

196. *The Rotatory Dispersion and Circular Dichroism of
2 : 2-Dinitrocamphane in the Ultra-violet.*

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OPTICALLY active organic substances containing the groups CO, CS, Ph, Cl, Br, I, N₃, ONO, and NO have been used by a number of observers for studying rotatory dispersion and circular dichroism (see Mitchell, "The Cotton Effect," London, 1933). We have now employed a compound containing the nitro-group. We had intended to use camphor- ψ -nitrol, but as it was too unstable for polarimetric work we examined its oxidation product, 2 : 2-dinitrocamphane.

Rotatory dispersion data for solutions of this substance in alcohol are given in Table I, and specific rotation, $[\alpha]$, is plotted against wave-length, λ , in the figure (curve 1, full line). The rotation falls to a negative maximum at about 3020 A., and thereafter increases, passing through zero at 2762 A. It was not found practicable to follow the curve further into the ultra-violet than 2666 A., owing to the strong absorption beyond this limit.

The absorption was examined with a Hilger sector spectrophotometer, a 2-cm. column of an alcoholic solution containing 0.0390 g./100 c.c. being used. In curve 2 (full line) the molecular extinction coefficient, ϵ , is plotted against wave-length, and the result is similar to that recorded for several aliphatic compounds containing the nitro-group (cf. Goodeve, *Trans. Faraday Soc.*, 1934, **30**, 504; Zelinsky and Rosanoff, *Z. physikal. Chem.*, 1912, **78**, 639).

Table II contains the circular dichroism data, alcohol being again used as solvent. The

TABLE I.

Solutions: (a) 0.1563, (b) 0.6250, (c) 0.3125 g./100 c.c.; $l = 0.99$ cm.; $t = 17^\circ$.

Soln.	λ .	α .	$[\alpha]$.	Soln.	λ .	α .	$[\alpha]$.
(a)	2980	-0.40°	-2586°	(b)	3720	-0.50°	-808°
	2946	-0.35	-2262		3558	-0.60	-970
	2912	-0.25	-1615		3350	-0.70	-1132
	2869	-0.20	-1293		3248	-0.80	-1293
	2833	-0.15	-970	3222	-0.90	-1454	
	2804	-0.10	-647	(c)	3193	-0.50	-1616
	2762	0.00	0		3126	-0.70	-2262
	2706	+0.10	+647		3047	-0.80	-2586
	2689	+0.15	+970				
	2666	+0.20	+1293				

TABLE II.

Concn. = 0.1563 g./100 c.c.; $l = 0.99$ cm.; $t = 17^\circ$.

λ .	Ellipticity.	$\epsilon_l - \epsilon_r$.	ϵ .	$(\epsilon_l - \epsilon_r)/\epsilon$.	λ .	Ellipticity.	$\epsilon_l - \epsilon_r$.	ϵ .	$(\epsilon_l - \epsilon_r)/\epsilon$.
3030	-0.20°	-0.90	101	-0.009	2778	-0.75°	-3.35	283	-0.012
3009	-0.30	-1.34	113	-0.012	2739	-0.75	-3.35	293	-0.011
2972	-0.35	-1.56	138	-0.011	2666	-0.65	-2.91	308	-0.009
2957	-0.40	-1.79	152	-0.012	2644	-0.55	-2.46	311	-0.008
2946	-0.45	-2.01	162	-0.012	2620	-0.50	-2.24	315	-0.007
2920	-0.50	-2.24	189	-0.012	2580	-0.40	-1.79	323	-0.006
2900	-0.55	-2.46	210	-0.012	2550	-0.35	-1.56	338	-0.005
2885	-0.65	-2.91	227	-0.013					

molecular ellipticity (col. 3) is given by $\epsilon_l - \epsilon_r = (4\tau \times 0.4343)/lc$, where τ is the observed ellipticity expressed in radians, l the length of tube in cm., and c the concentration in g.-mols./litre. When the molecular ellipticity is plotted against wave-length, a symmetrical curve is obtained (curve 3, full line) which has a negative maximum at 2770 A., very close to where the rotation curve crosses the axis. Values of ϵ shown in col. 4 of Table II were read off from the absorption curve for the required wave-lengths. The last column contains the dissymmetry factor $(\epsilon_l - \epsilon_r)/\epsilon$, which is fairly constant down to 2778 A., after which it decreases.

