146. *The Rotatory Dispersion and Circular Dichroism of* l-*Menthyl* d-β-*Chloro*-β-*nitrosobutyrate.*

By Stotherd Mitchell and George K. Simpson.

The absorption spectrum of *l*-menthyl *d*-β-chloro-β-nitrosobutyrate (in alcoholic solution) shows a double band near the middle of the visible spectrum due to the nitroso-group. We have made measurements of rotation and circular dichroism in the neighbourhood of this band.

When molecular extinction coefficients ε and circular dichroism $(\varepsilon_l - \varepsilon_r)$ are plotted against wave-length, the curves obtained are very similar in form and each can be represented as the sum of two probability curves. The anisotropy factors $(\varepsilon_l - \varepsilon_r)/\varepsilon$ found from the corresponding component curves have the same maximum value. Using Lowry and Hudson's modification of an equation formulated by Kuhn, we have calculated partial rotations from the two circular dichroism components, and when the sum of these is subtracted from the experimental rotation curve a difference curve is obtained in which the anomaly due to the nitroso-group is completely smoothed out.

It is well known that the introduction of a chromophoric group into an optically active molecule impresses a characteristic form on its rotatory dispersion curve. The partial rotation due to such a group can be separated from the total rotation of the molecule by mathematical analysis. Bruhat (*Ann. Physique*, 1915, **3**, 442) was the first to attack this problem, but the equations he used were not very accurate. Better results were obtained by Kuhn and his collaborators (*Z. physikal. Chem.*, 1930, *B*, **8**, 281; 1931, *B*, **15**, 59; 1932, *B*, **18**, 32; 1935, *B*, **29**, 1, 256) who investigated a number of substances containing the groups N_3, ONO, Ph, Cl, Br, and I. At first they employed an equation which took into consideration the form of the absorption curve expressed as a probability distribution of frequencies, but afterwards they made use of circular dichroism data treated in the same way. Lowry and Hudson (*Phil. Trans.*, 1933, *A*, **232**, 117) pointed out that absorption curves are never quite symmetrical when plotted on a frequency scale, but many show more perfect symmetry if wave-lengths are used in place of frequencies. The same is also true of circular dichroism curves. By suitable modification of Kuhn's equation they obtained very striking results with a number of xanthates in the neighbourhood of the CS·S band. When the equation was extended to compounds with CHO and CO groups, however, the results were not so convincing (J., 1933, 1179; 1935, 696, 709). Mitchell and Gordon (J., 1936, 853) used the same equation in connection with the nitro-group, but the residual curve obtained was not free from ripples. We have now applied the equation with more success to a substance containing the nitroso-group, *viz.*, l-*menthyl* d-β-*chloro*-β-*nitrosobutyrate.*

Experimental.

Preparation of l-*Menthyl* d-β-*Chloro*-β-*nitrosobutyrate*, $CH_3{\cdot}CCl(NO){\cdot}CH_2{\cdot}CO_2C_{10}H_{19}$.—Menthyl acetoacetate, prepared by heating ethyl acetoacetate with menthol (Rupe, *Annalen*, 1912, **395**, 87), was treated with hydroxylamine hydrochloride and sodium acetate in aqueous alcohol, and after the alcohol had been distilled off the oxime was obtained as a yellow oil. It was dissolved in concentrated hydrochloric acid, and sufficient water added to form an oily suspension. This was kept at about 0°, and chlorine passed in with occasional shaking. A blue solid formed; after being separated, washed with water, and dried, it had m. p. 58—60°. It crystallised from alcohol in blue needles, but the m. p. rose considerably with successive crystallisations: after the seventh, it remained constant at 71° (Found: C, 58·1; H, 8·2; N, 5·0; Cl, by Stepanow's method, 11·9. $C_{14}H_{24}O_3NCl$ requires C, 58·0; H, 8·3; N, 4·8; Cl, 12·2%).

Kägi (*Annalen*, 1920, **420**, 68) records that the m. p. of *l*-menthyl benzylacetoacetate similarly increased with fractional crystallisation, and after examining the rotations of his initial and his final product he concluded that the former was the *dl*-benzylacetoacetate and the latter the *l*-ester. In our case we took readings of both rotation and ellipticity in alcoholic solution for sodium light (c = 0·6500 g./100 c.c.; l = 6 cm.; t = 18°) and found:

	α_{5893}.	Ellipticity.
Initial product (m. p. 58—60°)	−0·43°	+ (just detectable)
Final product (m. p. 71°)	−1·39	+1·41°

From these data we concluded that our final product was 1-*menthyl* d-β-*chloro*-β-*nitrosobutyrate.*

Absorption Spectrum.—The absorption due to the nitroso-group was examined photographically with a Spekker spectrophotometer, a 1 cm. column of a 0·0774M-solution in alcohol being used. In Fig. 1 the molecular extinction coefficient, ε, is plotted against wave-length λ (full line). The curve shows two overlapping bands conveniently situated near the middle of the visible spectrum.

