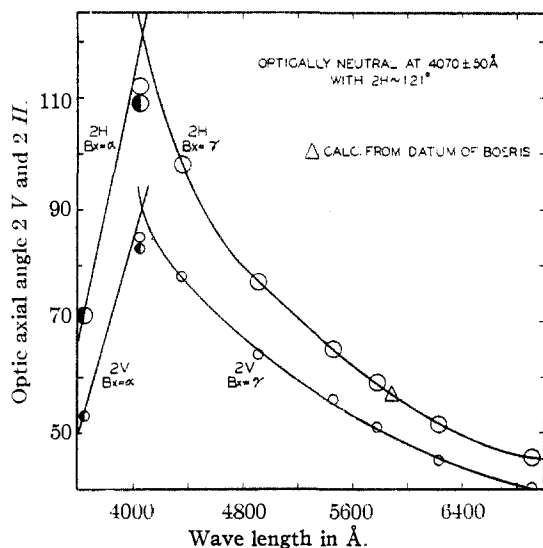

Fig. 1.—Axial dispersion with change of sign in stilbene.

Fig. 2.—Axial dispersion with change of sign in stilbene.

axial dispersion with change of sign. The interference figures of the β'-γ' section show the presence of crossed dispersion (14° for interval 5461 − 3650 Å.) and a corresponding amount of horizontal dispersion is apparent in the α'-β' section.

Refractive indices by Merwin's method are

REFRACTIVE INDEX AT 25 ± °C.

λ	α	β	γ
3650	(1.797)	(1.975)	(2.03)
4047	1.769	(1.864)	(1.973)
4358	1.751	1.823	(1.940)
4916	1.726	1.772	1.893
5461	1.712	1.743	1.860
5780	1.706	1.732	1.848
6234	1.699	1.721	1.835
6908	1.691	1.708	1.818

The indices in parentheses are extrapolations. These should involve little error in the case of α and γ as the dispersion curves were quite "normal," each coinciding with that of a single immersion liquid through most of the visible spectrum. The refractive index of α-bromonaphthalene was measured as far down the spectrum as 3650 Å.[13]

intersection of the two experimental curves determines the wave length at which 2 V equals 90°, in this case 4070 ± 50 Å. The 2 H values for both bisectrices coincide at this wave length and are equal to about 121°. This value was calculated from the relation sin H = β sin $V/1.515$. The experimental 2 H values, 112 and 109° at 4047 Å., are low due to observational difficulties; the correct values should be near 123 and 119°, respectively. Figure 2 indicates more clearly the relationship between the two sets of data. The photographs in Fig. 3 show the phenomenon of

