

Optical Rotatory Power. Part IV: Rotatory Dispersion of Bornyl and Menthyl Xanthates, Especially in the Region of Absorption

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V. *Optical Rotatory Power. Part IV.—Rotatory Dispersion of Bornyl and Menthyl Xanthates, especially in the Region of Absorption.*

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A.—INTRODUCTORY.

1. *Rotatory Dispersion.*

During a period of over 20 years, investigations have been carried out by one of us with a view to determining the form of the curve of rotatory dispersion, *e.g.*, in the cases of quartz* and of a large number of typical organic compounds.† These measurements were always made within the range of wave-lengths for which the medium under examination was completely transparent, since only under these conditions could the precision of the measurements be raised to a maximum by increasing the concentration of the optically-active compound and the length of the column traversed in the polarimeter. The general result has been to prove that the equation $\alpha = \Sigma \frac{k_n}{\lambda^2 - \lambda_n^2}$, by which DRUDE in 1899 proposed to represent the optical rotatory power of transparent media, can be used to express the rotatory dispersion of compounds of every available type, up to the limits set by the experimental errors and by the range of transparency of the medium. Thus, crucial experiments, in which every effort was made to secure a maximum of experimental accuracy, have shown that in this region it is possible to express the “normal” rotatory dispersion of octyl alcohol by a single term of DRUDE’s equation,‡ whilst the “anomalous” rotatory dispersion of ethyl tartrate can be expressed with equal accuracy by two terms of opposite sign.§ Only for quartz has the introduction of a fifth constant been found necessary|| in order to express the data up to the limit set by the experimental errors. It is therefore clear that *in the region of complete transparency* each partial rotation is a hyperbolic function of α and λ^2 , tending asymptotically towards an infinite value of α when the value of λ corresponds to a characteristic frequency of the medium.

This frequency would be expected to correspond to the “head” of an absorption-band, *i.e.*, to a maximum of selective absorption by the medium; but in nearly every

* LOWRY, ‘Phil. Trans.’ A, vol. 212, p. 261 (1912); LOWRY and COODE-ADAMS, *ibid.*, vol. 226, p. 391 (1927); LOWRY and SNOW, ‘Proc. Roy. Soc.’ A, vol. 127, p. 271 (1930).

† LOWRY, ‘Trans. Chem. Soc.’ vol. 103, p. 1062 (1913), *et seq.*

‡ LOWRY and RICHARDS, ‘Trans. Chem. Soc.’ vol. 125, p. 1593 (1924).

§ LOWRY and CUTTER, ‘Trans. Chem. Soc.’ vol. 121, p. 532 (1922).

|| LOWRY and COODE-ADAMS, ‘Phil Trans.’ A, vol. 226, p. 391 (1927).

case which has been examined hitherto, a definite divergence has been found between the frequency deduced from observations of optical rotatory dispersion and the observed frequency of the head of the band,* when this is accessible to direct observation. This divergence may be due to the fact that accessible absorption bands are only observed in unsaturated compounds, which necessarily possess also a characteristic absorption in the Schumann region, so that some mutual influence between them may be expected; but in the derivatives of camphor it can be attributed to the composite character of the absorption band, the optical activity of which is concentrated in a part of the band nearest to the visible spectrum.†

In order to obtain further information in reference to the relation between absorption and rotatory dispersion, experiments were undertaken some years ago with Mr. GLYN OWEN, in order to extend the measurements of rotatory dispersion into the region of absorption, and thus to determine the form of the dispersion curve which is associated with the COTTON phenomenon. The choice of suitable compounds for this purpose is of primary importance, since the observed rotations are often reduced to immeasurably small values (as with nicotine) when the solution is diluted to a sufficient extent to allow of the transmission of light in the region of maximum absorption. Since it was essential that the absorption bands should be readily accessible, experiments were begun with the optically active xanthates, prepared and studied by TSCHUGAEFF,‡ but the work was interrupted before it was possible either to complete the measurements or to make an analysis of the form of the curves.

2. Circular Dichroism.

In the meanwhile, the problem was attacked from the physical side by KUHN,§ who made an important advance by including the measurement of circular dichroism within the range of his experimental observations. This property, which is a measure of the difference of the *molecular extinction-coefficients*, ε_r and ε_l , of the medium for right and left circularly polarized light, does not directly determine the optical rotatory power of the medium, which depends (as FRESNEL showed) on the difference of the *refractive indices* n_r and n_l for right and left circularly polarized light; but it is to be expected that the rotatory dispersion of the medium will be related to its circular dichroism in

* LOWRY and RICHARDS, 'J. Chem. Soc.,' vol. 125, p. 2521 (1924); LOWRY and CUTTER, *ibid.*, vol. 127, p. 611, (1925); CUTTER, BURGESS and LOWRY, *ibid.*, p. 1266; RICHARDS and LOWRY, *ibid.*, p. 1507; LOWRY and LLOYD, *ibid.*, p. 1775 (1929); LOWRY and ALLSOPP, *ibid.*, p. 1613 (1932).

† KUHN and GORE, 'Z. phys. Chem.,' B, vol. 12, p. 389 (1931); LOWRY and FRENCH, 'J. Chem. Soc.,' p. 2654 (1932); see also WEDENEWA, 'Ann. Physik,' vol. 72, p. 122 (1923), on camphorquinone.

‡ 'J. Russ. Phys. Chem. Soc.,' vol. 35, p. 1116 (1903), and vol. 36, p. 988 (1904).

§ KUHN, 'Z. phys. Chem.,' B, vol. 4, p. 14 (1929); 'Trans. Faraday Soc.,' vol. 26, p. 293 (1930); KUHN and BRAUN, 'Z. phys. Chem.,' B, vol. 8, pp. 281, 445 (1930); KUHN and LEHMANN, 'Z. Electrochem.,' vol. 37, p. 549 (1931); KUHN and SZABO, 'Z. phys. Chem.,' B, vol. 15, p. 59 (1931).

just the same way as the refractive dispersion of the medium is related to its power of absorbing unpolarized light of suitable frequency. If, therefore, the circular dichroism of a medium be known, its *rotatory dispersion* may be predicted from the position of the maximum and the magnitude of the half-width of the band of circular dichroism, with the help of similar formulæ to those which are used to predict the *refractive dispersion* of a medium from the position of the maximum and the magnitude of the half-width of its absorption bands. Since, however, there are very few cases in which the circular dichroism of a medium is known (and there are very many cases in which it cannot at present be measured), it is often necessary to assume that the circular dichroism and the absorption of unpolarized light are proportional to one another, and to correlate the rotatory dispersion of the medium with its ordinary absorption, or, in other words, to assume that the wave-length of maximum absorption and the "half-width" of the band are the same for the absorption ε of unpolarized light and for the *difference*, $\varepsilon_r \sim \varepsilon_l$, between the absorptions of circularly polarized light of opposite signs. Justification for this procedure can be found in KUHN's experiments, which show that the ratio of these two quantities* is often approximately constant for a given absorption band, or more accurately is proportional to the frequency of the light. In the xanthates, however, the circular dichroism of two adjacent absorption bands is of opposite sign, so that the curve cuts the axis of wave-lengths, whilst the two maxima of absorption are necessarily on the same side of the axis.

3. *Correlation of Absorption and Dispersion.*

Quantitative relations between absorption and dispersion were first suggested by MAXWELL in 1869† and worked out by SELLMEIER‡ in 1872. They were extended into the region of absorption in 1875 by HELMHOLTZ,§ whose equations were modified by KETTELER|| to a form which is in harmony with the electro-magnetic theory of light. The corresponding equations for rotatory dispersion in the region of transparency were given in 1893 by DRUDE,¶ who in 1906** extended them into the region of absorption by re-introducing a "frictional" term, which had been neglected in the simplified equation cited above. DRUDE's equation then showed a difference (which had been discovered

* The ratio, $g = (\varepsilon_r \sim \varepsilon_l)/\varepsilon$, was described by KUHN as the "anisotropy factor"; but this term is definitely incorrect when applied to media which are not "anisotropic" but "dissymmetrically isotropic," (DRUDE, "Lehrbuch der Optik," p. 401, 1900). In the present paper, therefore, we have described this ratio as the "dissymmetry factor," since it is the dissymmetry of the medium and not its isotropy or anisotropy, which gives rise to circular dichroism, circular double refraction and optical rotatory power.

† 'Math. Trip.' (1869).

‡ 'Ann. Phys. Chem.,' vol. 145, pp. 399, 520 (1872); vol. 147, pp. 386, 525 (1872).

§ 'Ann. Phys. Chem.,' vol. 154, p. 582 (1875).

|| 'Phil. Mag.,' vol. 2, pp. 332, 414, 508 (1876). 'Ann. Phys. Chem.,' vol. 160, p. 466 (1877); vol. 7, p. 658 (1879); vol. 12, p. 481 (1881).

¶ 'Wied. Ann.,' vol. 48, p. 536 (1893).

** "Theory of Optics," English trans., pp. 415-417 (1907).

experimentally by COTTON* in 1896) in the absorption coefficients for left and right circularly polarized light, but his expression for rotatory dispersion was not in a form which could be applied directly to the experimental data. In 1908, however, NATANSON† developed a formula for rotatory dispersion which bears the same relation to DRUDE's simplified formula as the KETTELER-HELMHOLTZ formula for refractive dispersion bears to that of SELLMEIER.

In 1929, KUHN deduced an equation of similar form to NATANSON's by making use of a system of dissymmetrically coupled vibrators.‡ He tested this equation by calculating, with the help of a single arbitrary parameter, the partial rotations due to a particular absorption band. On subtracting these from the observed total rotations he obtained a curve of differences to represent the residual partial rotations due to bands in the SCHUMANN region. The curve of differences was quasi-hyperbolic, and the validity of the analysis was tested by the extent to which the loop, which is such a conspicuous feature of the curves of rotatory dispersion in the region covered by the absorption band, was eliminated.

Subsequent investigations by KUHN and BRAUN§ showed that this elimination was far from complete, since the curves of differences included two "shoulders," which could not be got rid of by any re-adjustment of the constants of the equation. This discrepancy was attributed to the fact that the hypothesis of "damped" vibrators is not applicable to the broad absorption bands of a liquid. The absorption curves based on this hypothesis show two non-existent shoulders, one on either side of the head of the band, and these are reproduced in the curves of rotatory dispersion deduced by means of this absorption-law.

Absorption curves which show a much closer resemblance to those observed experimentally can be deduced, as BIELECKI and HENRI|| have shown, by using an exponential formula to express the distribution of frequencies amongst the various vibrators. When, therefore, KUHN and BRAUN developed an equation based on a Maxwellian distribution of frequencies, they were able to eliminate almost completely the sinuosities from their curves of anomalous rotatory dispersion.

4. *Application to the Xanthates.*

In the work described below, KUHN and BRAUN's method of analysis has been applied in a modified form to the bornyl and menthyl xanthates. Independent evidence has been

* 'Ann. Chim. Phys.,' vol. 8, p. 347 (1896).

† 'Acad. Sci. Cracow,' Bull. No. 8, pp. 764-783, Oct., 1908; 'J. de Physique,' vol. 8, p. 321 (1909).

‡ 'Z. phys. Chem.,' B, vol. 4, p. 14 (1929); 'Trans. Faraday Soc.,' vol. 26, p. 293 (1930); compare BORN, 'Phys. Z.,' vol. 16, p. 251 (1915). 'Ann. Physik,' vol. 55, p. 177 (1918); OSEEN, 'Ann. Physik,' vol. 48, p. 1 (1915); LANDÉ, 'Ann. Physik,' vol. 56, p. 225 (1918); GANS, 'Z. Physik,' vol. 17, p. 353 (1923); vol. 27, p. 164 (1924); 'Ann. Physik,' vol. 79, p. 548 (1926); ROSENFELD, 'Z. Physik,' vol. 52, p. 161 (1928).

§ 'Z. phys. Chem.,' B, vol. 8, p. 281 (1930).

|| 'Phys. Z.,' vol. 14, p. 516 (1913).

obtained of the inadequacy of the HELMHOLTZ type of equation, as deduced by NATANSON and tested by KUHN, since our curves of differences, when calculated on this basis, again include two conspicuous humps in the region of absorption. On the other hand, the general validity of the Maxwellian distribution of frequencies has been established by a detailed study of the form of the absorption curves, although the equation of BIELECKI and HENRI does not agree exactly with our experimental data. A corresponding improvement in the analysis of the curves of rotatory dispersion was effected by using KUHN and BRAUN's equation instead of NATANSON's as a means of segregating the rotations due to the nearest absorption band. Their equations, however, do not represent accurately the form either of the absorption bands or of the curves of rotatory dispersion of our xanthates. We were therefore led to develop modified equations for this purpose. These equations represent the molecular extinction coefficients of the xanthates with an accuracy almost within the limits of experimental error, and give rise to difference curves which fall short of normal curves only in showing slight ripples within the region covered by the absorption band.

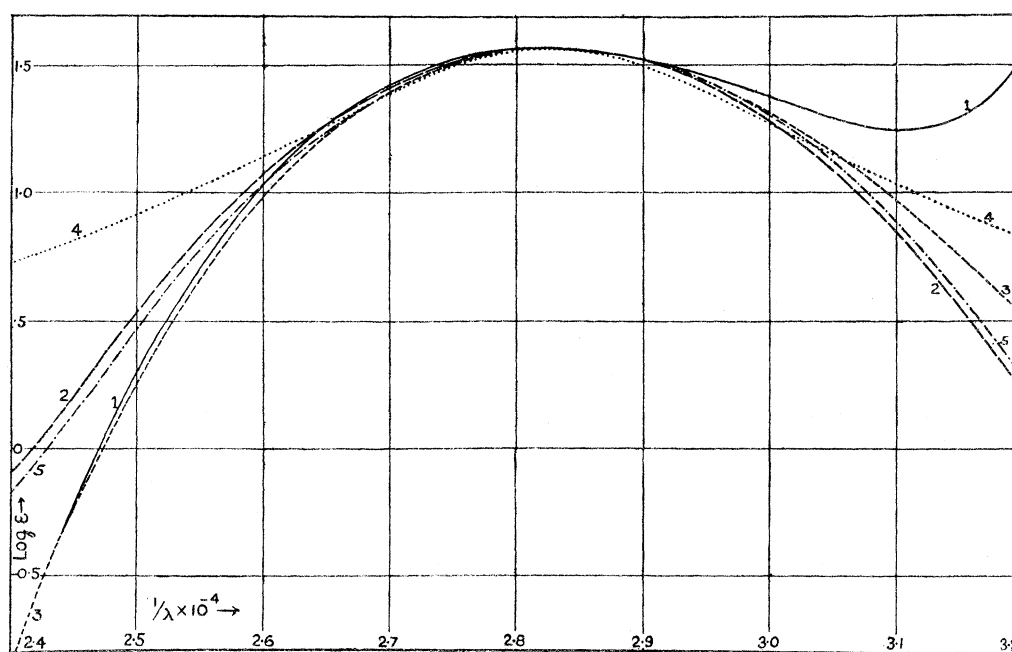


FIG. 1.—Analysis of first absorption band of methyl *d*-bornyl xanthate.

1. ——— Experimental curve; 2. — — — Curve calculated from equation (ii) of KUHN and BRAUN.
 3. - - - - Curve calculated from our equation (iv) $\epsilon = \epsilon_{\max} \cdot e^{-\left[\frac{\nu_0}{\nu} \left(\frac{\nu_0 - \nu}{\theta}\right)\right]^2}$; 4. Curve calculated from KETTELER-HELMHOLTZ equation (i); 5. - · - · - Curve calculated from equation (iii) of BIELECKI and HENRI.

The principal feature of our new equations consists in the fact that they represent the absorption curves as being symmetrical on a scale of *wave-lengths*. The equations of KUHN and BRAUN, on the other hand, postulate a symmetrical distribution of *frequencies*, whilst the equation of BIELECKI and HENRI is of an intermediate type. Our adoption

of the hypothesis of a symmetrical distribution of wave-lengths was based exclusively on experiment, since the curves reproduced in figs. 2 to 10 are clearly of this type. Other absorption curves which have been plotted in this laboratory and elsewhere (*e.g.*,

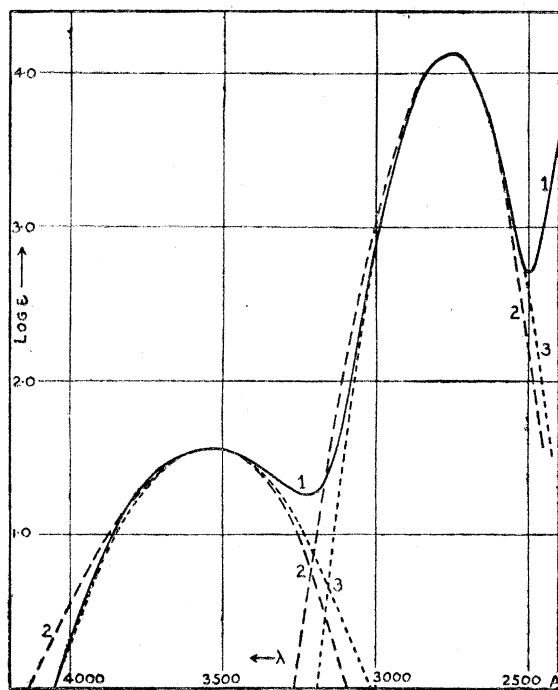


FIG. 2.—Molecular extinction coefficients of methyl *d*-bornyl xanthate.

1 = Experimental curve ; 2 = Theoretical curve calculated from KUHN and BRAUN's equation (ii) ; 3 = Theoretical curve calculated from our equation (iv).