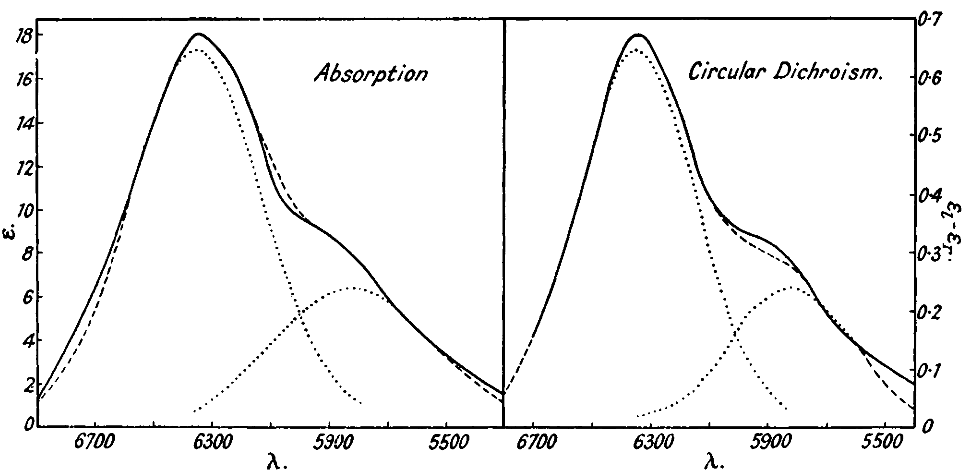

FIG. 1.

Rotatory Dispersion.—The rotation measurements were made visually with a spectropolarimeter constructed from a Hilger polarimeter and a Zeiss–Winkel monochromator. A 100 c.p. Pointolite lamp served as light source. Readings taken at intervals between 6800 A. and 4800 A. are set out in Table I, and the rotatory dispersion curve is shown in Fig. 2 (full line).

TABLE I.

Rotatory Dispersion in Alcohol.

(c = 0·6500 g./100 c.c.; t = 18°.)

λ.	α.	[α].	λ.	α.	[α].	λ.	α.	[α].
				l = 6 cm.				
4800	−1·02°	−261·5°	5500	−1·47°	−376·9°	5900	−1·38°	−353·8°
4900	−1·07	−274·4	5600	−1·60	−410·2	6000	−1·33	−341·0
5000	−1·09	−279·5	5660	−1·62	−415·4	6100	−1·28	−328·2
5200	−1·17	−300·0	5700	−1·61	−412·8	6200	−1·05	−269·3
5400	−1·37	−351·3	5800	−1·51	−387·2	6300	−0·21	− 53·8
				l = 2 cm.				
6400	+0·28°	+215·4°	6600	+0·63°	+484·6°	6800	+0·46°	+353·9°
6500	+0·55	+423·2	6700	+0·56	+430·8			

Circular Dichroism.—Ellipticity readings were taken with the spectropolarimeter used for the rotation measurements but with a $\lambda/4$ attachment added behind the Lippich polarising system (cf. Mitchell and Cormack, J., **1932**, 415). The results are set out in Table II, and the circular dichroism curve is shown in the right-hand section of Fig. 1 (full line).

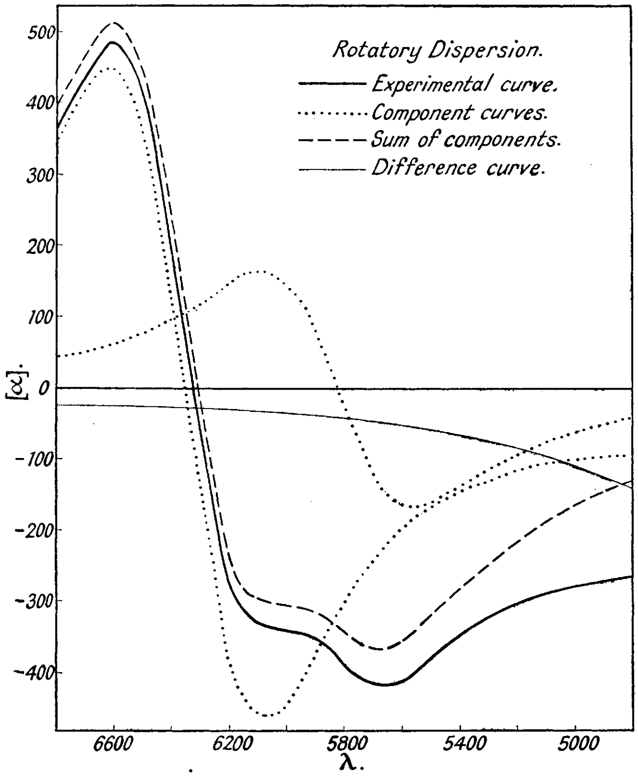

FIG. 2.

TABLE II.

Circular Dichroism in Alcohol.