(12) Emmons (*Am. Mineral.*, **13**, 504 (1928); **14**, 414 (1929)) has developed a valuable technique where both wave length and temperature are varied to attain an index match between a liquid and a mineral. The success of this "double variation method" is based on the fact that minerals generally are insoluble in organic immersion liquids and have a negligible temperature coefficient of refractive index compared with the rather large values for organic liquids. Many crystalline organic compounds are relatively soluble in the usual liquids and have large temperature coefficients, hence do not lend themselves well to temperature variation methods. For this reason the present work has been restricted to variation of wave length only.
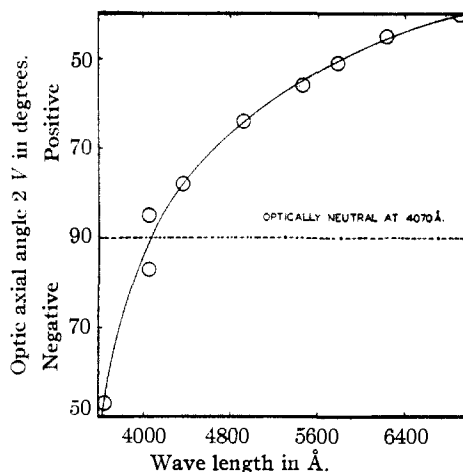
(13) The refractive index of this liquid was measured at 3650 Å. by the method of minimum deviation using a one-circle goniometer, the regular telescope eyepiece of which had been replaced by an improvised "fluorescence eyepiece." The latter consisted of a brass tube the same length and diameter as the regular ocular, but containing instead of the usual crosshairs, a glass disk with a ground surface facing the telescope objective. The ground surface was cross-ruled lightly with India ink, rubbed with powdered anthracene and placed at the conjugate focus of the objective where in ultraviolet light a sharp fluorescence image of the slit was formed and was visible through the back of the translucent disk along with the silhouette of the ink cross lines. A 14x aplanatic dissecting lens was fitted into the eye end of the brass tube and focused on the blue-green fluorescence image. By refocusing the whole eyepiece slightly the visible mercury lines could be viewed also. The following results were obtained with α-bromonaphthalene: n^{25} = 1.761 (3650), 1.720 (4047), 1.701 (4358), 1.664 (5461), 1.658 (5780). The same scheme has been used to measure the refractive index of ultraviolet transmitting liquids at 2536 Å., using quartz objectives and a hollow prism of Corning 791 glass.
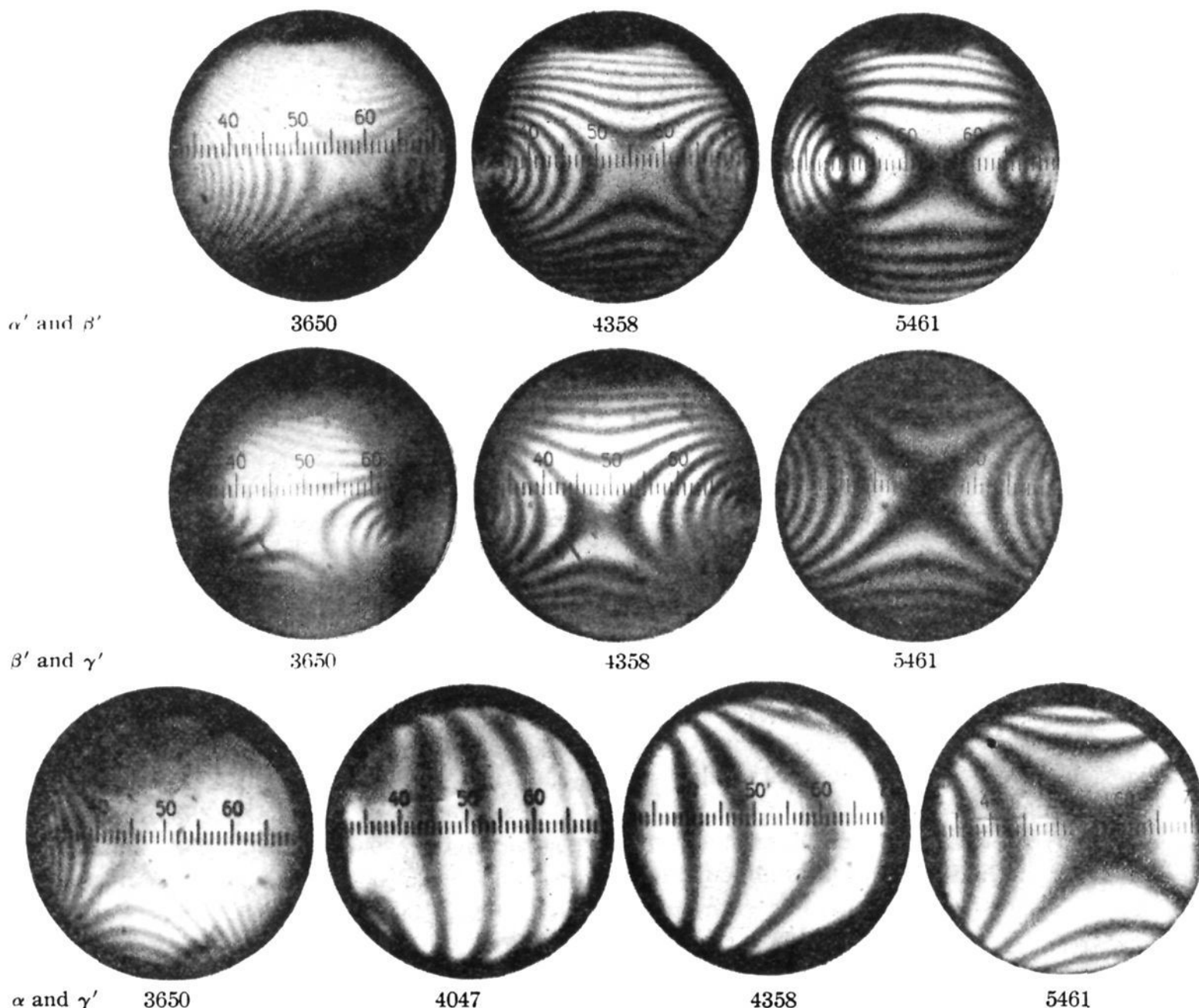
Fig. 3.—Interference figures of stilbene in monochromatic light: axial dispersion with change of sign; monoclinic crossed dispersion present in ultraviolet; wave lengths in Å.