This constancy of the dissymmetry factor over the long-wave portion of the absorption band suggests that the selective absorption due to the nitro-groups covers the same wave-length range as the ellipticity. Furthermore, the form of the rotatory dispersion curve indicates that it is controlled to a great extent by the same absorption band. It is possible to test these assumptions in the following manner.

The molecular ellipticity may be expressed by the equation

$$(\epsilon_l - \epsilon_r) = (\epsilon_l - \epsilon_r)_{\max} e^{-[(\lambda - \lambda_0)/\theta]^2} \quad (1)$$

which is essentially that used by Kuhn and Szabo (*Z. physikal. Chem.*, 1931, *B*, 15, 63), but with wave-lengths substituted for frequencies. In this equation, the parameter θ is defined by $\lambda' = 1.6651\theta$, where λ' is the half-width of the band. The values $(\epsilon_l - \epsilon_r)_{\max} = -3.37$, $\lambda' = 400$ A., and $\lambda_0 = 2770$ A. are read from the full-line curve 3, and equation (1) then gives the broken curve 3.

The form of the rotatory absorption band may now be calculated from the parameters λ_0 and θ , obtained from the curve of circular dichroism, using the equation

$$\epsilon = \epsilon_{\max} e^{-[(\lambda - \lambda_0)/\theta]^2} \quad (2)$$

(cf. Kuhn and Braun, *Z. physikal. Chem.*, 1930, *B*, 8, 281; Lowry and Hudson, *Phil. Trans.*, 1933, *A*, 232, 117).

Since the dissymmetry factor remains constant at 0.012 over the long-wave side of the absorption band (Table II), it follows that ϵ_{\max} must have a value very near to $3.37/0.012 \approx 280$, and the broken curve 2 can now be calculated.

Finally, an approximate calculation of the contribution of the nitro-groups to the rotatory dispersion of the molecule may be made by means of equation (3), which is a modi-

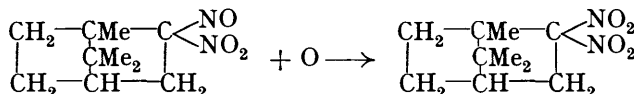
fication by Lowry and Hudson (*loc. cit.*) of an equation formulated by Kuhn and Braun (*loc. cit.*) :

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

where $[\phi]$ = maximum value of $[\alpha]$ which occurs at wave-length λ_ϕ , m = maximum value of the terms within the large brackets, λ_0 and θ have values as above, and the other symbols have their usual significance. The result is shown as the broken curve 1, and it is clear from the figure that the difference curve (not shown) obtained from this and the full-line curve 1 must cross the axis of zero rotation at several points, so that it is not possible to decide whether the residual rotation should be regarded as positive or negative. The ripples in the residual curve are probably due partly to experimental error and partly to the approximate nature of equation (3). Similar results have been obtained by Hudson, Wolfrom, and Lowry (J., 1933, 1189) with tetra-acetyl μ -arabinose, and by Baldwin, Wolfrom, and Lowry (J., 1935, 700) with penta-acetyl μ -fructose. In the present case it would appear that the contribution of the nitro-groups accounts for essentially the whole of the observed rotation.

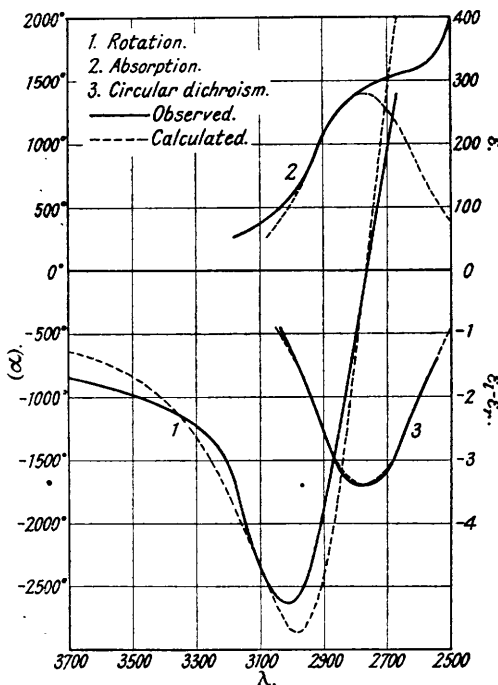
EXPERIMENTAL.

