## 50. *The Rotation Dispersion and Circular Dichroism of Bornylene Nitrosite.*

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THE interesting results which followed from a study of the blue nitrosites of caryophyllene and humulene (Mitchell, J., 1928, 3258; 1930, 1829) made it desirable to extend this line of research. We turned first to other nitrosites which could be obtained in an optically active form, in the hope that they would show circular dichroism : those of bornylene, phellandrene, and zingiberene seemed promising, and a quantity of each was prepared. They are white crystalline solids which dissolve in organic solvents to give practically colourless solutions at room temperature. On warming, solutions of bornylene nitrosite develop a blue colour which deepens as the temperature is raised ; up to 70° no appreciable decomposition takes place, and the solution loses its colour again on cooling. Several nitroso-compounds have been found to behave in this way (compare Piloty, *Ber.*, 1902, 35, 3092), the colour being attributed to dissociation of white double molecules into blue single ones. Henderson and Heilbron (J., 1911, 99, 1897) determined the molecular weight of bornylene nitrosite by the elevation of the boiling point of acetone and obtained an average value of 379. $(C_{10}H_{16}O_3N_2)_2$ requires 424, so the amount of dissociation is small at 56°. The phellandrene and zingiberene nitrosites give solutions which, in comparison with those of the bornylene compound, are much less stable towards heat, and do not turn blue appreciably. They were therefore unsuitable for our work.

A toluene solution of bornylene nitrosite was employed for rotation dispersion measurements at 14° and 63°. At the latter temperature the solution is quite blue, whilst at the former it is

practically colourless. The concentration (1·596 g. per 100 c.c. of solution at 14°) was chosen so that with a 6-cm. tube readings could be taken as far into the red as 6700 Å.U. at the higher temperature. The blue solution shows circular dichroism and it was decided to determine what has recently been called the anisotropy factor (Kuhn, *Trans. Faraday Soc.*, 1930, **26**, 299; *Z. physikal. Chem.*, 1930, *B*, **8**, 445). This factor is useful for assessing the suitability

Wave-length, Å.U.
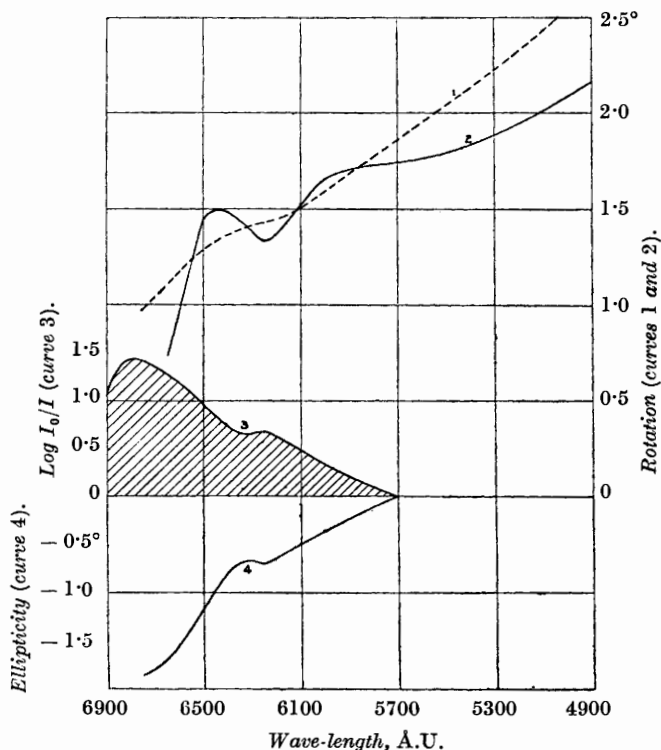
1 *and* 2.   *Rotations at* 14° *and* 63° *respectively.*
3. *Absorption at* 63°.   4. *Ellipticity at* 63°.

of a circularly dichroic substance for asymmetric photochemical experiments. It may be defined as $(\chi_l - \chi_r)/\chi$, where χ_l, χ_r, and χ are respectively the extinction coefficients for left-handed, right-handed, and ordinary light. In practice, it is determined from ellipticity readings and absorption measurements with ordinary light. In the present case these were made with the same solution under the same conditions so the expression given above becomes equal to $4\tau \times 0.4343/\log (I_0/I)$, where τ is the observed ellipticity expressed in radians and I_0/I is the ratio of the intensity of the

incident to that of the emergent light. Log I_0/I is read directly from the photometer scale.

At 14° the solution is just beginning to absorb red light, and in consequence the rotation dispersion curve at this temperature shows a slight irregularity between 6000 and 6700 Å.U. (curve 1). A trace of ellipticity is also present in this region, but it is too small to be measured with any accuracy. At 63° two absorption bands have developed, a weak one with its head about 6250 Å.U. and a stronger one with its head about 6800 Å.U. (curve 3). The influence of these bands on the rotation dispersion (curve 2) and the ellipticity (curve 4) is clearly seen. In the table are given the complete experimental data and also the calculated anisotropy factors. The latter are remarkably constant in the middle of the weak band.