Solutions : (*a*) 0·6500 g./100 c.c. ; l = 6 cm. ; t = 18°.
(*b*) 0·6440 g./100 c.c. ; l = 2 cm. ; t = 18°.

	λ.	Ellipticity.	$\epsilon_l - \epsilon_r$.	λ.	Ellipticity.	$\epsilon_l - \epsilon_c$.	λ.	Ellipticity.	$\epsilon_l - \epsilon_r$.
(*a*)	5200	+0·27°	+0·061	5600	+0·63°	+0·142	5900	+1·48°	+0·333
	5400	+0·35	+0·079	5700	+0·86	+0·194	6000	+1·52	+0·342
	5500	+0·51	+0·115	5800	+1·20	+0·270	6100	+1·75	+0·394
(*b*)	6200	+0·77	+0·525	6400	+0·95	+0·648	6600	+0·45	+0·307
	6300	+0·95	+0·648	6500	+0·66	+0·450	6700	+0·22	+0·150

DISCUSSION.

Analysis of the Curves of Absorption and Circular Dichroism.—The absorption curve was assumed to consist of two components of the type given by the equation :

$$\varepsilon = \varepsilon_{\text{max.}}\, e^{-[(\lambda - \lambda_0)/\theta]^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

λ_0 is the wave-length corresponding to $\varepsilon_{\text{max.}}$, and θ is defined by $\lambda' = 1{\cdot}6651\ \theta$ where λ' is the half-width of the band. These component curves are shown dotted in Fig. 1. For the larger curve $\varepsilon_{\text{max.}} = 17{\cdot}2$, $\lambda_0 = 6350$, $\theta = 324$, and for the smaller, $\varepsilon_{\text{max.}} = 6{\cdot}35$, $\lambda_0 = 5820$, $\theta = 396$. The sum of these two curves is shown as a broken line, which is in good agreement with the full-line experimental curve.

For the analysis of the circular dichroism curve we used the corresponding equation:

$$(\varepsilon_l - \varepsilon_r) = (\varepsilon_l - \varepsilon_r)_{\text{max.}} e^{-[(\lambda - \lambda_0)/\theta]^2} . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

with $(\varepsilon_l - \varepsilon_r)_{\text{max.}} = 0{\cdot}650$ at 6350 A. and 0·240 at 5820 A. for the larger and smaller components respectively, and $\theta = 300$ in each case. The agreement between the addition curve (broken line) and the experimental curve (full line) is again quite good.

Anisotropy Factor.—Table III gives values of ε and $(\varepsilon_l - \varepsilon_r)$ obtained from each of the component curves for a number of wave-lengths. From these the anisotropy factor $(\varepsilon_l - \varepsilon_r)/\varepsilon$ is calculated. It will be seen that in the middle of each band the factor has the same value (0·038). It falls away considerably from this maximum value in the case of the smaller band, but remains more constant within the larger band.

TABLE III.

Large band.				Small band.			
λ.	ϵ.	$\epsilon_l - \epsilon_r$.	$(\epsilon_l - \epsilon_r)/\epsilon$.	λ.	ϵ.	$\epsilon_l - \epsilon_r$.	$(\epsilon_l - \epsilon_r)/\epsilon$.
5950	3·74	0·110	0·029	5420	2·30	0·041	0·018
6050	7·30	0·239	0·033	5520	3·58	0·088	0·025
6150	11·75	0·417	0·035	5620	4·92	0·154	0·031
6250	15·63	0·582	0·037	5720	5·96	0·215	0·036
6350	17·20	0·650	0·038	5820	6·35	0·240	0·038
6450	15·63	0·582	0·037	5920	5·96	0·215	0·036
6550	11·75	0·417	0·035	6020	4·92	0·154	0·031
6650	7·30	0·239	0·033	6120	3·58	0·088	0·025
6750	3·74	0·110	0·029	6220	2·30	0·041	0·018

Calculation of Partial Rotations from Circular Dichroism.—The contributions to the rotatory dispersion curve associated with each of the component circular dichroism curves were calculated by means of the equation

$$[\alpha] = \frac{[\phi]}{m} \frac{\lambda_\varphi}{\lambda} \left[e^{-[(\lambda - \lambda_0)/\theta]^2} \int_0^{(\lambda - \lambda)/\theta} e^{x^2} dx + \frac{\theta}{2(\lambda + \lambda_0)} \right] \quad . \quad . \quad . \quad . \qquad (3)$$

$[\phi]$ is the maximum value of $[\alpha]$ which occurs at λ_0, m is the maximum value of the terms inside the large brackets, and the other symbols have their usual significance. In Fig. 2 the partial rotation curves are dotted and their sum is shown as a broken line. The difference curve (thin full line) obtained from this and the experimental curve (heavy full line) represents the rotatory dispersion of the rest of the molecule after the partial rotation due to the nitroso-group has been subtracted. In few of the cases so far studied has it been possible to eliminate so completely the anomaly due to a chromophoric group.

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UNIVERSITY OF GLASGOW.

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