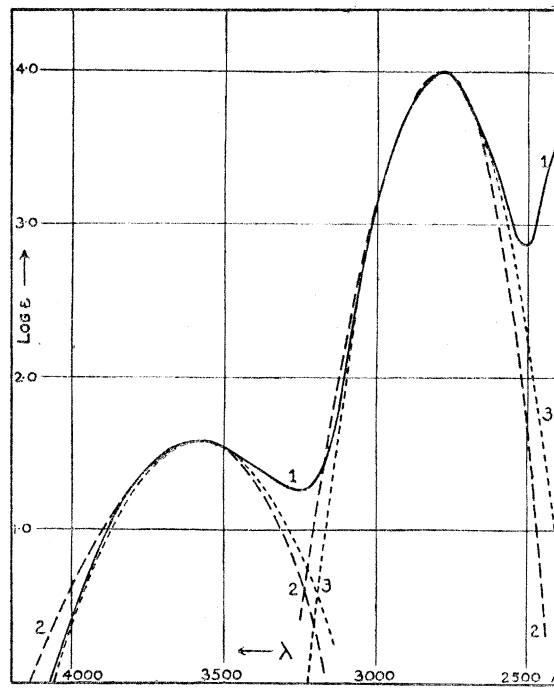


FIG. 3.—Molecular extinction coefficients of ethyl *d*-bornyl xanthate.

1 = Experimental curve ; 2 = Theoretical curve calculated from equation (ii) ; 3 = Theoretical curve calculated from equation (iv).

the curves for nicotine and its derivatives*) are obviously unsymmetrical ; but they are invariably steeper on the side of longer wave-lengths. It has often been supposed that these unsymmetrical curves may be caused by a superposition of two or more symmetrical bands ;† but the phenomenon is far too general to be treated as an anomaly, and we prefer to think that our symmetrical curves may perhaps represent a limiting form which is reached only in extreme cases. On the other hand, the equations of KUHN and BRAUN, and of BIELECKI and HENRI, lead to absorption curves of a type which we have not yet recognized amongst any of the organic compounds which we have examined, in that they are steeper on the side of shorter wave-lengths.‡

* LOWRY and LLOYD, 'J. Chem. Soc.', p. 1376 (1929) ; LOWRY and GORE, 'J. Chem. Soc.', p. 319 (1931).

† BRUHAT and PAUTHENIER, 'Ann. Physique,' vol. 5, p. 440 (1926).

‡ Curves of this type have, however, been recorded for the absorption by van der Waals' molecules, *e.g.*, in compressed xenon (McLENNAN and TURNBULL, 'Proc. Roy. Soc.' A, vol. 129, p. 266 (1930). See also WINANS, 'Phil. Mag.', vol. 7, p. 555 (1929) ; OLDENBURG, 'Z. Physik,' vol. 55, p. 1 (1929) ; FRANCK, 'Naturwiss.' vol. 19, p. 217 (1931).

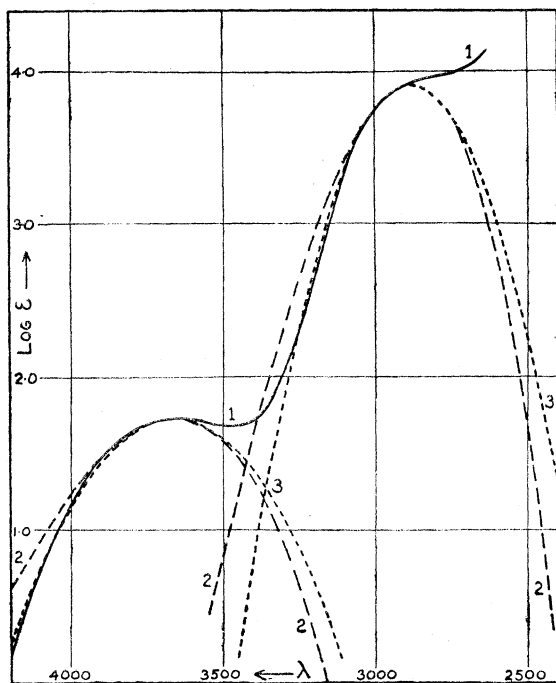


FIG. 4.—Molecular extinction coefficients of *d*-bornyl dixanthogenide.

1 = Experimental curve; 2 = Theoretical curve calculated from equation (ii); 3 = Theoretical curve calculated from equation (iv).

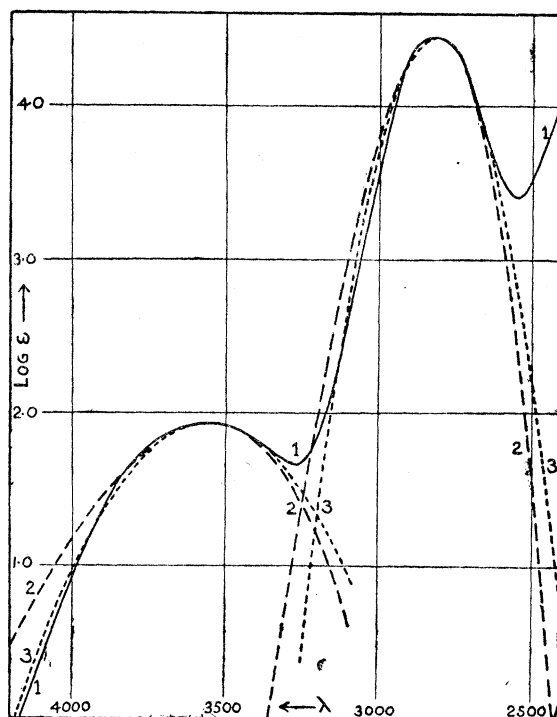


FIG. 5.—Molecular extinction coefficients of methylene *d*-bornyl xanthate.

1 = Experimental curve; 2 = Theoretical curve calculated from equation (ii); 3 = Theoretical curve calculated from equation (iv).

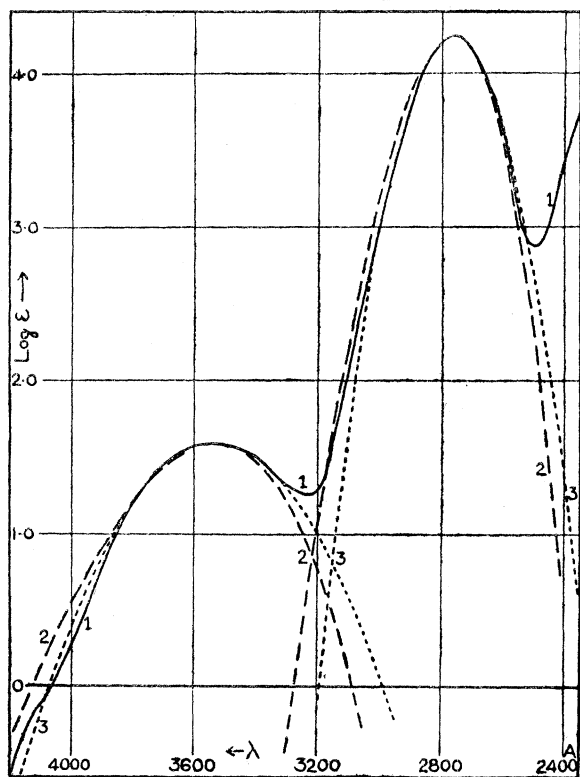


FIG. 6.—Molecular extinction coefficients of methyl *l*-menthyl xanthate.

1 = Experimental curve; 2 = Theoretical curve calculated from equation (ii); 3 = Theoretical curve calculated from equation (iv).

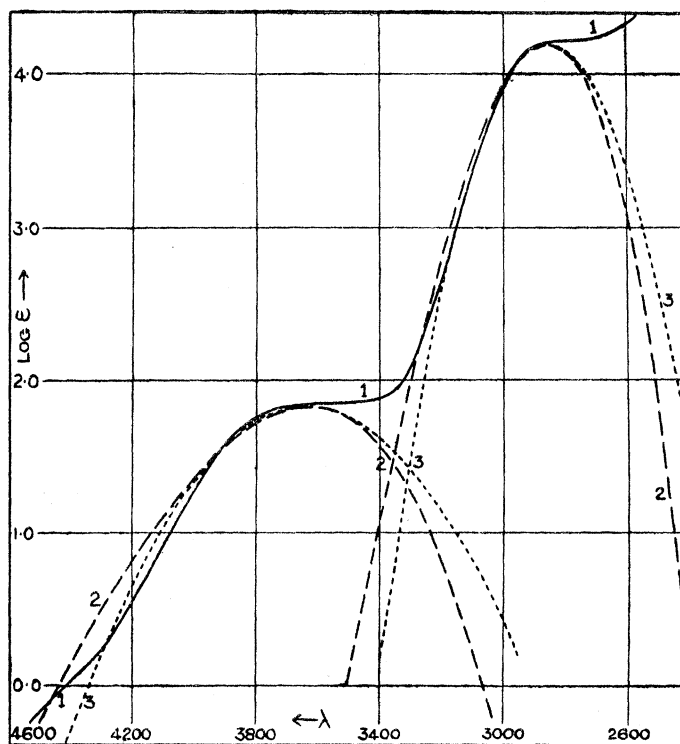


FIG. 7.—Molecular extinction coefficients of *l*-menthyl dixanthogenide.

1 = Experimental curve; 2 = Theoretical curve calculated from equation (ii); 3 = Theoretical curve calculated from equation (iv).

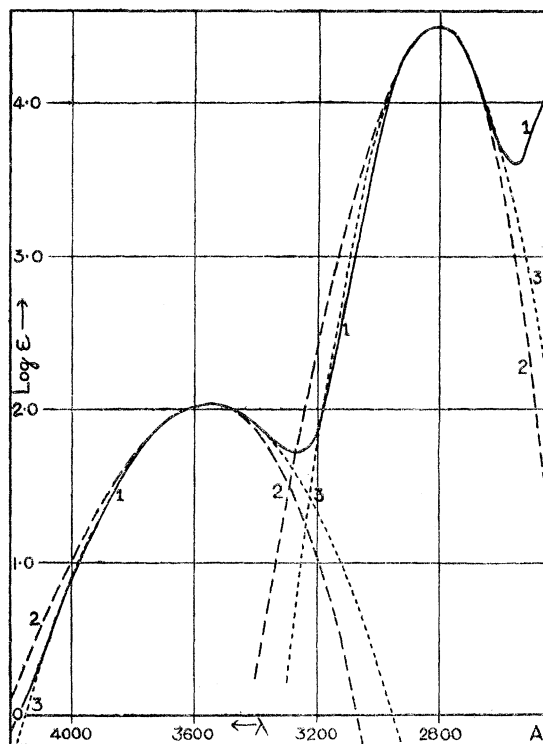


FIG. 8.—Molecular extinction coefficients of methylene *l*-menthyl xanthate.

1 = Experimental curve ; 2 = Theoretical curve calculated from equation (ii) ; 3 = Theoretical curve calculated from equation (iv).

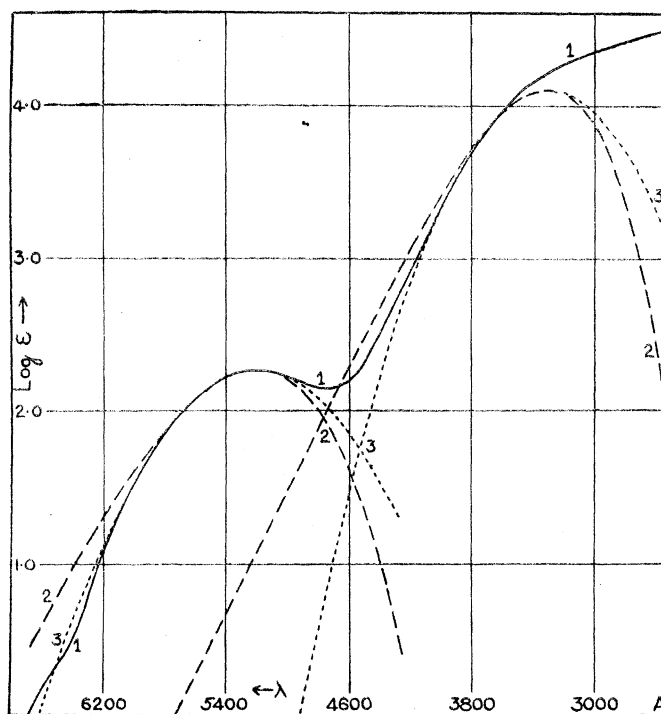


FIG. 9.—Molecular extinction coefficients of diphenyl *d*-bornyl dithiourethane.

1 = Experimental curve ; 2 = Theoretical curve calculated from equation (ii) ; 3 = Theoretical curve calculated from equation (iv).

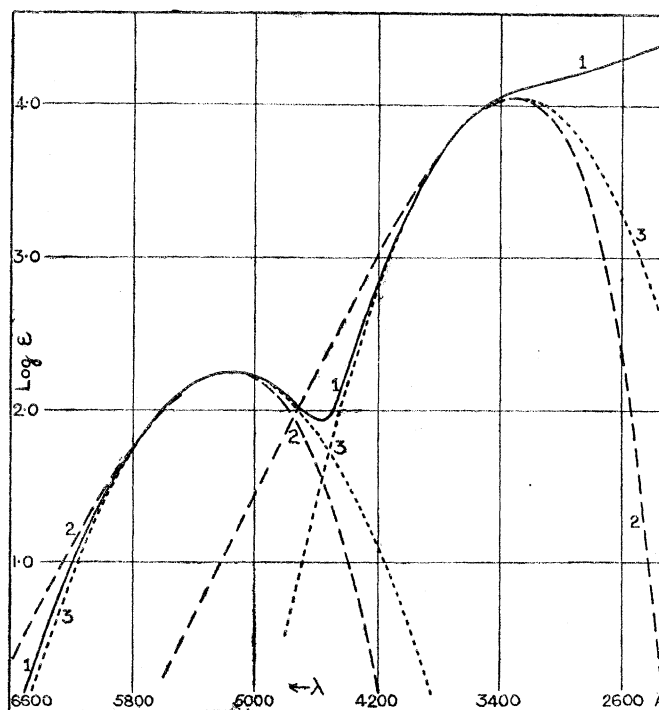


FIG. 10.—Molecular extinction coefficients of diphenyl *l*-menthyl dithiourethane.

1 = Experimental curve ; 2 = Theoretical curve calculated from equation (ii) ; 3 = Theoretical curve calculated from equation (iv).

B.—EXPERIMENTAL METHODS.

5. *Materials.*

The nine compounds used in the present investigation are set out in Table I.

TABLE I.

Substance.	Formula.	Melting-point.
		°C.
I.—Methyl <i>d</i> -bornyl xanthate	$C_{10}H_{17}O \cdot CS \cdot S \cdot CH_3$	57
II.—Ethyl <i>d</i> -bornyl xanthate	$C_{10}H_{17}O \cdot CS \cdot S \cdot C_2H_5$	52
III.— <i>d</i> -Bornyl dioxanthogenide	$C_{10}H_{17}O \cdot CS \cdot S \cdot S \cdot CS \cdot O \cdot C_{10}H_{17}$	82.5
IV.—Methylene <i>d</i> -bornyl xanthate	$C_{10}H_{17}O \cdot CS \cdot S \cdot CH_2 \cdot S \cdot CS \cdot O \cdot C_{10}H_{17}$	108
V.—Methyl <i>l</i> -menthyl xanthate	$C_{10}H_{19}O \cdot CS \cdot S \cdot CH_3$	39
VI.— <i>l</i> -Menthyl dioxanthogenide	$C_{10}H_{19}O \cdot CS \cdot S \cdot S \cdot CS \cdot O \cdot C_{10}H_{19}$	93
VII.—Methylene <i>l</i> -menthyl xanthate	$C_{10}H_{19}O \cdot CS \cdot S \cdot CH_2 \cdot S \cdot CS \cdot O \cdot C_{10}H_{19}$	137
VIII.—Diphenyl <i>d</i> -bornyl dithiourethane	$C_{10}H_{17}O \cdot CS \cdot N(C_6H_5) \cdot CS \cdot C_6H_5$	87
IX.—Diphenyl <i>l</i> -menthyl dithiourethane	$C_{10}H_{19}O \cdot CS \cdot N(C_6H_5) \cdot CS \cdot C_6H_5$	106

They were prepared by the method of TSCHUGAEFF,* and were purified by repeated recrystallization from mixtures of ether and alcohol until the melting-points were sharp and constant.

The seven xanthates are colourless or pale yellow, but they exhibit anomalous rotatory dispersion, in the same way as the tartaric esters. They differ, however, from these esters in showing two strong ultra-violet absorption bands at 3600 and 2800 Å. (approx.), instead of a weak general absorption. The dithiourethanes are of a bright red colour, but their optical properties are very similar to those of the xanthates, from which they differ mainly in the fact that the absorption bands are displaced in the direction of longer wave-lengths to 5200 and 3300 Å. (approx.), respectively.

The strongest ultra-violet absorption band of the xanthates is at 2800 Å. (approx.). It may be attributed provisionally to the $>C=S$ group, since PURVIS, JONES and TASKER† and HANTZSCH and SCHARF‡ found a strong band between 2750 and 3050 Å. in a number of thion-, thionthio- and trithio-carbonates, all of which contain the $>C=S$ group. The much weaker band at 3600 Å. (approx.) (which was not recorded by TSCHUGAEFF§) may be attributed to the group $-S \cdot CS-$, since HANTZSCH and SCHARF found a weak band of similar wave-length (3509 Å.) in diethyl thionthiocarbonate, $C_2H_5 \cdot O \cdot CS \cdot S \cdot C_2H_5$, but not in diethyl thioncarbonate,



* 'Ber. deuts. chem. Ges.,' vol. 35, p. 2470 (1902); 'J. Russ. Phys. Chem. Soc.,' vol. 35, p. 1116 (1903); vol. 36, p. 988 (1904).