Wave-length, Å.U.	Temp. 14°. Rotation.	Temperature 63°.			
		Rotation.	Ellipticity.	Log I_0/I.	Anisotropy factor.
6700	1·04°	0·38°	—1·81°	1·35	—0·041
6600	1·17	0·93	—1·59	1·20	—0·040
6500	1·29	1·44	—1·18	0·94	—0·038
6400	1·36	1·48	—0·80	0·74	—0·033
6350	1·38	1·44	—0·71	0·69	—0·031
6300	1·41	1·39	—0·69	0·65	—0·032
6250	1·42	1·33	—0·71	0·68	—0·032
6200	1·44	1·36	—0·66	0·63	—0·032
6100	1·52	1·52	—0·50	0·49	—0·031
6000	1·59	1·66	—0·37	0·33	—0·034
5800	1·76	1·72	—0·10	0·10	—0·030
5500	2·04	1·79	—	—	—
5000	2·66	2·08	—	—	—

Additional absorption readings taken at 6900 and 6800 Å.U. gave values for log I_0/I of 1·05 and 1·44 respectively.

EXPERIMENTAL.

Preparation of Bornylene Nitrosite.—The bornylene used for the preparation of the nitrosite was obtained from *l*-borneol by the xanthate method of Tschugaev (*Annalen*, 1912, **388**, 280). The most troublesome part of the process is the decomposition of methyl bornyl xanthate to bornylene. For this stage and the subsequent distillations over sodium, a Pyrex flask was used with a long, wide side-arm fitting directly into a well-cooled receiver. The distillations were carried out under slightly reduced pressure in order to eliminate, as far as possible, the nauseating odour of the sulphur by-products. Four distillations over sodium were necessary. The bornylene was then finally purified with hydrogen peroxide as described by Henderson and Caw (J., 1912, **101**, 1416). The borneol used as starting material showed $[\alpha]_{5790}^{19°} - 37\cdot9°$ ($c = 11\cdot52$ in alcohol), and the bornylene obtained gave $[\alpha]_{5790}^{19°} + 22\cdot8°$ ($c = 7\cdot63$ in light petroleum).

The bornylene nitrosite was prepared by the method of Henderson and Heilbron (*loc. cit.*). After being crystallised several times from acetone, it was obtained as white silky needles, m. p. 163°.

Apparatus.—The rotation measurements were made with a spectro-polarimeter constructed from a Hilger polarimeter and a Hilger constant-deviation spectroscope. Two symmetrical slits were fitted, the one next the polarising prisms having a lateral adjustment. A light source was required which would permit readings to be taken far into the red, and a 1000 c.p. Pointolite lamp was found to be suitable. A mercury-vapour lamp was used for calibration purposes. The light from the Pointolite lamp was condensed directly on the front slit of the spectroscope, whilst that from the mercury-vapour lamp came from the side and was focused on a small totally reflecting prism which could be moved away from the slit when not required.

For ellipticity measurements, we used the method recently described by Bruhat (*Bull. Soc. chim.*, 1930, **47**, 251). This employs a λ/4 plate in conjunction with an ordinary Lippich polarimeter, the plate, mounted in a special holder, being introduced behind the polarising system of the instrument. The type of holder described by Bruhat is very suitable, but we did not fit it with a scale and vernier as recommended because they would have been incon-venient to read when a thermostat was being used with our polari-meter. The ellipticities under consideration do not exceed a few degrees, so we found it better to control the rotation of the λ/4 plate by an arrangement exactly similar to the analyser fine-adjustment and to fit both regulating screws with graduated drums. One division on each drum corresponded to a rotation of 0·012°.

For all measurements, the solution was contained in a 6-cm. glass tube with cemented end pieces. To avoid the use of glass windows in the thermostat, the ends of the tube were held in brass sleeves which passed through rubber stoppers in the walls of the thermostat. Short pieces of rubber tubing, fitting over both sleeves and observation tube, made the arrangement water-tight. The thermostat temperature was controlled by a thermoregulator of the type described by Patterson (*J. Soc. Chem. Ind.*, 1902, **21**, 456).

Measurements of rotation and ellipticity were made in the following way. The spectroscope drum was set for the desired wave-length and a suitable half-shadow angle chosen. Next, the analyser was adjusted to its zero position, the λ/4 plate (λ = 5890 Å.U.) introduced, and its orientation regulated to maintain equal illumination in the triple field. The solution under examination was introduced, the λ/4 plate removed, and a determination of the rotation made in the usual way. The λ/4 plate was then re-introduced, and if the solution exhibited circular dichroism the

equality of the illumination was destroyed. Equality was restored by turning both the λ/4 plate and the analyser in the same direction through the same angle. This angle gives the amount of the ellipticity. In order to determine its sign, the simplest method is to examine a solution of known ellipticity in the apparatus. Alkaline solutions of copper d-tartrate give negative ellipticities and are convenient for this purpose.

The absorption measurements were made with a Hilger–Nutting photometer which was kindly lent to us by Professor E. Taylor Jones, of the Natural Philosophy Department of this University. This was employed along with the constant-deviation spectroscope referred to above. The polarimeter thermostat was adapted for use with this arrangement by fitting an additional tube for the solvent. This could be done easily, since the centres of the two apertures of the photometer were separated horizontally by 38 mm. A 100 c.p. Pointolite lamp was used as light source.