and the resulting curve used as a guide in extrapolating α and γ. At 4070 Å. $1/\alpha^2 - 1/\beta^2$ is equal to $1/\beta^2 - 1/\gamma^2$ so that γ could be readily located. The dispersion curve of β was much different from those of the index liquids used but could be safely extrapolated to 4070 Å. The values of β and γ at 3650 Å. were chosen to conform with the optic axial angle. The three dispersion curves are plotted in Fig. 4. That they are in reasonable accord with the optic axial angle data is evident from the following table.

β	Optic axial angle, 2 V	
	Calcd. from 2 H and β	Calcd. from α, β and γ
3650	53°	(53°)
4047	85, 97	(90)
4358	78	80½
4916	64	67
5461	56	57½
5780	51	53½
6234	45	50
6908	40	45

The nearly constant separation of β and γ is confirmed by the almost negligible change in the isochromatic curves of the section with wave length contrasted with the large change observed in the $\alpha' - \beta'$ section (Fig. 3). Other optical data include: Optical character, neutral at 4070 $\pm$ 50 Å., positive above and negative below this wave length. Orientation: b = α; ax. pl. $\perp\{010\}$, $Bx_a = \gamma$ (above 4070) or α (below 4070). The above observations are consistent with Robertson, Prasad and Woodward's[14] assignment of the monoclinic space group $C_{2h}^6 - P2_1/C$. The only optical study of stilbene that could be found in the older literature was that of Boeris[15] who reported the optic axial angle for sodium light as $2E = 91° 33'$. This result is in harmony with the present study.

(14) Robertson, Prasad and Woodward, *Proc. Roy. Soc.*, **154**, 187 (1936).
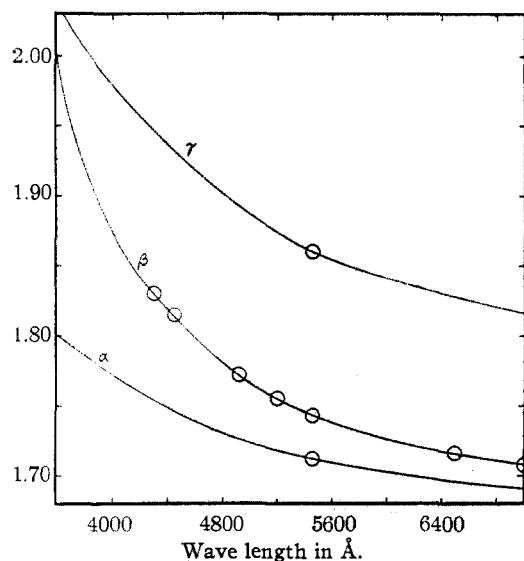
(15) Boeris, *Z. Krist.*, **34**, 300 (1901).

Fig. 4.—Refractive indices of stilbene.

Fig. 5.—Refractive indices and birefringence of benzil
birefringence data: ⊕, Jelley; ⊖, Bryant.

Benzil.—Jelley[5] has shown that the positive birefringence of this uniaxial substance decreases with decreasing wave length, becomes zero in the visible violet and then increases again with a negative sign. Since the only literature values of the refractive indices were for sodium light,[16] the dispersion curves of ϵ and ω were determined by the immersion method at 25 ± 3° supplemented by Merwin's dispersion method.

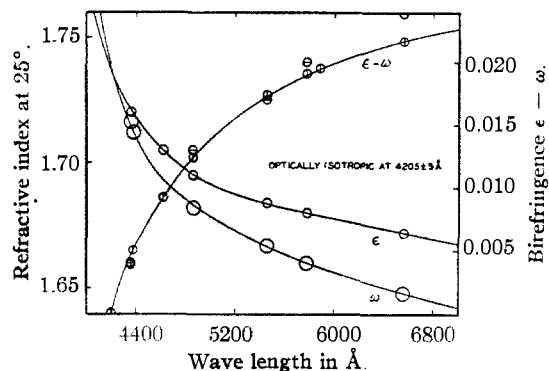| λ	ω	ϵ	$\epsilon - \omega$	$\epsilon - \omega$ (Jelley)
4205(±3)	(1.737)	(1.737)	(0.000)	0.0000
4358	1.716	1.720	.004	.0039
4380	1.712	(1.718)	(.006)	.0050
4620	(1.694)	1.705	(.011)	.0092
4860	1.682	1.695	.013	.0124
5461	1.667	1.684	.017	.0174
5780	1.660	1.680	.020	.0191
5893	(1.658)	(1.679)	.021	.0195
6560	1.648	1.672	.024	.0217

(The figures in parentheses were obtained graphically.)