† 'J. Chem. Soc.,' vol. 97, p. 2287 (1910).

‡ 'Ber. deuts. chem. Ges.,' vol. 46, p. 3570 (1913).

§ TSCHUGAEFF and OGORODNIKOFF, 'Z. phys. Chem.,' vol. 85, p. 481 (1913).

PURVIS, JONES and TASKER do not record any band in this region for diethyl thionthio- and trithio-carbonates, both of which contain the group $-\text{S} \cdot \text{CS}-$, but this may be merely because they worked with solutions which were too dilute.

A band of still longer wave-length was detected by HANTZSCH and SCHARF at 4082 Å. in ethyl xanthogenic thioanhydride, $\text{C}_2\text{H}_5 \cdot \text{O} \cdot \text{CS} \cdot \text{S} \cdot \text{CS} \cdot \text{O} \cdot \text{C}_2\text{H}_5$, and may be attributed to the group $-\text{CS} \cdot \text{S} \cdot \text{CS}-$. In the same way, the band at 5200 Å. (approx.), which gives rise to the red colour of the dithiourethanes, may be attributed to the $-\text{CS} \cdot \text{NR} \cdot \text{CS}-$ group.* In each of these cases the group which gives rise to visible colour contains *two* $>\text{C}=\text{S}$ groups, separated by an atom of variable valency.

These chromophoric groups do not usually exhibit optical activity; but they become optically-active in the dissymmetric field of the bornyl or menthyl radical, and therefore exhibit the phenomenon of "induced dissymmetry."†

The solvent used throughout this series of measurements was cyclohexane. It was purified by shaking repeatedly with fresh portions of 14 per cent. oleum, washing with water to which calcium carbonate was added, and distilling twice from lime and from fused calcium chloride in an all-glass apparatus. It was then fractionally crystallized until the freezing-point was constant at about 6° C.

6. *Methods of Measurement.*

(a) The methods used for the measurement of *optical rotatory power* in the visible and ultra-violet regions of the spectrum have already been described in earlier papers of this series.‡ The rotatory power of each compound was determined for about 20 lines in the visible and (by a photographic method) for at least an equal number of lines in the ultra-violet region. The measurements were carried right through the first absorption band to a point where further readings were rendered impossible by the growing intensity of the second absorption band.

(b) The *molecular extinction coefficients* of the xanthates were measured over a range of wave-lengths from 4200 to 2300 Å., and those of the dithiourethanes from 6500 to 2300 Å. (approx.) by means of a BELLINGHAM and STANLEY spectrophotometer.

(c) The *circular dichroism* of each compound in the first absorption band was measured by the method of KUHN and BRAUN,§ but using a FRESNEL rhomb of uviol glass. The circular dichroism in the second absorption band could not be measured, on account of

* TSCHUGAEFF, 'Ber. deuts. chem. Ges.,' vol. 35, p. 2470 (1902), formulated these compounds as iminoxanthogenides, $\text{R} \cdot \text{C} (: \text{NR}) \cdot \text{S} \cdot \text{CS} \cdot \text{OR}'$, and attributed their colour to the chromophoric group $-\text{CS} \cdot \text{S} \cdot \text{C} : \text{N}-$; the dithiourethane structure, $\text{R} \cdot \text{CS} \cdot \text{NR} \cdot \text{CS} \cdot \text{OR}'$, was established by JAMIESON ('Chem. Zbl.,' p. 1002 (1904, i)).

† LOWRY and WALKER, 'Nature,' vol. 113, p. 565 (1924); LOWRY, 'Nature,' vol. 131, p. 563 (1933).

‡ LOWRY, 'Phil. Trans.,' A, vol. 212, p. 261 (1912); LOWRY and AUSTIN, *ibid.*, vol. 222, p. 249 (1922); LOWRY and COODE-ADAMS, *ibid.*, vol. 226, p. 391 (1927).

§ 'Z. phys. Chem.,' B, vol. 8, p. 445 (1930).

the much greater intensity of the absorption. The circular dichroism of the first band was, however, complicated by the overlapping of the opposite circular dichroism of the second band.

C.—ABSORPTION.

7. *Experimental Results.*

The molecular extinction-coefficients of seven xanthates and two dithiourethanes are represented graphically as curve 1 in figs. 2 to 10, whilst the first absorption band of methyl *d*-bornyl xanthate is shown on a larger scale as curve 1 in fig. 1. The numbers from which these curves are plotted have been tabulated, but are not reproduced in the present paper.

- (i) Methyl, ethyl and methylene *d*-bornyl and *l*-menthyl xanthates each show two absorption bands, of which the first, at 3550 Å. (approx.), is roughly 300 times less intense than the second, at 2800 Å. (approx.).
- (ii) *d*-Bornyl and *l*-menthyl dixanthogenides, on the other hand, show only two "step-outs," which are nearer, by about 100 Å., to the visible spectrum than the corresponding bands. This displacement of the bands is in agreement with VICTOR HENRI'S observations on molecules containing two chromophoric groups at various distances from each other.
- (iii) The dithiourethanes show a band which is almost reduced to a "step-out," at 5200 Å. (approx.), and a "step-out," without a maximum, at 3300 Å.

8. *Analysis of Absorption Curves.*

Three equations were used to calculate theoretical values of the molecular extinction-coefficients for wave-lengths inside the first absorption band:—

- (a) An approximate equation of the KETTELER-HELMHOLTZ type, as used by KUHN,* namely,

$$\varepsilon = \varepsilon_{\max} \frac{\nu^2 \nu'^2}{(\nu_0^2 - \nu^2)^2 + \nu^2 \nu'^2} \simeq \varepsilon_{\max} \frac{\nu'^2}{4(\nu_0 - \nu)^2 + \nu'^2}, \quad \dots \dots (i)$$

where

ε = molecular extinction coefficient at frequency ν .

ε_{\max} = maximum molecular extinction coefficient at frequency ν_0 .

ν_0 = frequency corresponding to head of band.

ν' = range of frequencies corresponding to the half-width of the band.†

* 'Z. phys. Chem.,' B, vol. 4, p. 14 (1929); 'Trans. Faraday Soc.,' vol. 26, p. 293 (1930).

† In deducing theoretical values for the molecular extinction coefficients by means of equations (i) and (ii), it was not always possible to determine the half-width of the bands directly from the experimental curves, owing to the upward trend of the curves on the side of shorter wave-lengths. The half-width was then taken as twice the "semi-half-width" as observed on the side of longer wave-lengths.

- (b) An exponential equation, based on a Maxwellian distribution of frequencies, as used by KUHN and BRAUN,* namely,

$$\varepsilon = \varepsilon_{\max} e^{-\left(\frac{\nu_0 - \nu}{\theta}\right)^2}, \quad \dots \dots \dots (ii)$$

where the parameter θ is defined, in terms of the half-width (ν') of the band,† by the equation

$$\nu' = 1.6651 \theta.$$

- (c) An exponential equation suggested by BIELECKI and HENRI‡:—

$$\varepsilon = \alpha \nu e^{-\beta (\nu_0 - \nu)^2}, \quad \dots \dots \dots (iii)$$

where

$$\alpha = \varepsilon_{\max} / \nu_0$$

β = constant embodying the half-width of the band.

The values calculated from these three equations are represented graphically for the typical case of methyl *d*-bornyl xanthate in fig. 1, where $\log \varepsilon$ is plotted against $1/\lambda$. In comparing the theoretical and observed curves, attention must be concentrated on the long wave-length side of the maximum, since the form of the curve on the side of shorter wave-lengths is influenced by the close proximity of the second and much more intense band; but none of the calculated absorption curves represents the experimental data satisfactorily, since the observed absorption falls off much more rapidly than that calculated by means of the preceding equations.

The character and origin of the deviations between the observed and calculated molecular extinction coefficients, for the *first* absorption band became clear when the same methods of analysis were applied to the *second* absorption band of the xanthates, which is developed much more fully on the side of shorter wave-lengths. The absorption curves deduced from equation (ii) of KUHN and BRAUN for *both* absorption bands are represented graphically as curve 2 in figs. 2 to 10. § As for the first band, the observed and calculated values diverge somewhat widely; but the reason for this discrepancy is now obvious, since the theoretical curves are symmetrical on a scale of *frequencies* (and are therefore less steep on the side of longer wave-lengths), whilst the observed curves are definitely symmetrical on a scale of *wave-lengths*. In order to represent this characteristic feature of the observed data, a new absorption equation (iv) was developed, as follows:—

$$\varepsilon = \varepsilon_{\max} e^{-\left[\frac{\nu_0}{\nu} \left(\frac{\nu_0 - \nu}{\theta}\right)\right]^2}. \quad \dots \dots \dots (iv)$$

As in equation (ii), θ is defined by

$$k\theta = \nu', \dagger$$

* 'Z. phys. Chem.,' B, vol. 8, p. 281 (1930).

† See footnote †, p. 127.

‡ 'Phys. Z.,' vol. 14, p. 516 (1913).

§ The parameters used in these calculations are set out in Table II, p. 129.

KUHN's empirical value of k was usually adopted, but in four cases the value of this constant was adjusted in order to give the closest possible agreement between observed and calculated values.

The parameters of the new equation (iv) are set out in Table II, and the calculated molecular extinction coefficients *for both absorption bands* are plotted as curve 3 in figs. 2 to 10. The agreement is now so close as to approach the limits of experimental error throughout those parts of the curves in which there is no serious overlapping of the

TABLE II.

(a) Parameters of First Absorption Band.

Compound.	Head of Band.		Maximum Intensity.	Half-width.			
				For equations (i), (ii) and (iii).		For equation (iv).	
	λ_0	$\nu_0 \times 10^{-14}$	$\log \epsilon_{\max}$	λ'	$\nu' \times 10^{-14}$	λ'	$\nu' \times 10^{-14}$
I.— $C_{10}H_{17}O \cdot CS \cdot S \cdot Me \dots$	3540	8.474	1.565	445	1.062	470	1.131
II.— $C_{10}H_{17}O \cdot CS \cdot S \cdot Et \dots$	3580	8.379	1.570	425	0.990	452	1.059
III.— $[C_{10}H_{17}O \cdot CS \cdot S]_2 \dots$	3660	8.196	1.72	490	1.092	524	1.179
IV.— $[C_{10}H_{17}O \cdot CS \cdot S]_2CH_2 \dots$	3550	8.451	1.92	504	1.194	540	1.293
V.— $C_{10}H_{19}O \cdot CS \cdot S \cdot Me \dots$	3530	8.499	1.590	443	1.062	470	1.137
VI.— $[C_{10}H_{19}O \cdot CS \cdot S]_2 \dots$	3630	8.265	1.82	540	1.224	580	1.329
VII.— $[C_{10}H_{19}O \cdot CS \cdot S]_2CH_2 \dots$	3550	8.451	2.030	443	1.026	460	1.098
VIII.— $C_{10}H_{17}O \cdot CS \cdot NPh \cdot CS \cdot Ph \dots$	5200	5.769	2.270	937	1.032	1020	1.143
IX.— $C_{10}H_{19}O \cdot CS \cdot NPh \cdot CS \cdot Ph \dots$	5150	5.826	2.250	898	1.008	974	1.113

(b) Parameters of Second Absorption Band.

I.— $C_{10}H_{17}O \cdot CS \cdot S \cdot Me \dots$	2760	10.869	4.12	230	0.909	230	0.909
II.— $C_{10}H_{17}O \cdot CS \cdot S \cdot Et \dots$	2790	10.752	3.99	230	0.882	230	0.882
III.— $[C_{10}H_{17}O \cdot CS \cdot S]_2 \dots$	2880	10.416	3.90	311	1.158	311	1.158
IV.— $[C_{10}H_{17}O \cdot CS \cdot S]_2CH_2 \dots$	2820	10.638	4.44	233	0.882	233	0.882
V.— $C_{10}H_{19}O \cdot CS \cdot S \cdot Me \dots$	2760	10.869	4.24	230	0.909	230	0.909
VI.— $[C_{10}H_{19}O \cdot CS \cdot S]_2 \dots$	2850	10.527	4.20	287	1.056	300	1.113
VII.— $[C_{10}H_{19}O \cdot CS \cdot S]_2CH_2 \dots$	2810	10.677	4.48	260	0.990	260	0.990
VIII.— $C_{10}H_{17}O \cdot CS \cdot NPh \cdot CS \cdot Ph \dots$	3300	9.090	4.10	771	2.094	860	2.409
IX.— $C_{10}H_{19}O \cdot CS \cdot NPh \cdot CS \cdot Ph \dots$	3300	9.090	4.05	771	2.094	860	2.409

bands. When, however, the calculated values for the first band are plotted on a large scale, as in curve 3 of fig. 1, it is clear that the small remaining deviations are systematic in character. We cannot therefore claim to have found the ideal equation, although one of its essential characteristics appears to be adequately established.

D.—CIRCULAR DICHROISM.

9. *Experimental Results.*

Measurements of circular dichroism, $\varepsilon_l \sim \varepsilon_r$, were restricted to the range of wavelengths covered by the first absorption band, since the intensity of the second absorption band is too great (in comparison with its circular dichroism) for useful measurements to be possible. Even in this range, the results are not very exact; but the data for the menthyl compounds are more accurate than those for the bornyl compounds, where the rotatory power and circular dichroism are approximately three times smaller. For diphenyl *d*-bornyl dithiourethane, where the "dissymmetry factor" is exceptionally small, our photographic measurements were less exact than the visual measurements of BRUHAT,* and have therefore not been reproduced.

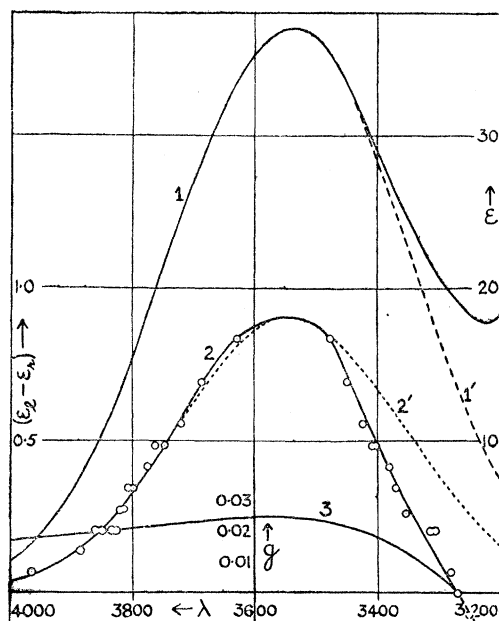


FIG. 11.—Circular dichroism of methyl *d*-bornyl xanthate.

1 = Experimental absorption curve; 1' = Theoretical absorption curve calculated from equation (iv); 2 = Experimental circular dichroism curve; 2' = Theoretical circular dichroism curve calculated from equation (v); 3 = Dissymmetry factor.

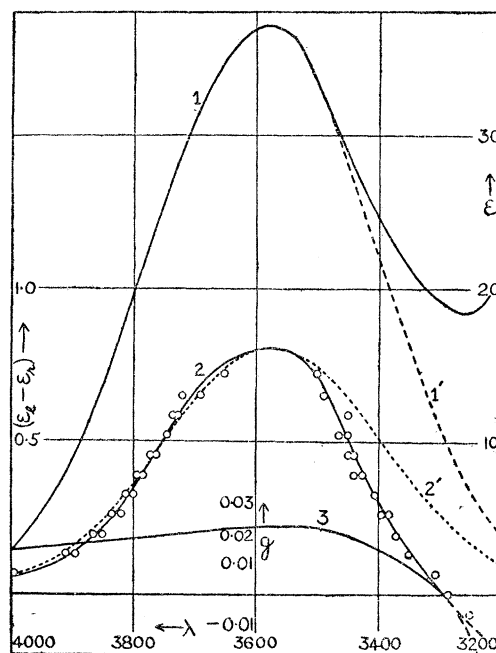


FIG. 12.—Circular dichroism of ethyl *d*-bornyl xanthate.

1 = Experimental absorption curve; 1' = Theoretical absorption curve calculated from equation (iv); 2 = Experimental circular dichroism curve; 2' = Theoretical circular dichroism curve calculated from equation (v); 3 = Dissymmetry factor.

As with the molecular extinction coefficients, the values recorded for the circular dichroism of this series of compounds can be expressed with sufficient accuracy by graphical methods. The tables in which these data were collected have therefore been omitted from the present paper, but the principal constants have been collected in Table III, p. 134 and the data have been plotted as curve 2 in figs. 11 to 18. For

* 'Ann. Physique,' vol. 3, p. 232 (1915).

the purpose of comparison, the observed molecular extinction coefficients ϵ are also shown in these figures as curve 1, whilst curve 1' shows the molecular extinction coefficients on the short wave-length side of the band, as calculated from equation (iv). The "dissymmetry factor," $g = (\epsilon_l \sim \epsilon_r)/\epsilon$, which represents the ratio of the numbers

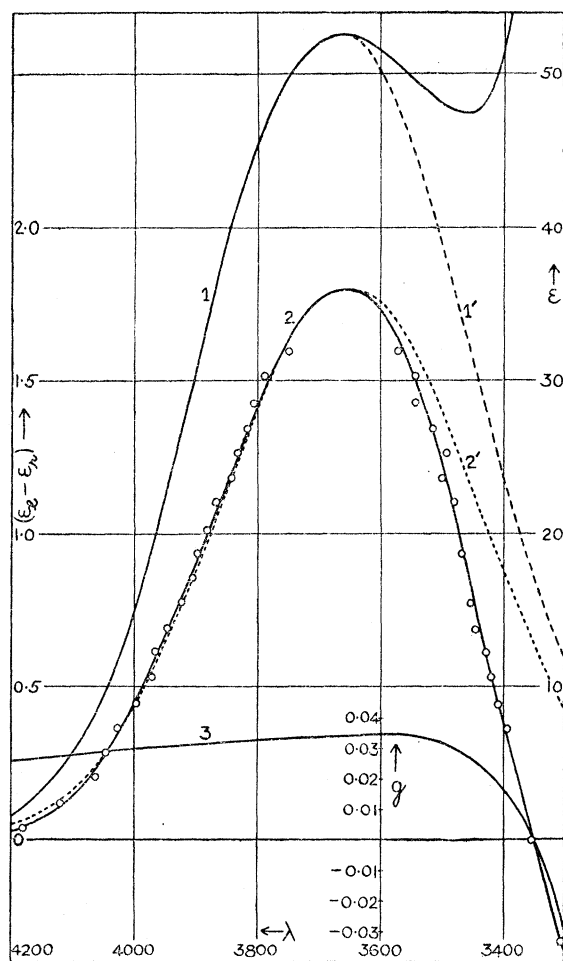


FIG. 13.—Circular dichroism of *d*-bornyl dixanthogenide.