Preparation of 2 : 2-Dinitrocamphane. — Charlton, Earl, Kenner, and Luciano (J., 1932, 37) observed that when camphor- ψ -nitrol was freshly prepared it melted at 60°, but on standing over-night the m. p. fell to 52°. We found that the blue nitrol readily absorbs oxygen and loses its colour. By exposing a quantity of the nitrol to the air on a porous plate, a camphor-like product was obtained which, after being crystallised several times from aqueous alcohol, had m. p. 107.5—108.5° (Found : C, 53.0; H, 7.0; N, 12.5. C₁₀H₁₆N₂O₄ requires C, 52.6; H, 7.0; N, 12.3%), and was concluded to be 2 : 2-dinitrocamphane :



Apparatus.—For measuring the rotations, an ultra-violet polarimeter of the type described by Kuhn (*Ber.*, 1929, 62, 1727) was constructed. The optical parts and graduated circles were obtained from Messrs. Adam Hilger, Ltd., the castings for the iron bed and standards were made from patterns prepared in our workshop, and the instrument was assembled by Mr. Robert McCulloch.

A simple Rochon prism of left-handed quartz, 4 cm. long and 2 × 2 cm. aperture, served as analyser. The polariser was made from a right-handed quartz prism of the same dimensions and had a fixed half-shadow angle of 5°. Both polariser and analyser were provided with a graduated circle, and each was mounted as a separate unit which could be moved as required on the slides of the iron bed. The condensing lens fitted in front of the polariser was a plano-convex quartz lens of 5" focal length, and the projection lens fitted behind the analyser was an achromatic quartz fluorite doublet of focal length 8.27". As light source we used an iron arc with a current of 3 amps., the coil of an electromagnet being inserted in the circuit to steady the arc as recommended by Houstoun ("Treatise on Light," London, 1930, p. 250). The arc was focused on a small circular hole in a metal screen by means of a plano-convex quartz lens of 1.5" focal



length. End pieces for the observation tube were made from selected pieces of fused silica, free from strain, supplied by The Thermal Syndicate, Ltd.

The polarimeter was used in conjunction with a Hilger medium quartz spectrograph. Only the ordinary rays from the polariser were allowed to enter the observation tube (cf. Lowry and Gore, *Proc. Roy. Soc.*, 1932, *A*, **135**, 13), and only the ordinary rays from the analyser were permitted to pass into the spectrograph, the dividing line of the polariser being focused with the projection lens across the centre of the slit and the height of the slit being adjusted to 4 mm. by means of a V-shaped slide. After the zero had been determined, a series of photographs was taken for different positions of the analyser, and the wave-lengths were found for which the contiguous parts of each photograph had equal intensity. Ilford Iso-Zenith plates (H and D 650) were used throughout, and the exposures were varied from 2 to 40 minutes, depending on the amount of absorption of the light at the point of interest on the plate.

For measuring the ellipticities, we used the method of Kuhn and Braun (*Z. physikal. Chem.*, 1930, *B*, **8**, 445), in which a Fresnel rhomb was placed between the polariser and the observation tube. Different settings were given to the polariser, and the wave-lengths for which these gave equal intensity were found from a photographic plate in the same way as for the rotations. Kuhn and Braun constructed a rhomb suitable for use in the ultra-violet by fitting a brass case of the required shape with windows of fused silica and then filling it with water, but as fused silica of optical quality is now available (cf. Lowry and French, *J.*, 1932, 2654), our rhomb was made of this material; it had an aperture 1.7×1.7 cm., and an angle of $51^\circ 47'$ which was calculated from Fresnel's equation (*Ann. Chim. Phys.*, 1831, **46**, 256) by using the value $n_{2743} = 1.4964$ for fused silica. The rhomb was inserted after the polariser, and optical alinement was then restored by raising the optical train from the rhomb to the light source. To facilitate this, the tubular bearing for the graduated circle of the polariser passed through a block which could be raised between vertical guides by means of a screw, the rhomb holder being slid into grooves at the back of the block.

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