S T U D I E S I N C I R C U L A R D I C H R O I S M

THESIS

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C O N T E N T S

STUDIES IN CIRCULAR DICHROISM.

SECTION I - INTRODUCTION

No attempt to deal in any detail with the phenomena associated with circular dichroism can proceed without reference to the pioneer work of Cotton in this direction, work which has stood the acid test of repetition by practically every investigator in this field. Indeed one of the most recent publications is a repetition of Cotton's work in order to discuss it from a modern theoretical standpoint (23).

It was in 1895-6 that Cotton first published the results of his investigations on the optical properties of complex salts of copper and chromium (4, 5). In particular he found that for sulutions of potassium chromium tartrate and alkaline solutions of copper tartrate an incident plane polarised beam of light emerged not only with its plane of polarisation turned through an angle relative to the plane of incidence, but, in addition the emergent light was elliptical not plane. These effects/

effects Cotton found to be associated with a given absorption band. The optical rotation showed a maximum on one side of the band and a mimimum on the other, the rotation passing through zero at the head of the band, at which point also the ellipticity of the emergent light attained a maximum. These associated phenomena, now termed the "Cotton Effect", may be illustrated by the diagram below:

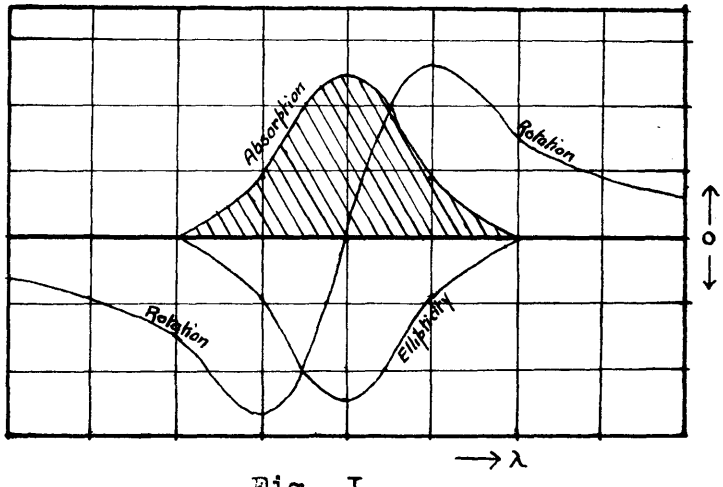


Fig. I

On theoretical grounds and as shown experimentally by Fresnel, ordinary optical rotation is due to the different refractive indices (or speeds) of the two circular components of the plane polarised beam. Cotton suggested that the elliptical polarisation might be explained on the assumption of different absorption coefficients for the two components in addition to their differing refractive indices.

Direct measurement of the two extinction coefficients fully confirmed this hypothesis and to this unequal absorption of the two forms of circularly polarised light the term "circular dichroism" is applied.

The remarkable rotation effects associated with the appearance of circular dichroism inside the absorption band indicated that further investigation along these lines was likely to yield valuable results, and recent developments in photochemistry fully justify this view. In order to explain the occurrence in nature of compounds which rotate the plane of polarisation of light the initial production at some time of an asymmetric compound must be postulated. By extension of the pioneer work of Pasteur and Fischer several methods have been developed for the separation of optically active compounds provided there is an asymmetric agent available at some stage in the process, but these do not furnish any explanation of the ultimate origin of asymmetry. In answer to the problem the "vitalists" maintained that in the enormous asymmetric bias in nature it is indicated that the production and use of single optically active substances is the very prerogative of life itself, and that before life there were no optically active compounds (9, 10).

In contrast to the contention of vitalism it may be postulated/

postulated that the formation of the initial optically active isomer must have occurred by dissymmetrical influences outside all living organisms, and to support this theory some means must be suggested for producing a total asymmetric synthesis. The photochemical action of circularly polarised light is a case in point. If a substance exhibits unequal absorption of the two forms of circularly polarised light (circular dichroism) and is moreover decomposed by light of the wave length for which the dichroism is pronounced, then it is to be expected that different decomposition rates will be obtained on irradiation by the two forms of circularly polarised light.