1 = Experimental absorption curve; 1' = Theoretical absorption curve calculated from equation (iv); 2 = Experimental circular dichroism curve; 2' = Theoretical circular dichroism curve calculated from equation (v); 3 = Dissymmetry factor.

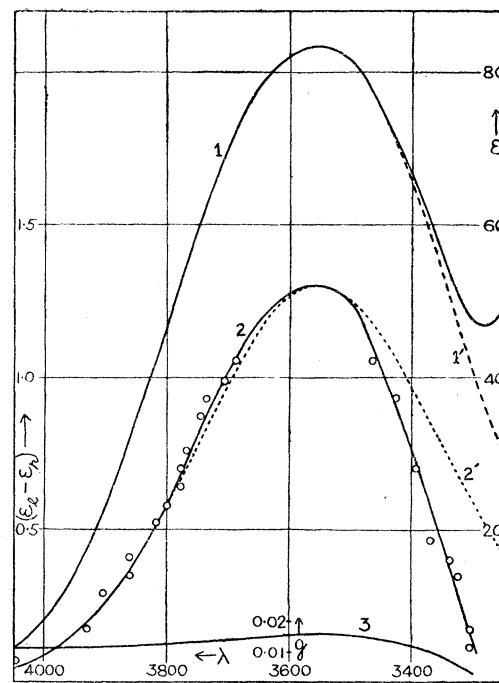


FIG. 14.—Circular dichroism of methylene *d*-bornyl xanthate.

1 = Experimental absorption curve; 1' = Theoretical absorption curve calculated from equation (iv); 2 = Experimental circular dichroism curve; 2' = Theoretical circular dichroism curve calculated from equation (v); 3 = Dissymmetry factor.

plotted in curves 1 and 2, is shown as curve 3 in the same figures. This factor does not vary much in the range of wave-lengths covered by the first band, but the form of the curve on the side of short wave-lengths is complicated by overlapping with the second band.

10. *Analysis of the Curves of Circular Dichroism.*

In accordance with the theoretical deductions of KUHN, we find that the "dissymmetry factor" g , instead of remaining constant in the range of wave-lengths covered by the first absorption band, increases in an approximately linear manner as the wave-length

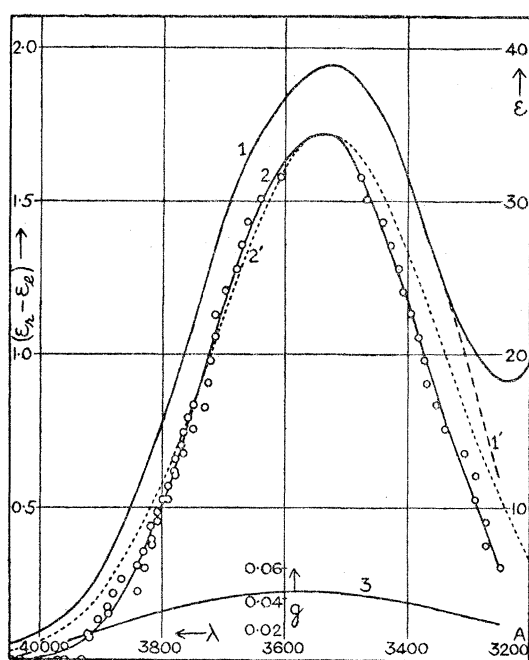


FIG. 15.—Circular dichroism of methyl *l*-menthyl xanthate.

1 = Experimental absorption curve; 1' = Theoretical absorption curve calculated from equation (iv); 2 = Experimental circular dichroism curve; 2' = Theoretical circular dichroism curve calculated from equation (v); 3 = Dissymmetry factor.

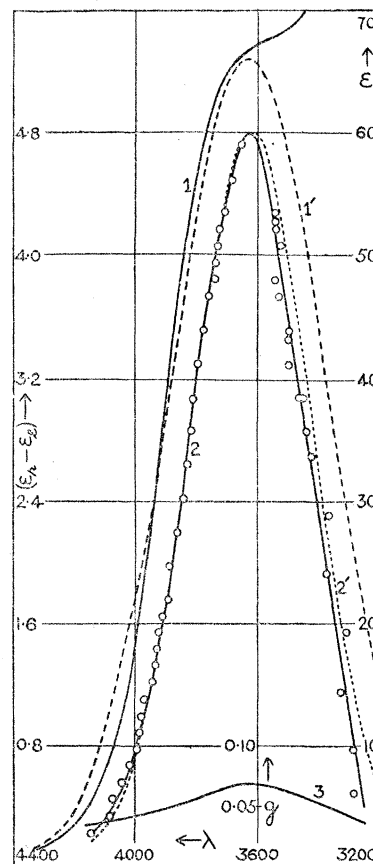


FIG. 16.—Circular dichroism of *l*-menthyl dixanthogenide.

1 = Experimental absorption curve; 1' = Theoretical absorption curve calculated from equation (iv); 2 = Experimental circular dichroism curve; 2' = Theoretical circular dichroism curve calculated from equation (v); 3 = Dissymmetry factor.

decreases, and is, in fact, roughly proportional to the frequency, thus indicating that the whole band is governed by a single characteristic frequency. It has, however, already been shown, in § 8 above, that the molecular extinction coefficients of all the xanthates of this series can be represented to a very close approximation by the expression

$$\epsilon = \epsilon_{\max} e^{-\left[\frac{\nu_0}{\nu} \left(\frac{\nu_0 - \nu}{\theta}\right)\right]^2}.$$

Since the factor g is approximately proportional to the frequency ν , it should be possible to represent the curves of circular dichroism by the expression

$$(\varepsilon_l \sim \varepsilon_r) = (\varepsilon_l \sim \varepsilon_r)_{\max} \frac{\nu}{\nu_0} e^{-\left[\frac{\nu_0}{\nu} \left(\frac{\nu_0 - \nu}{\theta}\right)\right]^2} \dots \dots \dots (v)$$

since

$$g = \frac{\varepsilon_l \sim \varepsilon_r}{\varepsilon} \text{ and } g = \frac{g_0 \nu}{\nu_0}.$$

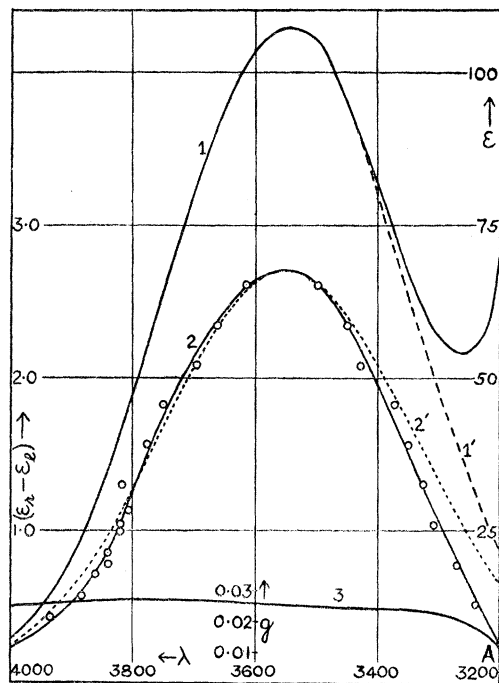


FIG. 17.—Circular dichroism of methylene *l*-menthyl xanthate.

1 = Experimental absorption curve; 1' = Theoretical absorption curve calculated from equation (iv); 2 = Experimental circular dichroism curve; 2' = Theoretical circular dichroism curve calculated from equation (v); 3 = Dissymmetry factor.

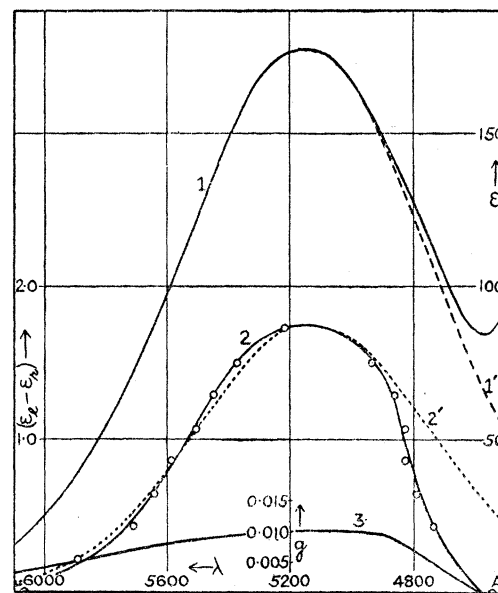


FIG. 18.—Circular dichroism of diphenyl *l*-menthyl dithiourethane.

1 = Experimental absorption curve; 1' = Theoretical absorption curve calculated from equation (iv); 2 = Experimental circular dichroism curve; 2' = Theoretical circular dichroism curve calculated from equation (v); 3 = Dissymmetry factor.

It will be noticed that the above expression is analogous to the absorption equation of BIELECKI and HENRI—

$$\varepsilon = \varepsilon_{\max} \nu/\nu_0 e^{-\beta(\nu_0 - \nu)^2},$$

in that both contain the factor ν/ν_0 .

By means of equation (v), theoretical curves were calculated to represent the circular dichroism of each compound. These theoretical curves are shown as dotted lines (2') in figs. 11 to 18, and the values of ν_0 , ν' and $(\varepsilon_l \sim \varepsilon_r)_{\max}$ used in the calculations are given

in Table III. In every case there is a very close agreement between the experimental and theoretical values of $(\epsilon_l \sim \epsilon_r)$ on the long wave-length side of the maximum. On the short wave-length side there is an increasing divergence between experimental and theoretical values, the former decreasing more rapidly than the latter. This divergence is most obvious in the curves for the methyl and ethyl xanthates and dixanthogenide of *d*-borneol, which cross the axis at 3200 to 3400 Å. and give rise to negative values of $(\epsilon_l - \epsilon_r)$ below about 3300 Å.; but it is also characteristic of the whole series of curves, since the partial rotation due to the second band (and therefore the sign of its circular dichroism) is always opposite to that of the first band.

The experimental and theoretical curves of the three menthyl xanthates diverge much less widely than those of the bornyl xanthates or dithiourethane, indicating that the two maxima of circular dichroism are more widely separated in the menthyl xanthates; this conclusion is also supported by the analysis of the curves of rotatory dispersion, as set out under E below.

TABLE III.—Parameters of Curves of Circular Dichroism.

Compound.	Position of Maximum.		Maximum Circular Dichroism	$\theta \times 10^{-14}$.
	λ_0 .	$\nu_0 \times 10^{-14}$.		
I.— $C_{10}H_{17}O \cdot CS \cdot S \cdot Me$	3550	8.451	$(\epsilon_l - \epsilon_r)_{max}$ 0.90	0.613
II.— $C_{10}H_{17}O \cdot CS \cdot S \cdot Et$	3580	8.379	0.80	0.597
III.— $[C_{10}H_{17}O \cdot CS \cdot S]_2$	3660	8.196	1.80	0.655
IV.— $[C_{10}H_{17}O \cdot CS \cdot S]_2CH_2$	3560	8.427	1.30	0.649
V.— $C_{10}H_{19}O \cdot CS \cdot S \cdot Me$	3540	8.475	$(\epsilon_r - \epsilon_l)_{max}$ 1.72	0.616
VI.— $[C_{10}H_{19}O \cdot CS \cdot S]_2$	3630	8.265	4.80	0.631
VII.— $[C_{10}H_{19}O \cdot CS \cdot S]_2CH_2$	3560	8.427	2.70	0.685
IX.— $C_{10}H_{19}O \cdot CS \cdot NPh \cdot CS \cdot Ph$	5150	5.826	$(\epsilon_l - \epsilon_r)_{max}$ 1.75	0.604

E.—ROTATORY DISPERSION.

11. *Experimental Results.*

The investigation described in the present paper was undertaken with the primary purpose of determining the mathematical form of the curves of rotatory dispersion, especially in the region of absorption. The extreme complexity of these curves can be seen at once from an inspection of figs. 19 to 27; but, whereas measurements of molecular extinction coefficients and of circular dichroism are always comparatively rough, measurements of rotatory dispersion are of a much higher order of accuracy, and are therefore susceptible to mathematical analysis of a degree of precision which is much greater than that with which the curves are plotted. The numerical data on which these curves are based are therefore recorded in detail in Tables IV to IX, since

TABLE IV.—Specific Rotations of *d*-Bornyl Xanthates.
(Visual Readings.)

λ.	Methyl Ester.				Ethyl Ester.				Dixanthogenide.				Methylene Ester.			
	<i>c</i> = 10·2245 <i>g</i> /100 c.c.				7·3563 <i>g</i> /100 c.c.				7·0579 <i>g</i> /100 c.c.				7·2144 <i>g</i> /100 c.c.			
	<i>l</i> = 4 dm.				4 dm. (1 dm. for Hg 4358.)				4 dm. (1 dm. for Hg 4358.)				4 dm. (1 dm. for Li 4602, Hg 4358.)			
α.	[α].		Diff. (O-C.)		α.	[α].		Diff. (O-C.)		α.	[α].		α.	[α].		Diff. (O-C.)
			1	2				1	2							
Li 6708	11·82	28·91	±	+0·05	7·60	25·81	±	+0·02	13·04	46·17	±	—	—0·28	—0·97	—0·12	—0·01
Cd 6438	12·56	30·72	—0·04	+0·01	8·04	27·32	—0·05	—0·02	13·95	49·41	—0·20	—	—0·62	—2·15	—0·16	—0·05
Zn 6362	12·78	31·24	—0·05	±	8·18	27·78	—0·03	±	14·27	50·54	±	±	—0·69	—2·39	±	+0·11
Li 6104	13·54	33·10	+0·04	+0·08	8·59	29·18	—0·09	—0·03	15·21	53·87	—0·07	—0·16	—1·20	—4·16	—0·06	+0·03
Na 5893	14·07	34·32	—0·08	—0·07	8·93	30·35	+0·03	+0·09	16·02	56·72	—0·01	—0·04	—1·76	—6·09	—0·07	±
Cu 5782	14·33	35·04	±	+0·03	9·06	30·79	+0·02	+0·08	16·42	58·15	±	—0·02	—2·12	—7·36	—0·09	—0·04
Hg 5780	14·34	35·06	+0·01	+0·02	9·04	30·72	—0·07	±	16·45	58·25	+0·08	+0·04	—2·10	—7·29	±	+0·06
Cu 5700	14·49	35·44	—0·02	—0·01	9·11	30·97	—0·09	—0·01	16·67	59·03	—0·14	—0·16	—2·46	—8·53	—0·19	—0·15
Ag 5468	—	—	—	—	—	—	—	—	17·41	61·64	—0·02	—0·01	—3·55	—12·13	+0·06	+0·05
Hg 5461	14·83	36·27	±	±	9·24	31·42	—0·02	+0·02	17·43	61·72	±	±	—3·55	—12·32	±	—0·01
Cu 5219	14·70	35·95	—0·07	—0·12	9·04	30·73	+0·03	+0·02	17·76	62·91	—0·14	—0·06	—5·24	—18·14	+0·07	±
Ag 5209	—	—	—	—	9·01	30·62	—0·02	—0·03	—	—	—	—	—	—	—	—
Cu 5153	14·58	35·65	+0·01	—0·01	8·87	30·15	—0·04	—0·06	17·70	62·67	—0·34	—0·23	—5·81	—20·13	+0·13	+0·06
Cu 5106	14·41	35·24	—0·01	—0·03	8·75	29·72	+0·02	—0·02	17·66	62·56	—0·25	—0·14	—6·30	—21·83	+0·08	—0·01
Cd 5086	14·35	35·09	+0·03	+0·03	8·68	29·51	+0·03	±	17·62	62·40	—0·20	—0·16	—6·54	—22·64	±	—0·10
Zn 4811	12·08	29·53	+0·02	+0·02	6·90	23·46	—0·01	—0·10	15·97	56·57	+0·01	±	—10·40	—36·04	±	±
Cd 4800	11·91	29·11	—0·04	—0·04	6·80	23·10	±	—0·10	15·83	56·07	—0·01	—0·06	—10·63	—36·81	—0·09	—0·07
Zn 4722	10·63	26·00	—0·03	—0·01	5·87	19·95	—0·01	—0·09	14·70	52·06	+0·34	+0·05	—12·19	—42·24	—0·11	+0·03
Zn 4680	9·82	24·01	+0·09	+0·09	5·29	17·98	+0·09	+0·03	13·92	49·29	+0·69	+0·15	—13·17	—45·62	—0·44	+0·08
Li 4602	7·80	19·08	—0·01	±	3·91	13·28	+0·05	+0·08	11·86	42·02	+1·09	—0·22	—3·84	—53·23	—0·80	—0·26
Hg 4358	—3·98	—9·72	—0·09	—0·46	—1·03	—13·94	—1·38	—0·01	—0·15	—8·50	+7·09	—5·20	—6·37	—88·30	—3·35	—0·14

1. Difference for two-term equation of Table X.

2. Difference for three-term equation of Table X.

TABLE V.—Specific Rotations of *l*-Menthyl Xanthates.
(Visual Readings.)