The wave length of isotropy and the birefringences given in the last column are recent unpublished results obtained by E. E. Jelley.[17] The refractive index measurements were made using aqueous glycerol solutions of K_2HgI_4 after preliminary difficulties were traced to the considerable solubility in organic immersion oils. However saturated solutions of benzil in organic liquids are satisfactory immersion media. The maximum

uncertainty in ϵ and ω is estimated at less than ± 0.003. The refractive indices and principal birefringences are plotted in Fig. 5. The crystal symmetry conforms to one of two enantiomorphous trigonal space groups, $D_2^6 - C3_22$ or $D_3^4 - C3_12$.[18]

Thiourea.—The strong axial dispersion of this compound in the visible region becomes crossed axial plane dispersion in the near ultraviolet. The optic axial angle, 2 H_a has the following values: 2 H_a = 25.0° (3650) {100}; 0° (3780 ± 40 Å.); 22.0° (4047), 32.5° (4358), 40.0° (4916), 44.0° (5461), 45.5° (5780), 46.5° (6234), 48.0° (6908), {001}, all ± 0.5°. These data are given in Fig. 6. Figure 7 shows the interference figures of thiourea for different wave lengths.
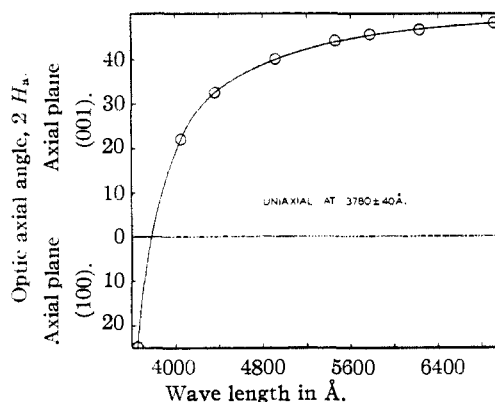

Fig. 6.—Crossed axial plane dispersion in thiourea.

Groth[19] gives 2 E values by Hintze for the wave lengths 5893 and 6708 Å. These data calculated to 2 H_a yield 45° and 46°, respectively, in fair agreement with the above results.

The refractive indices and corresponding bire-

(16) Groth, Vol. V, p. 200.
(17) Private communication. Dr. Jelley has very kindly permitted the writer to quote these data. The birefringences were obtained by the new and precise "method of lens crystals" (vide ref. 6) and the wave length of isotropy was from an interference micro-spectrogram.

(18) Z. Krist. Strukturbericht., 1913–1928, p. 727.
(19) Groth, Vol. III, p. 555.
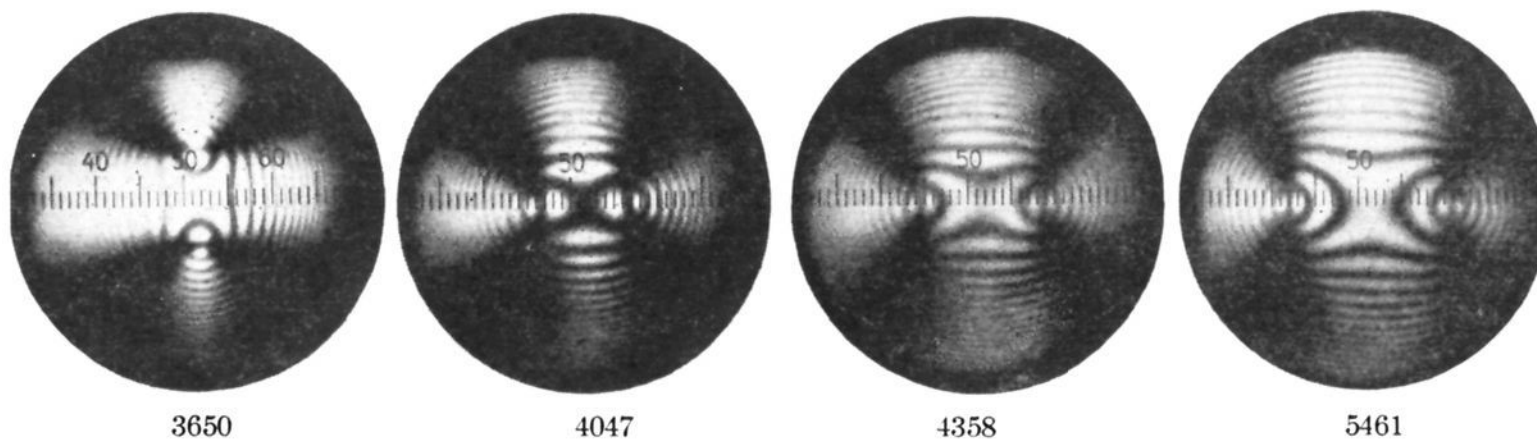
3650   4047   4358   5461