Methyl Ester.				Dixanthogenide.				Methylene Ester.				<i>d</i> -Bornyl.				<i>l</i> -Menthyl.			
$c = 5.9487 \text{ g/100 c.c.}$				$7.6608 \text{ g/100 c.c.}$				$7.1560 \text{ g/100 c.c.}$				2.972 gm. 0.9907 " 0.3302 " per 100 c.c.				2.614 gm. 0.8713 " 0.2904 " per 100 c.c.			
$l = 4 \text{ dm.}$				$\left\{ \begin{array}{l} 4 \text{ dm. for Cu 5700} \\ \text{" " Cd 4800} \\ \text{" " Zn 4680} \\ \text{" " Li 4602} \\ 1 \text{ cm. for Hg 4358.} \end{array} \right.$				4 dm. (1 cm. for Hg 4358.)				1 cm.				1 cm.			
λ .	α .			Diff. 1. (O-C.)			$[\alpha]$.	Diff. 1. (O-C.)			$[\alpha]$.	Diff. 2. (O-C.)			α .	Diff. 2. (O-C.)			$[\sigma]$.
	α .	$[\alpha]$.		α .	$[\alpha]$.			α .	$[\alpha]$.			α .	$[\sigma]$.			α .	$[\sigma]$.		
Li 6708	-15.57	-65.43	\pm	-56.33	-183.82	\pm	6.31	22.04	-0.14	-0.14	22.04	+0.24	+80	-0.24	-0.24	-0.24	+80	-0.24	90
Cd 6438	-16.67	-70.06	-0.18	-61.13	-199.49	-0.27	7.73	27.01	\pm	\pm	27.01	+0.40	+135	-0.39	-0.39	-0.39	+135	-0.39	150
Zn 6362	-16.95	-71.23	-0.04	-62.54	-204.09	-0.21	8.36	29.21	+0.60	+0.60	29.21	+0.49	+165	-0.48	-0.48	-0.48	+165	-0.48	185
Li 6104	-18.01	-75.69	\pm	-67.66	-220.80	\pm	10.05	35.11	\pm	\pm	35.11	+0.81	+275	-0.80	-0.80	-0.80	+275	-0.80	305
Na 5893	-18.90	-79.43	-0.05	-72.25	-235.78	+0.05	11.94	41.71	-0.13	-0.13	41.71	+1.11	+375	-1.20	-1.20	-1.20	+375	-1.20	460
Cu 5782	-19.37	-81.40	-0.15	-74.81	-244.13	-0.01	13.23	46.22	+0.09	+0.09	46.22	+0.41	+410	-0.47	-0.47	-0.47	+410	-0.47	540
Hg 5780	-19.30	-81.11	+0.17	-74.88	-244.36	-0.09	13.27	46.36	+0.14	+0.14	46.36	+0.40	+400	-0.48	-0.48	-0.48	+400	-0.48	550
Cu 5700	-19.72	-82.88	-0.29	-79.16	-250.11	+0.32	14.21	49.64	\pm	\pm	49.64	+0.13	+400	-0.17	-0.17	-0.17	+400	-0.17	590
Ag 5468	-20.48	-86.07	-0.09	-82.43	-269.00	-0.10	17.60	61.49	-0.33	-0.33	61.49	+0.07	+200	-0.13	-0.13	-0.13	+200	-0.13	450
Hg 5461	-20.48	-86.07	\pm	-82.57	-269.46	\pm	17.80	62.19	-0.04	-0.04	62.19	+0.05	+150	-0.12	-0.12	-0.12	+150	-0.12	400
Cu 5219	-21.02	-88.34	-0.14	-88.40	-288.48	+0.02	22.90	80.00	+0.17	+0.17	80.00	-0.13	+400	+0.04	+0.04	+0.04	+400	+0.04	150
Ag 5209	-21.02	-88.34	-0.10	-88.66	-289.33	-0.08	23.05	80.53	-0.11	-0.11	80.53	-0.15	+450	+0.05	+0.05	+0.05	+450	+0.05	175
Cu 5153	-21.03	-88.38	-0.03	-89.79	-293.02	+0.03	24.54	85.73	+0.03	+0.03	85.73	-0.19	+575	+0.09	+0.09	+0.09	+575	+0.09	300
Cu 5105	-21.02	-88.34	-0.04	-90.88	-296.57	+0.04	25.84	90.27	0.06	0.06	90.27	-0.24	+725	+0.14	+0.14	+0.14	+725	+0.14	500
Cd 5086	-20.94	-88.00	+0.23	-91.20	-297.62	+0.29	26.34	92.02	-0.36	-0.36	92.02	-0.24	+725	+0.16	+0.16	+0.16	+725	+0.16	550
Zn 4811	-19.76	-83.04	\pm	-94.58	-308.65	\pm	37.30	130.31	+1.42	+1.42	130.31	-0.45	+1350	+0.36	+0.36	+0.36	+1350	+0.36	1250
Cd 4800	-19.64	-82.54	+0.07	-93.65	-308.71	-0.11	37.56	131.22	+0.58	+0.58	131.22	-0.44	+1325	+0.36	+0.36	+0.36	+1325	+0.36	1250
Zn 4722	-18.70	-78.59	+0.16	-94.25	-307.57	-1.23	40.76	142.40	-2.43	-2.43	142.40	-0.49	+1500	+0.39	+0.39	+0.39	+1500	+0.39	1350
Zn 4680	-18.03	-75.77	+0.24	-93.34	-304.67	-1.33	43.91	153.40	-0.05	-0.05	153.40	-0.49	+1500	+0.40	+0.40	+0.40	+1500	+0.40	1400
Cd 4678	-18.00	-75.65	+0.21	-92.90	-298.92	-6.01	49.75	173.81	-0.06	-0.06	173.81	-0.51	+1550	+0.40	+0.40	+0.40	+1550	+0.40	1400
Li 4602	-16.39	-68.88	+0.48	-82.90	-219.30	-63.05	1.87	261	+7	+7	261	-0.54	+1650	+0.43	+0.43	+0.43	+1650	+0.43	1500
Hg 4358	-6.14	-25.80	-0.85	-1.68	-219.30	-63.05	1.87	261	+7	+7	261	-0.54	+1650	+0.43	+0.43	+0.43	+1650	+0.43	1500

1. Difference for two-term equation of Table X.

2. Difference for three-term equation of Table X.

TABLE VI.—Specific Rotations of Bornyl Xanthates.
(Photographic readings, $l = 1$ dm, $t = 20^\circ$.)

I.—Methyl- <i>d</i> -bornyl xanthate. Concentrations (<i>b</i>) 0·9295g/100 c.c. (<i>c</i>) 0·1549 „ (<i>d</i>) 0·0845 „			II.—Ethyl- <i>d</i> -bornyl xanthate. Concentrations (<i>b</i>) 0·6688g/100 c.c. (<i>c</i>) 0·1114 „ (<i>d</i>) 0·0608 „		
λ .	α .	$[\alpha]$.	λ .	α .	$[\alpha]$.
<i>b</i> 4307	−0·22	− 24·0	<i>b</i> 4294	−0·17	− 25·5
<i>b</i> 4271	−0·32	− 34·5	<i>b</i> 4272	−0·27	− 40·5
<i>b</i> 4233	−0·42	− 45·0	<i>b</i> 4219	−0·37	− 55·5
<i>b</i> 4203	−0·52	− 56·0	<i>c</i> 4202	−0·07	− 63
<i>b</i> 4171	−0·62	− 67·0	<i>b</i> 4176	−0·47	− 70·5
<i>b</i> 4143	−0·72	− 77·5	<i>b</i> 4132	−0·57	− 85·0
<i>b</i> 4118	−0·82	− 88·5	<i>b</i> 4119	−0·67	−100·0
<i>b</i> 4109	−0·92	− 99·0	<i>b</i> 4101	−0·77	−115·0
<i>b</i> 4085	−1·02	−110·0	<i>c</i> 4005	−0·27	−242
<i>b</i> 4070	−1·12	−120·5	<i>d</i> 3978	−0·17	−280
<i>b</i> 4055	−1·22	−131·5	<i>c</i> 3950	−0·37	−332
<i>c</i> 4046	−0·23	−147	<i>c</i> 3887	−0·47	−422
<i>c</i> 3979	−0·33	−212	<i>d</i> 3872	−0·27	−445
<i>c</i> 3949	−0·43	−276	<i>d</i> 3765	−0·27	−445
<i>c</i> 3900	−0·53	−341	<i>d</i> 3705	−0·17	−280
<i>c</i> 3858	−0·63	−405	<i>d</i> 3678	−0·07	−115
<i>c</i> 3801	−0·73	−470	<i>d</i> 3619	+0·03	+ 50
<i>d</i> 3765	−0·42	−490	<i>d</i> 3609	+0·13	+215
<i>d</i> 3611	−0·02	− 20	<i>d</i> 3525	+0·33	+545
<i>d</i> 3575	+0·18	+220			
<i>d</i> 3529	+0·38	+455			
<i>d</i> 3455	+0·78	+925			
III.— <i>d</i> -Bornyl dixanthogenide. Concentrations (<i>b</i>) 0·6416g/100 c.c. (<i>c</i>) 0·1069 „ (<i>d</i>) 0·0583 „			IV.—Methylene- <i>d</i> -bornyl xanthate. Concentrations (<i>b</i>) 0·6558g/100 c.c. (<i>c</i>) 0·0596 „		
λ .	α .	$[\alpha]$.	λ .	α .	$[\alpha]$.
<i>b</i> 4308	−0·17	− 26	<i>b</i> 4353	−0·60	− 92
<i>b</i> 4282	−0·37	− 57	<i>b</i> 4308	−0·70	−107·5
<i>c</i> 4234	−0·07	− 65	<i>b</i> 4272	−0·80	−122·5
<i>b</i> 4226	−0·57	− 89	<i>b</i> 4219	−0·90	−138
<i>b</i> 4204	−0·77	− 120	<i>b</i> 4185	−1·00	−153
<i>c</i> 4157	−0·17	− 159	<i>b</i> 4154	−1·10	−168·5
<i>c</i> 4101	−0·27	− 252	<i>b</i> 4132	−1·20	−183
<i>c</i> 4046	−0·37	− 346	<i>b</i> 4107	−1·30	−199
<i>d</i> 3969	−0·27	− 460	<i>b</i> 4070	−1·40	−214
<i>c</i> 3903	−0·47	− 486	<i>c</i> 4050	−0·14	−240
<i>d</i> 3860	−0·27	− 460	<i>c</i> 3997	−0·19	−325
<i>c</i> 3815	−0·37	− 346	<i>c</i> 3949	−0·20	−345
<i>d</i> 3805	−0·17	− 290	<i>c</i> 3826	−0·29	−490
<i>c</i> 3786	−0·27	− 252	<i>c</i> 3687	−0·20	−345
<i>c</i> 3758	−0·17	− 159	<i>c</i> 3687	−0·19	−325
<i>d</i> 3748	−0·07	− 120	<i>c</i> 3670	−0·14	−240
<i>c</i> 3735	−0·07	− 65	<i>c</i> 3649	−0·10	−175
<i>d</i> 3722	+0·03	+ 50	<i>c</i> 3607	−0·04	− 70
<i>d</i> 3670	+0·23	+ 395	<i>c</i> 3586	−0·005	− 10
<i>d</i> 3621	+0·43	+ 735	<i>c</i> 3586	±0·00	± 0
<i>d</i> 3552	+0·63	+1080	<i>c</i> 3586	+0·007	+ 10
			<i>c</i> 3554	+0·06	+ 95
			<i>c</i> 3535	+0·09	+160
			<i>c</i> 3525	+0·16	+265
			<i>c</i> 3507	+0·19	+325

TABLE VII.—Specific Rotations of Methyl-*l*-Menthyl Xanthate V.(Photographic readings, $l = 1$ cm., $t = 20^\circ$.)Concentrations (*a*) 5·9487, (*b*) 1·6996, (*c*) 0·9914 g/100 c.c.

λ .	α .	$[\alpha]$.	λ .	α .	$[\alpha]$.
<i>a</i> 4790	−0·48	− 80·5	<i>b</i> 3856	+1·02	+ 600
<i>a</i> 4560	−0·38	− 64·0	<i>b</i> 3815	+1·12	+ 659
<i>a</i> 4326	−0·08	− 13·5	<i>b</i> 3760	+1·12	+ 659
<i>a</i> 4282	+0·02	+ 3·5	<i>b</i> 3728	+1·02	+ 600
<i>a</i> 4240	+0·12	+ 20·0	<i>b</i> 3724	+0·92	+ 541
<i>a</i> 4216	+0·22	+ 37·0	<i>b</i> 3720	+0·92	+ 541
<i>a</i> 4185	+0·32	+ 54·0	<i>b</i> 3706	+0·82	+ 482
<i>a</i> 4155	+0·42	+ 70·5	<i>c</i> 3670	+0·22	+ 220
<i>a</i> 4137	+0·52	+ 87·5	<i>c</i> 3660	+0·12	+ 120
<i>a</i> 4123	+0·62	+104·0	<i>c</i> 3651	+0·02	+ 20
<i>a</i> 4101	+0·72	+121·0	<i>c</i> 3648	$\pm 0\cdot00$	± 0
<i>a</i> 4085	+0·82	+138·0	<i>c</i> 3631	−0·08	− 80
<i>a</i> 4075	+0·92	+154·5	<i>c</i> 3617	−0·18	− 180
<i>a</i> 4068	+1·02	+171·5	<i>c</i> 3603	−0·28	− 280
<i>a</i> 4046	+1·12	+188·0	<i>c</i> 3603	−0·38	− 380
<i>b</i> 4046	+0·32	+188	<i>c</i> 3595	−0·88	− 890
<i>a</i> 4032	+1·22	+205·0	<i>c</i> 3582	−0·48	− 485
<i>a</i> 4022	+1·32	+222·0	<i>c</i> 3582	−0·68	− 685
<i>b</i> 4015	+0·42	+247	<i>c</i> 3581	−0·78	− 785
<i>a</i> 4010	+1·42	+238·5	<i>c</i> 3577	−0·58	− 585
<i>a</i> 4005	+1·52	+255·5	<i>c</i> 3530	−1·08	−1089
<i>a</i> 3997	+1·62	+272·5	<i>c</i> 3525	−0·98	− 990
<i>a</i> 3986	+1·72	+289·0	<i>c</i> 3521	−1·18	−1190
<i>a</i> 3978	+1·82	+306·0	<i>c</i> 3498	−1·28	−1290
<i>b</i> 3971	+0·52	+306	<i>c</i> 3498	−1·48	−1495
<i>a</i> 3969	+1·92	+322·5	<i>c</i> 3490	−1·58	−1595
<i>a</i> 3966	+2·02	+339·5	<i>c</i> 3485	−1·68	−1695
<i>a</i> 3957	+2·12	+356·5	<i>c</i> 3477	−1·58	−1595
<i>a</i> 3953	+2·22	+373·0	<i>c</i> 3466	−1·78	−1795
<i>a</i> 3949	+2·32	+390·0	<i>c</i> 3466	−1·88	−1895
<i>b</i> 3942	+0·62	+365	<i>c</i> 3445	−1·98	−1995
<i>a</i> 3937	+2·42	+406·5	<i>c</i> 3427	−2·08	−2100
<i>b</i> 3908	+0·72	+424	<i>c</i> 3427	−2·18	−2200
<i>b</i> 3889	+0·82	+482	<i>c</i> 3407	−2·28	−2300
<i>b</i> 3887	+0·92	+541	(<i>c</i>) (3248)	(−2·28)	(−2300)
<i>b</i> 3879	+0·92	+541	(<i>c</i>) (3228)	(−2·18)	(−2200)

TABLE VIII.—Specific Rotations of *l*-Menthyl Dixanthogenide, VI.(Photographic readings, $l = 1$ cm., $t = 20^\circ$.)Concentrations (*a*) 7·6608, (*b*) 1·2768 g/100 c.c.

λ .	α .	$[\alpha]$.	λ .	α .	$[\alpha]$.
<i>a</i> 4384	−1·78	−232	<i>b</i> 3757	−0·58	− 454
<i>a</i> 4326	−1·58	−206	<i>b</i> 3748	−0·68	− 533
<i>a</i> 4282	−1·38	−180	<i>b</i> 3748	−0·78	− 611
<i>a</i> 4272	−1·28	−167	<i>b</i> 3727	−0·88	− 689
<i>a</i> 4272	−1·18	−154	<i>b</i> 3723	−0·98	− 768
<i>a</i> 4260	−1·08	−141	<i>b</i> 3720	−1·08	− 846
<i>a</i> 4245	−0·98	−128	<i>b</i> 3711	−1·18	− 924
<i>a</i> 4235	−0·88	−115	<i>b</i> 3707	−1·28	−1002
<i>a</i> 4226	−0·78	−102	<i>b</i> 3707	−1·38	−1081
<i>b</i> 4226	−0·08	− 63	<i>b</i> 3695	−1·48	−1160
<i>a</i> 4216	−0·68	− 89	<i>b</i> 3684	−1·58	−1235
<i>a</i> 4204	−0·58	− 75	<i>b</i> 3684	−1·68	−1316
<i>a</i> 4191	−0·38	− 49	<i>b</i> 3687	−1·78	−1394
<i>a</i> 4176	−0·18	− 23	<i>b</i> 3687	−1·88	−1492
<i>a</i> 4164	+0·02	+ 2·5	<i>b</i> 3677	−1·98	−1551
<i>b</i> 4148	+0·02	+ 16	<i>b</i> 3670	−2·08	−1629
<i>a</i> 4148	+0·22	+ 28·5	<i>b</i> 3670	−2·18	−1708
<i>a</i> 4132	+0·42	+ 55·0	<i>b</i> 3670	−2·28	−1785
<i>a</i> 4119	+0·62	+ 81·0	<i>b</i> 3660	−2·68	−2099
<i>b</i> 4107	+0·12	+ 94	<i>b</i> 3631	−3·38	−2647
<i>a</i> 4107	+0·82	+107	<i>b</i> 3619	−3·18	−2491
<i>a</i> 4101	+1·02	+133	<i>b</i> 3619	−3·68	−2882
<i>a</i> 4085	+1·22	+159	<i>b</i> 3607	−3·58	−2804
<i>a</i> 4071	+1·42	+185·5	<i>b</i> 3581	−3·78	−2961
<i>b</i> 4070	+0·22	+172	<i>b</i> 3565	−3·98	−3118
<i>b</i> 4046	+0·32	+251	<i>b</i> 3565	−4·18	−3274
<i>b</i> 4022	+0·42	+329	<i>b</i> 3542	−4·38	−3431
<i>b</i> 3969	+0·52	+407	<i>b</i> 3542	−4·58	−3588
<i>b</i> 3878	+0·52	+407	<i>b</i> 3542	−4·78	−3744
<i>b</i> 3856	+0·42	+329	<i>b</i> 3526	−4·68	−3665
<i>b</i> 3833	+0·32	+251	<i>b</i> 3525	−4·88	−3822
<i>b</i> 3814	+0·12	+ 94	<i>b</i> 3498	−4·98	−3900
<i>b</i> 3814	+0·02	+ 16	<i>b</i> 3497	−5·28	−4135
<i>b</i> 3798	−0·08	− 63	<i>b</i> 3490	−5·18	−4057
<i>b</i> 3788	−0·18	−141	<i>b</i> 3477	−5·38	−4214
<i>b</i> 3776	−0·28	−219	<i>b</i> 3477	−5·48	−4292
<i>b</i> 3766	−0·38	−298	<i>b</i> 3445	−5·68	−4448
<i>b</i> 3766	−0·48	−376	<i>b</i> 3440	−5·58	−4370

TABLE IX.—Specific Rotations of Methylene-*l*-Menthyl Xanthate, VII.(Photographic readings, $l = 1$ cm., $t = 20^\circ$.)Concentrations (*b*) 3·0550, (*c*) 1·0183, (*d*) 0·5092 g/100 c.c.

λ .	α .	$[\alpha]$.	λ .	α .	$[\alpha]$.
<i>b</i> 4353	0·82	268·5	<i>b</i> 3917	2·42	792
<i>b</i> 4308	0·92	301·0	<i>c</i> 3917	0·82	805
<i>b</i> 4267	1·02	334·0	<i>c</i> 3896	0·82	805
<i>b</i> 4226	1·12	366·5	<i>c</i> 3889	0·82	805
<i>b</i> 4191	1·22	399·5	<i>c</i> 3887	0·87	854
<i>b</i> 4176	1·32	432·0	<i>c</i> 3795	0·92	904
<i>b</i> 4144	1·42	465·0	<i>c</i> 3728	0·82	805
<i>c</i> 4107	0·47	462	<i>c</i> 3707	0·72	707
<i>b</i> 4085	1·52	497·5	<i>d</i> 3678	0·32	630
<i>c</i> 4085	0·52	510	<i>d</i> 3670	0·22	430
<i>b</i> 4062	1·62	530	<i>d</i> 3595	0·02	40
<i>b</i> 4032	1·72	563	<i>d</i> 3586	−0·08	−155
<i>b</i> 4032	1·82	596	<i>d</i> 3565	−0·18	−355
<i>c</i> 4032	0·62	609	<i>d</i> 3541	−0·28	−550
<i>b</i> 4015	1·92	628	<i>d</i> 3498	−0·38	−745
<i>d</i> 4005	0·32	630	<i>d</i> 3477	−0·48	−945
<i>b</i> 3984	2·02	661	<i>d</i> 3445	−0·58	−1140
<i>c</i> 3966	0·72	707	(<i>d</i>) (3257)	(−0·58)	(−1140)
<i>b</i> 3957	2·12	694	(<i>d</i>) (3254)	(−0·48)	(−945)
<i>b</i> 3949	2·22	727	(<i>d</i>) (3248)	(−0·38)	(−745)
<i>b</i> 3928	2·32	759			

only in this way is it possible for these measurements to be of lasting value in the analysis of the phenomenon of rotatory dispersion as our knowledge of the mechanism of the process develops.

The visual readings for seven xanthates are set out in Tables IV and V. The average error in the observed rotations is only a few hundredths of a degree, corresponding to an error of perhaps $0\cdot05^\circ$ in the specific rotations, except for the violet lines, where the readings were often taken with shorter columns of liquid, on account of incipient absorption of light of short wave-lengths.

In the region of absorption, readings could only be taken when shorter columns of liquid were used, *e.g.*, with a cell only 1 cm. in thickness, but with a greater aperture than that of the optical parts of the polarimeter. The concentrations of the solutions were also reduced as their absorptive power increased. Under these conditions, the error in the specific rotations was increased in direct proportion to the factor used in order to calculate them from the observed rotations; but the percentage error was not necessarily increased in the same proportion, since the specific rotations in the region of absorption rise to values which are many times greater than the maximum values in the region of transparency.

For the seven xanthates cited above, these limitations were encountered only in the violet and ultra-violet regions, including the mercury line, Hg 4358 of Tables IV and V.

and the whole of the photographic readings recorded in Tables VI to IX. But the specific rotations of the two coloured dithiourethanes, which are recorded in Table V, suffer from this limitation throughout the visible spectrum, since even at the red end of the spectrum the absorption was so strong that readings could only be taken when the observed rotations were reduced to less than 1/300 of the specific rotations.

The experimental error in the specific rotations is estimated as follows :—

For the seven xanthates—

- ± 0.05 in the visible region.
- ± 2.0 from 4300 to 4100 Å. approximately.
- $\pm 10^\circ$ from 4100 to 3800 Å. approximately.
- $\pm 20^\circ$ from 3800 to 3400 Å. approximately.

For the dithiourethanes—

- $\pm 7^\circ$ from 6708 to 5893 Å. approximately.
- $\pm 20^\circ$ from 5782 to 5780 Å. approximately.
- $\pm 50^\circ$ from 5700 to 4358 Å. approximately.

12. *General Character of the Curves of Rotatory Dispersion.*

The general results of the measurements of rotatory dispersion may be summarized as follows :—

(a) In the region of complete transparency the methyl and ethyl xanthates and the dioxanthogenides show all the usual characteristics of anomalous rotatory dispersion as they are observed for instance in the esters of tartaric acid, namely, (i) a point of inflexion in the red, (ii) a maximum in the green, and (iii) a reversal of sign in the violet. The bornyl and menthyl compounds give curves of exactly the same type, but of opposite sign, since the rotations in the middle of the visible spectrum are *positive* in the bornyl and *negative* in the menthyl xanthates.

(b) In the region covered by the first absorption band, a further series of anomalies is observed, of the same character as those observed by COTTON in the coloured tartrates. Thus, after passing through a zero value in the region of transparency, the specific rotations increase rapidly to a maximum of opposite sign in the near ultra-violet ; they then decrease again to zero at a wave-length near to that of maximum absorption, and finally rise to still larger values (of the same sign as in the middle of the visible spectrum) on entering the region covered by the second absorption band.

(c) The rotatory dispersion of the methylene esters differs from that of the methyl and ethyl esters, in that the reversal of sign in the region of transparency is shifted from the blue-violet to the extreme red end of the spectrum. The rotations are therefore negative for the bornyl xanthate and positive for the menthyl xanthate throughout the whole range of visual readings from Li 6708 to Hg 4358 and beyond. Within this range the dispersion is therefore apparently normal, since the rotations increase progressively with decreasing wave-length ; but this is only because the anomalies

have been displaced to longer wave-lengths. This conclusion was confirmed by the fact that a reversal of sign was detected in the methylene bornyl ester, IV, at about 7000 Å., where a zero reading was observed, whilst a small *positive* rotation, $\alpha = 0.06$, $[\alpha] = 0.2$, was observed at about 7100 Å., using a carbon arc as a source of red light. In the region of absorption, however, the curves of rotatory dispersion are of just the same type as those referred to above.

(d) A still further displacement is observed in the diphenyl dithiourethanes, where the first absorption band is shifted into the visible spectrum, so that the solutions have a strong red colour. The anomalies associated with the COTTON phenomenon are therefore also displaced into the visible spectrum, so that TSCHUGAEFF* was able to observe the anomalous rotations and BRUHAT† to measure also the circular dichroism in the region covered by the band. But the absorption by the second absorption band is too great to permit of photographic readings of either property in the ultra-violet. Apart from this displacement, however, the curves of rotatory dispersion of the dithiourethanes are very similar to those of the methylene esters, although the signs of the rotations are once more reversed.

13. *Analysis of the Curves of Rotatory Dispersion in the Region of Transparency.*

It has been found that anomalous rotatory dispersion, especially in the derivatives of tartaric acid, can be represented accurately, throughout the region of transparency, by two terms of DRUDE'S equation, representing partial rotations of opposite sign. Tables IV and V show that the same equation is also valid within extremely narrow limits, when applied to the rotatory dispersions of the four bornyl xanthates, I to IV, and of two menthyl xanthates, V and VI, in the range of wave-lengths covered by the visual readings. The rotatory dispersions of the two dithiourethanes do not lend themselves to similar calculations, since all the observations were made in a region of absorption, within which DRUDE'S equations are no longer valid.

The dispersion constants in the two-term equations for tartaric acid correspond to characteristic frequencies at $\lambda = 2330$ and 1750 Å. approximately.‡ Both constants appear to have a definite physical meaning, since the first wave-length agrees approximately with that of an absorption band, commonly assigned to the carboxyl group, near the end of the accessible ultra-violet region,§ whilst the second wave-length, in the middle of the SCHUMANN region, agrees with that of a characteristic frequency which has already been detected at about 1700 Å. in the secondary alcohols, and has therefore been attributed to the $-\text{CHOH}-$ group in these compounds.|| For the xanthates the dispersion constant of the low-frequency term corresponds to the

* OGORODNIKOFF, 'Z. phys. Chem.,' vol. 74, p. 503 (1910).

† 'Ann. Physique,' vol. 3, p. 232 (1915).

‡ BRUHAT and LEGRIS, 'Ann. Physique,' ser. 10, vol. 13, p. 5 (1930); BRUHAT, 'Trans. Faraday Soc.,' vol. 26, p. 400 (1930).

§ BRUHAT, *loc. cit.*

|| LOWRY and DICKSON, 'J. Chem. Soc.,' vol. 103, p. 1070 (1913).

wave-length of the first absorption band. But the high-frequency term is a composite expression, which has to cover the partial rotation of the second absorption band, as well as those of the bands in the SCHUMANN region which correspond to the saturated portions of the molecule. This term is therefore merely empirical and the dispersion-constant has no physical meaning.

As an alternative, values for the rotations were also calculated from a three-term equation. The low-frequency term in this equation again represents the partial rotation of the first absorption band; but there are now two high-frequency terms of similar sign. One of these represents the partial rotation of the second absorption band, whilst the other represents the partial rotations in the SCHUMANN region; the latter term has a zero value for the dispersion-constant, as in DRUDE's equation for quartz. The parameters of both equations are set out in Table X.

TABLE X.
Constants of Two-Term Drude Equations.

From
Absorption
Data.

—	k_1 .	k_2 .	λ_1^2 .	λ_2^2 .	λ_1 .	λ_2 .	λ_1 .	λ_2 .
I.— $C_{10}H_{17}O \cdot CS \cdot S \cdot Me...$	— 9.675	+24.043	0.13560	0.04716	3682	2170	3540	2760
II.— $C_{10}H_{17}O \cdot CS \cdot S \cdot Et...$	—19.555	+32.491	0.11976	0.06782	3461	2604	3580	2790
III.— $[C_{10}H_{17}O \cdot CS \cdot S]_2...$	— 6.973	+28.817	0.15597	0.03801	3949	1949	3660	2880
IV.— $[C_{10}H_{17}O \cdot CS \cdot S]_2CH_2$	—16.756	+19.658	0.11615	0.05160	3408	2272	3550	2820
V.— $C_{10}H_{19}O \cdot CS \cdot S \cdot Me...$	+ 9.973	—42.469	0.14477	0.01708	3805	1307	3530	2760
VI.— $[C_{10}H_{19}O \cdot CS \cdot S]_2...$	+ 9.816	—90.774	0.16701	0.03454	4087	1858	3630	2850
VII.— $[C_{10}H_{19}O \cdot CS \cdot S]_2CH_2$	—	—	—	—	—	—	3550	2810

Constants of Three-Term Drude Equations.

—	k_1 .	k_2 .	k_3 .	λ_1^2 .	λ_2^2 .	λ_1 .	λ_2 .
I.— $C_{10}H_{17}O \cdot CS \cdot S \cdot Me...$	—15.0524	+22.0484	+7.3393	0.12890	0.07896	3591	2810
II.— $C_{10}H_{17}O \cdot CS \cdot S \cdot Et...$	—13.892	+18.781	+8.329	0.12829	0.07784	3582	2790
III.— $[C_{10}H_{17}O \cdot CS \cdot S]_2...$	—17.729	+29.650	+9.685	0.13760	0.08585	3709	2930
IV.— $[C_{10}H_{17}O \cdot CS \cdot S]_2CH_2$	—10.901	+ 4.611	+9.242	0.12890	0.07952	3591	2820
VII.— $[C_{10}H_{19}O \cdot CS \cdot S]_2CH_2$	+16.390	+15.370	—32.020	0.13104	0.08352	3619	2890

Since the deviations from the two-term (4 constant) equations were already no larger than the inevitable errors of observations, no substantial improvement could be expected to result from the introduction of a fifth constant in the three-term equations; but the new values were at least equally good throughout the spectrum, and the concordance with the violet readings was definitely a little better. Since, however, there was so little room for improvement, it was not considered necessary to make similar calculations for the menthyl esters, V and VI.

It should be added that the equations (*see* section 14) which express the rotatory dispersions in the region of absorption show an incomparably worse agreement when attempts are made to use them to represent at the same time the vastly more accurate measurements in the region of complete transparency.

14. *Complete Analysis of Curves of Rotatory Dispersion.*

The first attempt to analyse the curves of rotatory dispersion, both in the region of complete transparency and within the first absorption band, was made by means of the equation of NATANSON* as used by KUHN† in the initial stages of his work on the α -azidopropionates, namely—

$$\alpha_n = \text{const.} \frac{v^2 (v_0^2 - v^2)}{(v_0^2 - v^2)^2 + v^2 v'^2},$$

or in wave-lengths—

$$\alpha_n = \text{const.} \frac{\lambda^2 - \lambda_0^2}{(\lambda^2 - \lambda_0^2)^2 + \lambda^2 \lambda'^2}, \quad \dots \dots \dots \text{(vi)}$$

where α_n = rotatory contribution of an absorption band and the other symbols have the same significance as in the previous section. From this equation the rotatory contribution of the first absorption band was calculated. The above expression represents a curve containing a positive and a negative maximum and a reversal of sign. The wave-lengths at which these occur are fixed by the values of λ_0 and λ' as determined by the absorption measurements, since the reversal of sign occurs at the maximum of absorption, and the positive and negative maxima occur approximately at the wave-lengths at which the absorption falls to one-half of its maximum value. The magnitude of the two maxima is determined by the constant, which depends entirely on the circular dichroism of the band.

The rotatory contributions of the first absorption band, deduced by means of this equation, are shown graphically, as curves 2, for the four bornyl xanthates in figs. 19 to 22, and for the two dithiourethanes in figs. 26 and 27. The difference curves 5 were obtained by subtracting curves 2 from the experimental curves 1, and thus represent the rotatory contributions of bands in the further ultra-violet. These difference curves should therefore show none of the anomalies present in the experimental curves in the region of the first absorption band. This result has been only partly achieved by means of this analysis, for the resultant curves all contain two conspicuous “humps,” which must be attributed to an inadequate representation by the above equation of the partial rotations due to the first absorption band. The cause of this can be traced to the fact that an absorption equation of the KETTELER-HELMHOLTZ type, on the basis of which the rotation equation was derived, could not be made to represent the absorption data.

* ‘Acad. Sci., Cracow,’ Bull. No. 8, p. 764, Oct., 1908.

† ‘Trans. Faraday Soc.,’ vol. 26, p. 293 (1930).

(a) A second attempt to analyse the rotatory dispersion curves was made by means of the equation of KUHN and BRAUN,* namely,

$$[M] = \frac{[\phi]}{0.541} \frac{\nu}{\nu_\phi} \left[e^{-\left(\frac{\nu_0 - \nu}{\theta}\right)^2} \int_0^{\frac{\nu_0 - \nu}{\theta}} e^{x^2} dx - \frac{\theta}{2(\nu_0 + \nu)} \right], \quad \dots \quad (\text{vii})$$

where

$[M]$ = molecular rotation at frequency ν .