Fig. 7.—Interference figures of thiourea in monochromatic light (crossed axial plane dispersion in the ultraviolet); wave length of light in Å.

fringences at $25 \pm 3°$ and $\lambda = 5461$ Å. are: $\alpha = 1.634 \pm 0.003$; $\beta = 1.789 \pm 0.005$; $\gamma = 1.806 \pm 0.005$; $\beta - \alpha = 0.155$; $\gamma - \beta = 0.017$; $\gamma - \alpha = 0.172$. Thiourea is optically negative, with the following orientation based on the data given in Groth: ax. pl. = $\{001\}$ (above 3780 Å.); = $\{100\}$ (below 3780 Å.); $Bx_a = \alpha = b$. It is orthorhombic with the space group $D_{2h}^{16} - Pnma$.[20]

Discussion

While it is true that strong dispersion of the optic axes and indicatrix axes occurs most frequently in substances made up of planar molecules, the exact nature and the amount of dispersion present are affected by small details of structure, and are not readily predictable, hence a property of this type has greater value for precise characterization than more commonly used optical properties such as refractive index or birefringence. In the author's experience identification of specific members of organic homologous series is accomplished more readily by properties that vary in a discontinuous or irrational manner through the series. This is true because differences in type of dispersion can be detected even where the effects are too small for precise measurement. At least seven distinct types of dispersion in interference figures can be recognized qualitatively, and can be placed on a quantitative basis where their intensity warrants it.

While there are few references to previous quantitative studies of the property the writer has called *axial dispersion with change of sign*, it appears that the existence of this obscure type of dispersion in certain minerals has been conceded on the basis of qualitative observations. A number of minerals have an optic axial angle $2 V$ of approximately $90°$ and at the same time strong

dispersion of the optic axes, and would therefore be expected to have this property.[21]

The extreme dispersion often associated with organic planar ring structures greatly increases the probability that this particular type of dispersion will occur. The intersection of the curves of the two optic axial angles, $2 H$, plotted against wave length indicates its presence and the particular wave length at which coincidence occurs may be called the *wave length of optical neutrality*, a useful subcriterion analogous to the wave length of uniaxiality in crossed axial plane dispersion. Symmetry considerations indicate that this type of dispersion, like crossed axial plane dispersion, may be present in the orthorhombic or in any lower symmetry classes.

The type of dispersion present in benzil has received much more attention than the frequency of its occurrence would suggest. The principal inorganic examples are members of the apophyllite[22] and gehlenite[23] groups of minerals, and the mix-crystal system: strontium and lead dithionates.[24] Here the optical character of a uniaxial material is altered by an interchange of the relative magnitudes of the ϵ and ω refractive indices. The approximate region of the spectrum at which this change occurs can be ascertained qualitatively in white light by observing the abnormal sequence of colors in the isochromatic curves of the interference figure. Ambronn has included some very fine color reproductions of this effect in his work on the dithionates. However, curves of the refractive indices and bire-

(20) *Z. Krist.* Strukturbericht., Vol. III, 1928–1932, p. 882.

(21) The writer is indebted to Dr. F. E. Wright of the Geophysical Laboratory in Washington, D. C., for the following list of minerals selected from Larsen and Berman, "The Microscopic Determination of the Nonopaque Minerals" (2nd ed., Geological Survey Bulletin 848, Washington, D. C. (1934)) in which change of sign should occur: Tellurite, Olivenite, Adamite, Tilleyite and Massicotite.