$[\phi]$ = maximum value of $[M]$, which occurs at frequency ν_ϕ , and is given by

$$g_0 \simeq \frac{2.85 [\Phi]}{100 \epsilon_{\max}}, \quad \text{or} \quad [\Phi] \simeq \frac{100 (\epsilon_l \sim \epsilon_r)_{\max}}{2.85}.$$

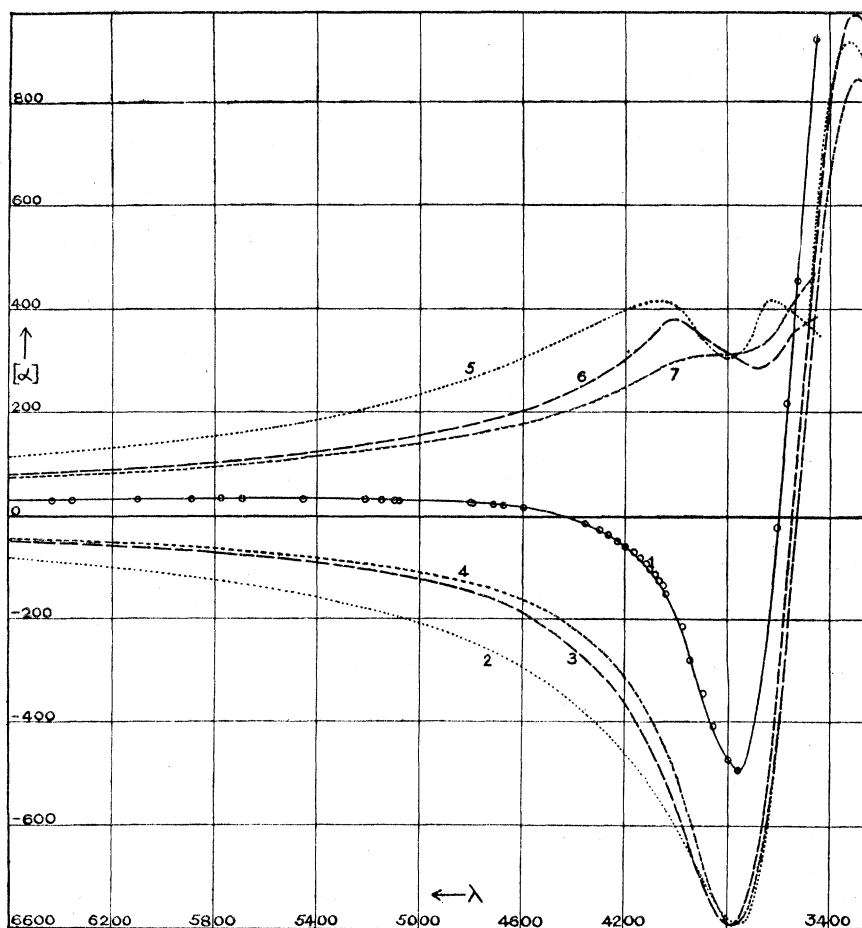


FIG. 19.—Rotatory dispersion of methyl *d*-bornyl xanthate.

- 1 = Experimental curve; 2 = Theoretical curve calculated from NATANSON's equation (vi);
 3 = Theoretical curve calculated from KUHN and BRAUN's equation (vii); 4 = Theoretical curve calculated from our equation (viii); 5 = Difference curve (curve 1 minus curve 2);
 6 = Difference curve (curve 1 minus curve 3); 7 = Difference curve (curve 1 minus curve 4).

* 'Z. phys. Chem.,' B, vol. 8, p. 281 (1930).

The other symbols have the same meaning as defined after equation (ii), p. 128, on which the above expression is based. The rotatory contributions of the first absorption band deduced by means of this equation are shown as curves 3 for the four bornyl xanthates in figs. 19 to 22, and for the two dithiourethanes in figs. 26 and 27. The difference curves 6, representing the partial rotations due to further ultra-violet bands,

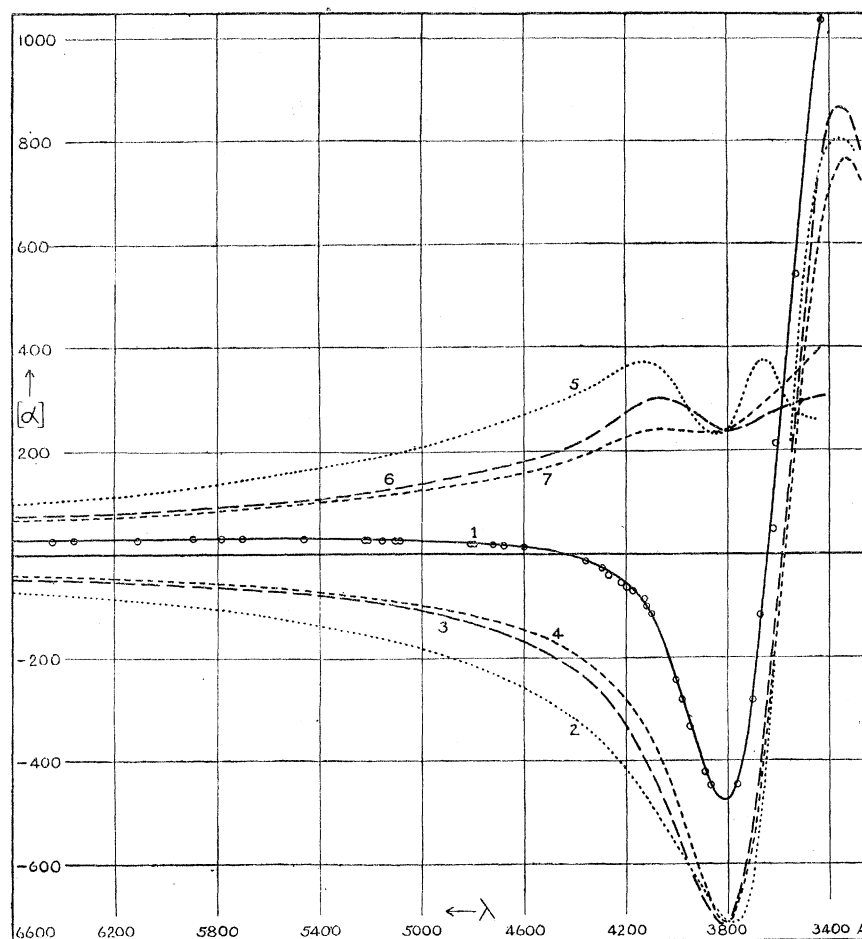


FIG. 20.—Rotatory dispersion of ethyl *d*-bornyl xanthate.

- 1 = Experimental curve; 2 = Theoretical curve calculated from equation (vi); 3 = Theoretical curve calculated from equation (vii); 4 = Theoretical curve calculated from equation (viii); 5 = Difference curve (curve 1 minus curve 2); 6 = Difference curve (curve 1 minus curve 3); 7 = Difference curve (curve 1 minus curve 4).

were obtained by subtracting curves 3 from the experimental curves 1. These curves differ from those obtained by the first analysis in that one of the "humps" has entirely disappeared and the other has been considerably reduced. Thus the equation of KUHN and BRAUN represents the rotatory contribution of an absorption band more accurately than that of NATANSON, although the analysis is by no means ideal.

(b) The third analysis of the dispersion curves was made by means of a modified expression (of the same type as that of KUHN and BRAUN), based on the new absorption equation (iv) which, as shown in a previous section, agrees more closely with our experimental absorption data than any of the others. The modified expression for

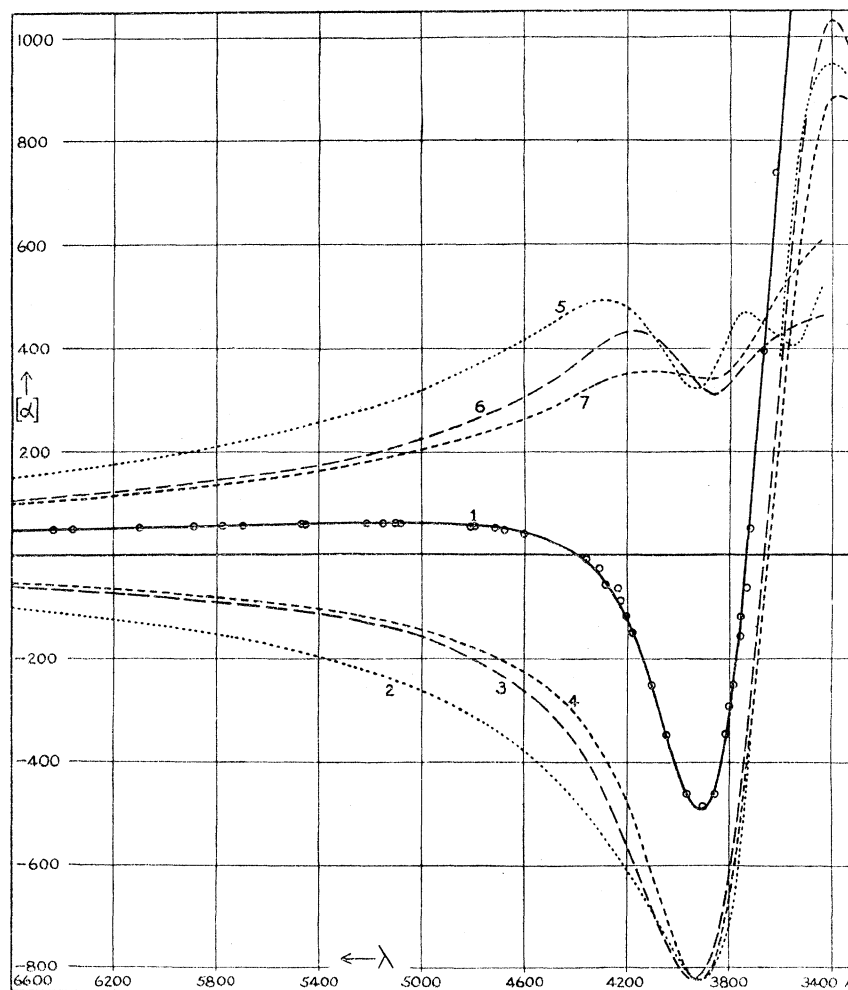


FIG. 21.—Rotatory dispersion of *d*-bornyl dixanthogenide.

- 1 = Experimental curve; 2 = Theoretical curve calculated from equation (vi); 3 = Theoretical curve calculated from equation (vii); 4 = Theoretical curve calculated from equation (viii); 5 = Difference curve (curve 1 minus curve 2); 6 = Difference curve (curve 1 minus curve 3); 7 = Difference curve (curve 1 minus curve 4).

rotatory dispersion was deduced on exactly the same lines as that used by KUHN and BRAUN. Thus, on page 287 of their paper, KUHN and BRAUN give the rotation produced by an optically active absorption band in the form

$$\phi = \frac{1}{2\pi} \frac{\nu^2}{\nu_0} g_0 \varepsilon_{\max} \int_{-\infty}^{+\infty} \frac{e^{-\left(\frac{\nu_0 - \nu_1}{\theta}\right)}}{\nu_1^2 - \nu^2} d\nu_1,$$

in which is incorporated their absorption equation

$$\varepsilon = \varepsilon_{\max} e^{-\left(\frac{\nu_0 - \nu}{\theta}\right)^2}.$$

In place of this we have introduced the modified absorption equation (iv), namely,

$$\varepsilon = \varepsilon_{\max} e^{-\left[\frac{\nu_0}{\nu} \left(\frac{\nu_0 - \nu}{\theta}\right)\right]^2}.$$

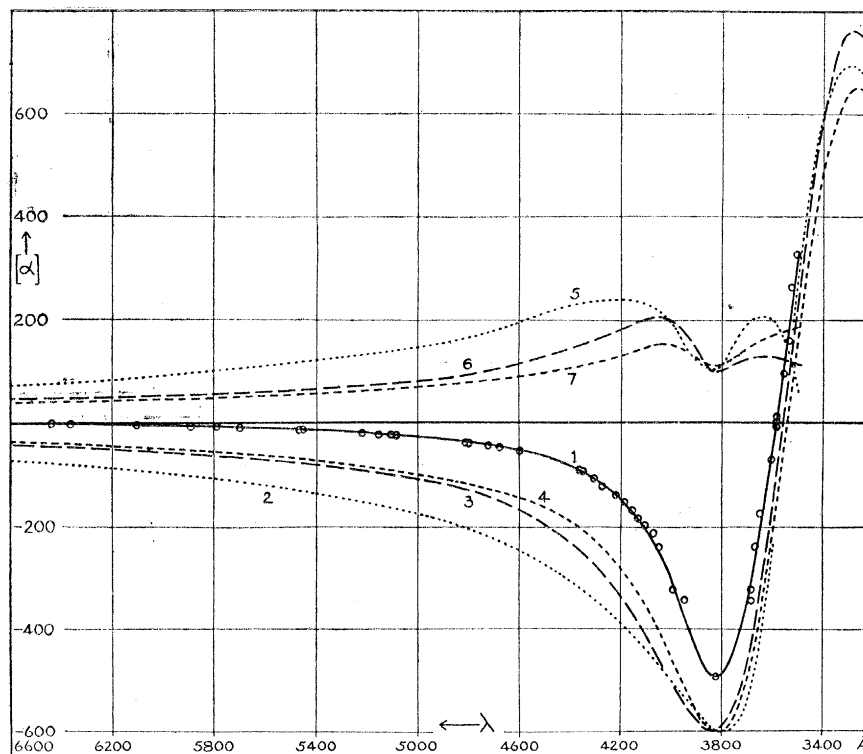


FIG. 22.—Rotatory dispersion of methylene *d*-bornyl xanthate.

- 1 = Experimental curve; 2 = Theoretical curve calculated from equation (vi); 3 = Theoretical curve calculated from equation (vii); 4 = Theoretical curve calculated from equation (viii); 5 = Difference curve (curve 1 minus curve 2); 6 = Difference curve (curve 1 minus curve 3); 7 = Difference curve (curve 1 minus curve 4).

The expression for the rotation then becomes

$$\phi = \frac{1}{2\pi} \frac{\nu^2}{\nu_0} g_0 \varepsilon_{\max} \int_{-\infty}^{+\infty} \frac{e^{-\left[\frac{\nu_0}{\nu_1} \left(\frac{\nu_0 - \nu_1}{\theta}\right)\right]^2}}{\nu_1^2 - \nu^2} d\nu_1.$$

By applying KUHN and BRAUN'S method of analysis, the expression for the molecular rotation becomes

$$[M] = \frac{[\Phi]}{m} \frac{\nu}{\nu_0} \left[e^{-\left[\frac{\nu_0}{\nu} \left(\frac{\nu_0 - \nu}{\theta}\right)\right]^2} \int_0^{\frac{\nu_0}{\nu} \left(\frac{\nu_0 - \nu}{\theta}\right)} e^{x^2} dx + \frac{\nu \theta}{2\nu_0 (\nu_0 + \nu)} \right] \dots \quad (\text{viii})$$

where m is the maximum value of the terms inside the bracket. For values of ν far removed from ν_0 the factor $\frac{\nu_0}{\nu} \left(\frac{\nu_0 - \nu}{\theta} \right)$ is large, and therefore the first term in the bracket of equation (viii) is approximately $\frac{\nu\theta}{2\nu_0(\nu_0 - \nu)}$. The whole expression thus reduces to

$$[M] = \frac{[\Phi]}{m} \frac{\nu}{\nu_\phi} \left[\frac{\nu\theta}{2\nu_0(\nu_0 - \nu)} + \frac{\nu\theta}{2\nu_0(\nu_0 + \nu)} \right]$$

$$= \frac{[\Phi]}{m\nu_\phi} \left[\frac{\nu^2\theta}{(\nu_0^2 - \nu^2)} \right] = \text{const.} \frac{\nu^2}{\nu_0^2 - \nu^2} = \frac{\text{const.}}{\lambda^2 - \lambda_0^2}.$$

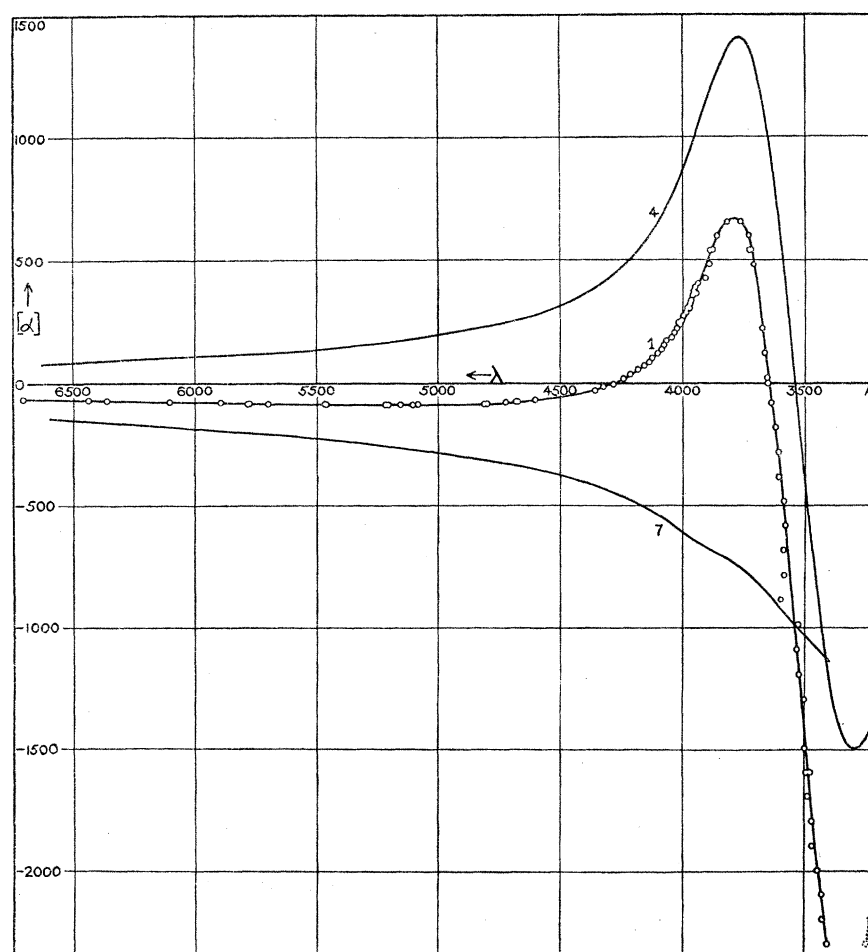


FIG. 23.—Rotatory dispersion of methyl *l*-menthyl xanthate.

1 = Experimental curve; 4 = Theoretical curve calculated from equation (viii); 7 = Difference curve (curve 1 minus curve 4).

Thus, for wave-lengths far removed from the absorption band, the modified expression (viii), like KUHN and BRAUN'S equation, becomes identical with DRUDE'S equation.

The rotatory contributions of the first absorption band were calculated by means of this equation, the value of $[\Phi]$ being chosen so that the first maximum was of the same magnitude as in the two previous analyses. These values are shown graphically as curves 4 in figs. 19 to 27. The difference curves 7, representing the rotatory contributions of further ultra-violet bands, were obtained by subtracting curves 4 from the

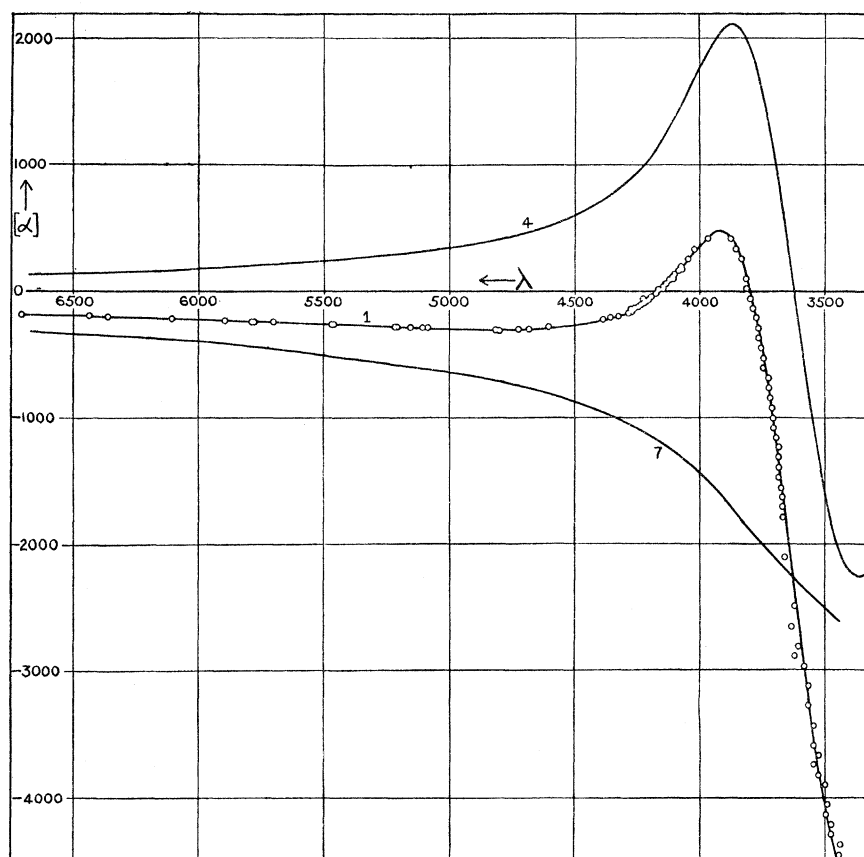


FIG. 24.—Rotatory dispersion of *l*-menthyl dixanthogenide.

1 = Experimental curve; 4 = Theoretical curve calculated from equation (viii); 7 = Difference curve (curve 1 minus curve 4).

experimental curves 1. These difference curves exhibit only slight ripples in the region of the first absorption band, thus showing that the above expression represents the partial rotation for the first xanthate band more accurately than either of the foregoing expressions. The elimination of the partial rotations for the first absorption band was particularly effective for the three menthyl xanthates, figs. 23–25, where direct measurements of circular dichroism were already available when the mathematical analysis of the curves was begun, so that the constants of the equation could be calculated from them. But we were not able to secure any improvement in the curves for the bornyl xanthates by making use of our subsequent measurements of the circular

dichroism of these compounds. The loop which has to be eliminated is indeed so dramatic, and the partial rotations in the region of absorption are so large and so difficult to measure accurately, that a complete smoothing of the curve is an almost unattainable ideal. The close proximity of a second optically active absorption band is also a disturbing factor, which may intrude to different extents in the different compounds of this series. Thus the second maximum due to the partial rotation of the first absorption band was realized experimentally only in methyl and methylene menthyl xanthates, since in the other compounds the overlapping of the second

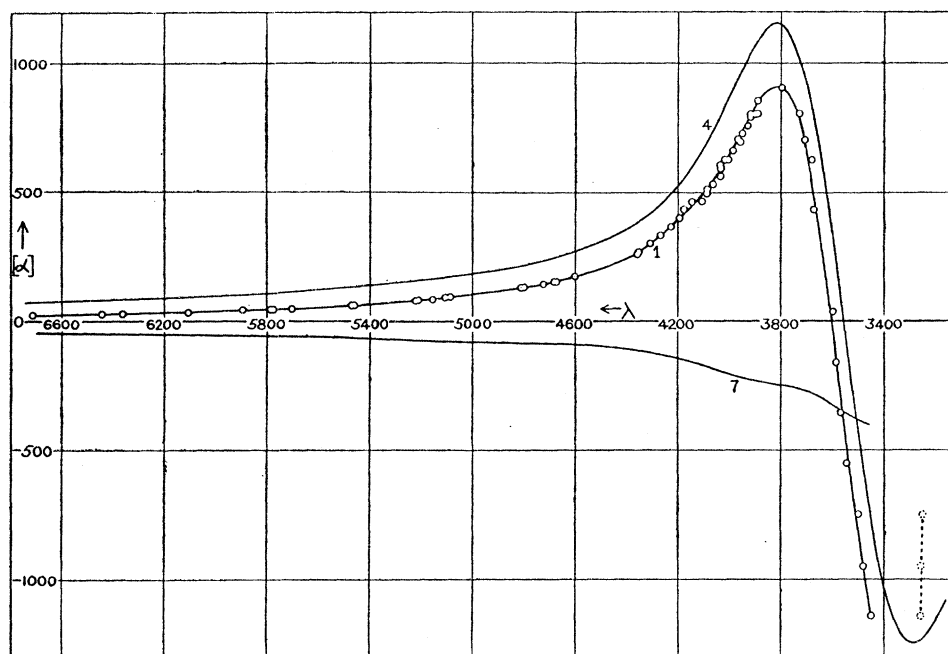


FIG. 25.—Rotatory dispersion of methylene *l*-menthyl xanthate.

1 = Experimental curve; 4 = Theoretical curve calculated from equation (viii); 7 = Difference curve (curve 1 minus curve 4).

absorption band prevented the measurements of rotatory power from being carried to a sufficiently short wave-length to reach this maximum. When this limitation was overcome by using excessively dilute solutions of methyl-*d*-bornyl xanthate, indications were obtained that the maximum had been converted into a mere step-out by the overlapping of a second partial rotation, which in this region is of the same sign as that for the first absorption band. Since measurements of circular dichroism also indicated that the overlapping of the two optically active bands was less in the menthyl than in the bornyl xanthates, it seems likely that the residual ripples in the curves for the other compounds may have been due to the overlapping of two contiguous bands. We therefore regard the results recorded in figs. 23 and 25 as sufficient evidence of the merits of our new equation and do not attach much importance to the ripples which are still left on the other curves.

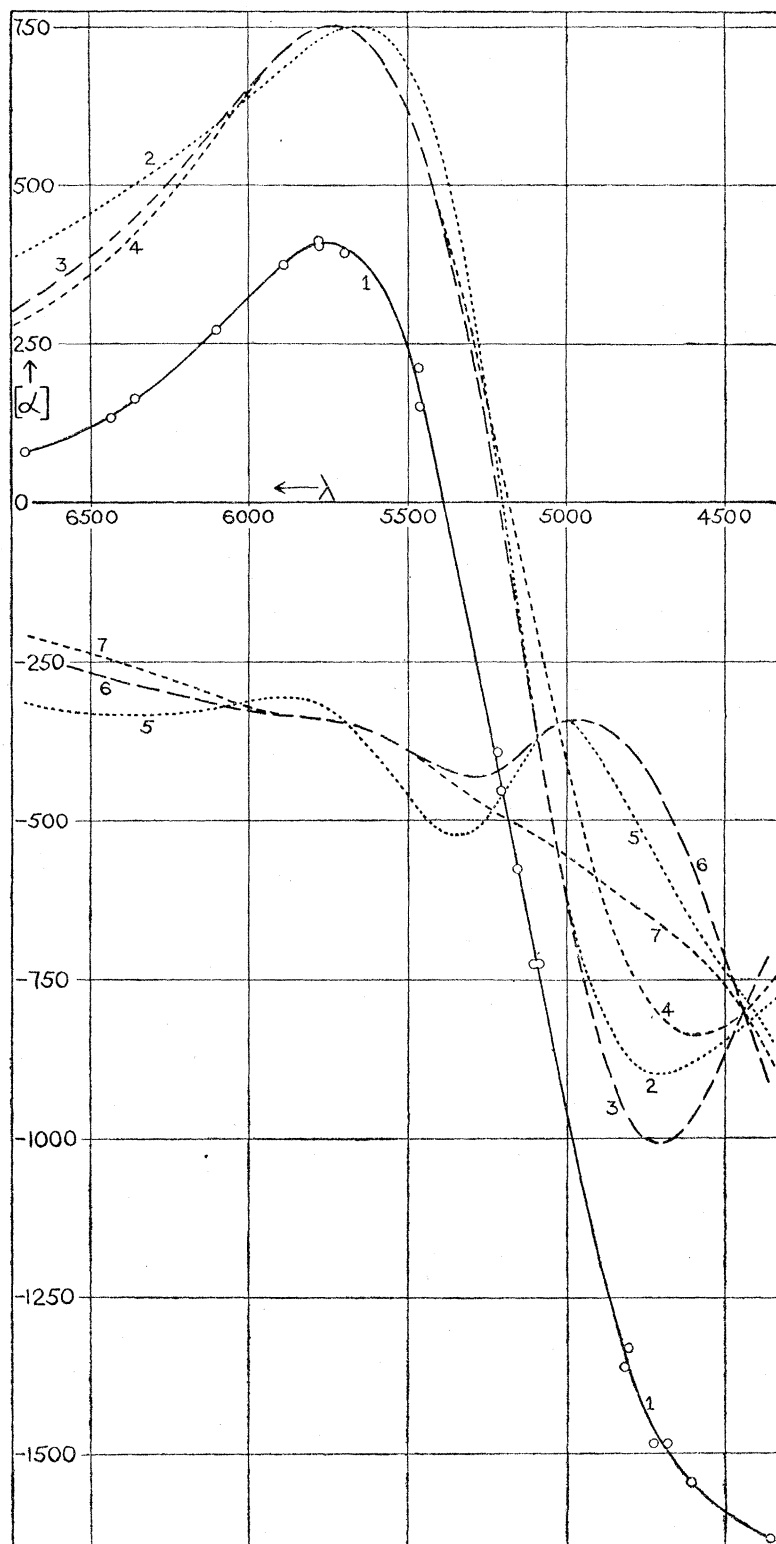
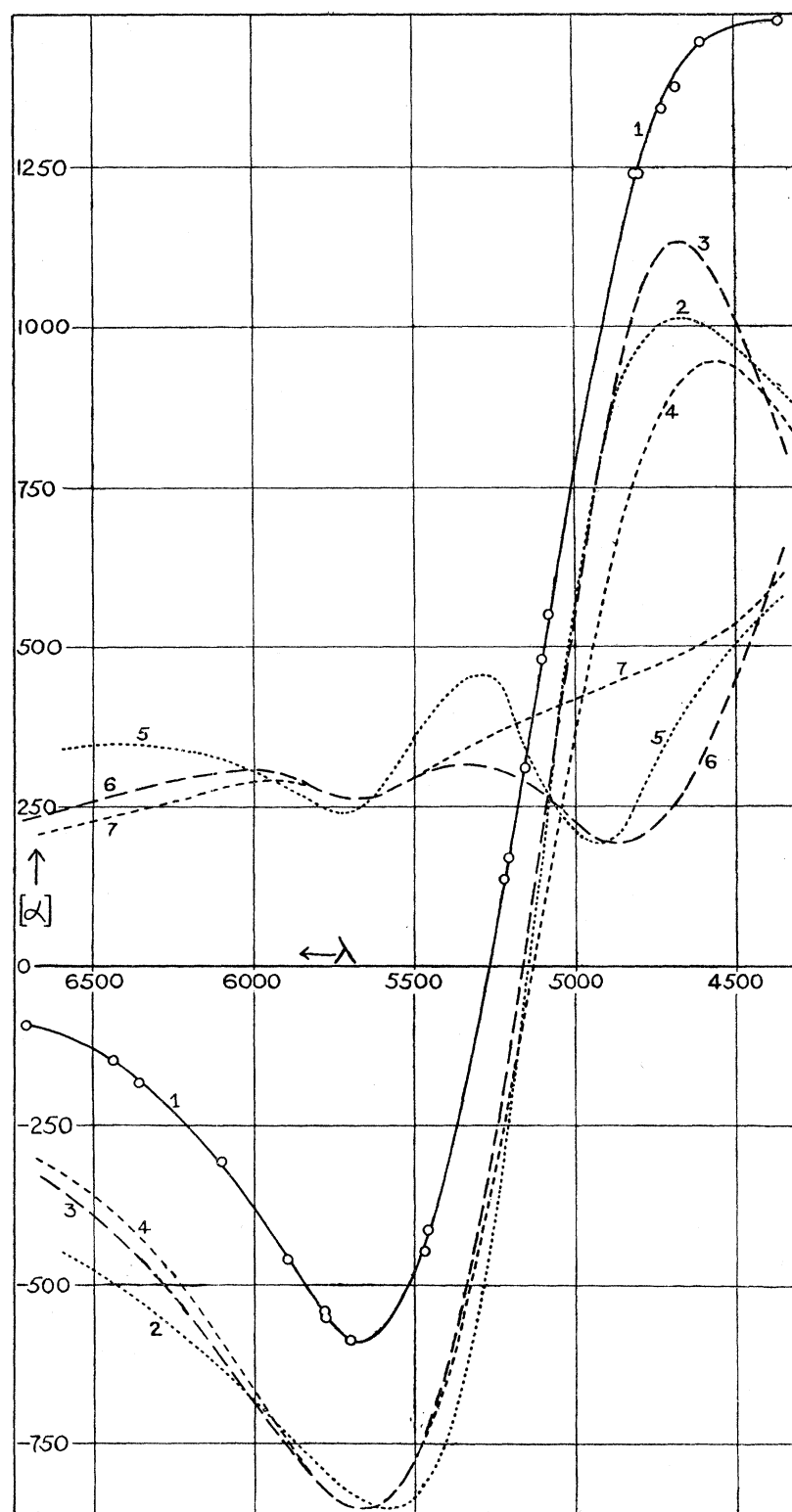


FIG. 26.—Rotatory dispersion of diphenyl *d*-bornyl dithiourethane.

- 1 = Experimental curve; 2 = Theoretical curve calculated from equation (vi); 3 = Theoretical curve calculated from equation (vii); 4 = Theoretical curve calculated from equation (viii); 5 = Difference curve (curve 1 minus curve 2); 6 = Difference curve (curve 1 minus curve 3); 7 = Difference curve (curve 1 minus curve 4).

FIG. 27.—Rotatory dispersion of diphenyl *l*-menthyl dithiourethane.

- 1 = Experimental curve; 2 = Theoretical curve calculated from equation (vi); 3 = Theoretical curve calculated from equation (vii); 4 = Theoretical curve calculated from equation (viii); 5 = Difference curve (curve 1 minus curve 2); 6 = Difference curve (curve 1 minus curve 3); 7 = Difference curve (curve 1 minus curve 4).

Summary.

(a) Measurements have been made of the absorption, circular dichroism and rotatory dispersion of a series of 9 bornyl and menthyl xanthates and related compounds, which had been prepared and partially investigated by TSCHUGAEFF.

(b) The seven xanthates show two absorption bands, the weaker band at longer wave-lengths being attributed to the —CS—S group and the stronger band at shorter wave-lengths to the >CS group. These bands cannot be represented by the equations of KETTELER and HELMHOLTZ, BIELECKI and HENRI, or KUHN and BRAUN, but conform closely to a new equation which has been developed to express the fact that the absorptions are symmetrical on a scale of wave-lengths.

(c) The circular dichroism in the first absorption band follows a similar course to the absorption, the “dissymmetry factor,” $(\epsilon_r \sim \epsilon_l)/\epsilon$, being approximately proportional to the frequency. Since, however, the circular dichroism of the second band is of opposite sign, this proportionality disappears where the two bands begin to overlap.

(d) The anomalous rotatory dispersion of the xanthates in the region of transparency can be expressed with great exactness by two terms of DRUDE’s equation, namely, a low-frequency term to represent the partial rotation of the first absorption band, and a high-frequency term of opposite sign to represent the combined effect of the second absorption band and of the hypothetical bands in the SCHUMANN region. Alternatively, a separate term can be used to represent the partial rotation of the second absorption band, and an inverse square term of the form k/λ^2 (with a zero value for the smaller dispersion constant, as in DRUDE’s equation for quartz) to represent the partial rotations of the bands in the SCHUMANN region.

(e) The anomalies of rotatory dispersion in the region of absorption cannot be expressed by the equations of NATANSON, or of KUHN and BRAUN, but have been represented in a more satisfactory manner by means of a new equation, corresponding with the new equations used to represent the absorption and circular dichroism of the band.