(22) Klein, *Sitz. preuss. Akad. Wiss.*, **18**, 217 (1892).

(23) Weinschenk, *Z. Krist.*, **27**, 577 (1896).

(24) Ambronn, *ibid.*, **52**, 48 (1912).

fringence form a more satisfactory basis for quantitative study. The wave length of isotropy (at which $\epsilon = \omega$) is an important fixed point on the birefringence–wave length curve.

Crossed axial plane dispersion in the near ultraviolet can be detected and measured photographically provided the wave length of uniaxiality is longer than that of the ultraviolet cut-off of the microscope system used. Thiourea becomes uniaxial at 3780 Å. and hence is a good experimental subject. Most organic substances have absorption bands in the ultraviolet and all types of dispersion tend to be intensified as these bands are approached from the high wave length side. For this reason many substances may have strong measurable dispersion in the visible violet or ultraviolet but very little in the balance of the visible spectrum. In such cases the dispersion may acquire sudden prominence over a relatively short wave length interval as illustrated by the sudden appearance of crossed dispersion in stilbene.

Summary

1. The dispersion of the optic axial angle in *trans*-stilbene has been measured. This substance is optically positive for wave lengths above 4070 Å. and optically negative for shorter wave lengths. The rare type of dispersion giving rise to this effect has tentatively been called *axial dispersion with change of sign*. Strong crossed dispersion is also present.

2. Dispersion of the refractive indices α, β, and γ in stilbene has been determined by Merwin's method.

3. The refractive indices ϵ and ω of benzil were measured over a wide range of wave lengths. As shown by Jelley, this substance is optically isotropic at 4205 Å., optically positive above, and negative below this wave length.

4. The optical properties of thiourea have been measured. This compound exhibits crossed axial plane dispersion near 3780 Å. in the ultraviolet.

[COMMUNICATION NO. 878 FROM THE KODAK RESEARCH LABORATORIES]

# The Inversion of Menthone with Trichloroacetic Acid in Aprotic Solvents

BY A. WEISSBERGER

The reaction of diazoacetic ester with trichloroacetic acid in hexane yielding the trichloroaceto-glycolic ester, $CCl_3CO_2CH_2CO_2C_2H_5$, proceeds through a reactive complex composed of one molecule of the ester and two molecules of the acid.[1,2] The reaction is slowed down considerably by the addition of certain substances like ethers, ketones and alcohols.[2] This effect was attributed to the formation of compounds of the addenda with the acid, and a spectroscopic study of the salt formation of dimethylaminoazobenzene and trichloroacetic acid in benzene[3] corroborated this interpretation. Parallel with these investigations was studied the inversion of menthone.[4] This reaction also can be measured in aprotic solvents, but it differs from the decomposition of diazoacetic ester in some respects. In the latter reaction, carried out in aprotic solvents, the acid becomes part of the reaction product, *i. e.*, it "catalyzes its own reaction,"[5] while in the menthone inversion the reaction product is a stereoisomer of the starting material. It was, therefore, of interest to see whether the reactive complex in the menthone inversion is simpler than in the diazoester decomposition, and to investigate whether addenda have the same or a different effect in both processes. The investigation of the menthone inversion itself is reported in the following.

Menthone, 1-methyl-4-isopropyl-cyclohexane-3-one, has two asymmetric carbon atoms and exists in four optically active isomers. The two pairs of antipodes differ from one another by geometrical isomerism

Menthone   Isomenthone
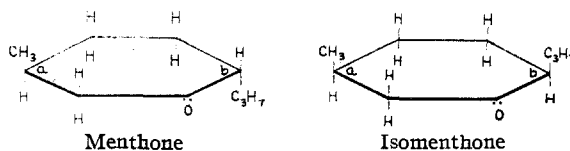
The *trans* formulas are attributed to menthone,

(1) Brönsted and Bell, THIS JOURNAL, **53**, 2478 (1931).

(2) Weissberger and Högen, Z. physik. Chem., **A156**, 321 (1931).

(3) Weissberger and Fasold, ibid., **A157**, 65 (1931).

(4) Wonneberger. Dissertation, Leipzig, 1930; Dörken. Dissertation, Leipzig, 1934.

(5) Bell, "Acid–Base Catalysis," Oxford University Press, New York, N. Y., 1941.