This idea was first advanced by Van't Hoff (34) and the first systematic investigations were carried out by Cotton in 1896, but although Cotton initiated the experimental attack in this field by a series of brilliant researches ultimate success was denied him, and it was not until 1929 that independent investigators, within a short time of each other, published results which definitely indicated the accomplishment of an asymmetric decomposition by circularly polarised light (16, 25).

The attainment of these positive results represents an enormous advance in stereochemistry and suggests/

suggests that closer examination of the phenomena of circular dichroism is likely to yield valuable results in the solution of many of the problems of optical activity, but any attempt to provide a theoretical basis for the interpretation of rotation phenomena must formulate expressions for the connection between the rotation dispersion and circular dichroism inside a given absorption band. Judged by these standards, the classical theory of optical activity due to Drude requires revision since the Drude function for the rotation dispersion becomes discontinuous at the head of the absorption bands and so cannot provide any quantitative relationship throughout the band. It is true that quantitative relationships have been derived and experimentally verified on this theory for the maximum and minimum of rotation compared to the ellipticity observed, (1), but these are only true for particular points and do not give any continuous relationship. Not the least achievement therefore of very recent theoretical work by Werner Kuhn is the mathematical formulation of quantitative relationships for the absorption, circular dichroism and rotation dispersion inside as well as outside the absorption band (13, 14). The results of measurements on these quantities have been very successfully utilised by Kuhn and his co-workers to confirm the theoretical/

theoretical formulations but so far most of the observations have been taken for wavelengths in the ultra violet and, beyond a very recent reference in Compt, rend., (36, 37), no attempts appear to have been made as yet by other workers to apply the analysis of Kuhn to other substances. It is therefore intended to deal in this thesis more fully with the theory due to Werner Kuhn, particularly with reference to the calculation of curves for rotation dispersion from experimental data for absorption and ellipticity. The work to be described has been carried out mainly towards the red end of the visible spectrum, and will thus provide an interesting test as to whether the formulae applied with such success to absorption bands in the ultra violet will be of equal value for absorption in the red.

There will be given first of all an account of an attempt to extend a former method for the direct determination of the absorption for the two forms of circular light, and this is followed by a description of an improved form of apparatus which was successfully employed to give quantitative measurements for absorption, rotation and circular dichroism throughout the visible spectrum. Observations made with the apparatus for various compounds are given, and the concluding section contains a discussion of the results in relation to the theory of Kuhn.

SECTION 2.

Examination of Ethyl ∝ - bromopropionate.

Circular dichroism is the term applied to the unequal absorption of the two forms of circularly polarised light, which manifests itself by the appearance of an emergent elliptically polarised beam from incident plane polarised light. The magnitude of the effect may therefore be expressed as the difference of the extinction coefficients for right and left circular light, respectively, or as the angle which characterises the ellipticity of the emergent vibration. In the earlier methods employed for the determination of either of these quantities progress was slow, due to the necessity for specially elaborate apparatus before even moderately satisfactory results could be obtained. An improvement towards simplicity of procedure is seen in the method successfully introduced by Mitchell for the study of the circular dichroism of caryophyllene nitrosite (24). This consists essentially of spectrophotographic examination of the absorption for the two forms of circular light, a Fresnel triprism being employed to give two contiguous beams of light, one right circular and the other left.

At the beginning of the work described in this thesis/

thesis the announcement of positive results in asymmetric photochemistry had just been made by Kuhn and Braun (16). From the form of the rotation dispersion curve for ethyl α- bromopropionate these authors assumed the existence of circular dichroism about 2800 A.U. and the positive results obtained on irradiation of the racemate by circularly polarised light of approximately that wave length justified their assumption.

It was decided to employ the method successfully used by Mitchell in the extreme red region of the spectrum and to test if it could be sufficiently modified for an examination of ethyl α- bromopropionate in the ultra violet.

Preparation of optically active ethyl α - bromopropionate. $CH_3CHBrCOOC_2H_5$

The starting product for the formation of this substance was commercial lactic acid syrup which usually shows a slight optical activity due to a preponderance of one of the active isomers. This activity is enhanced by the formation of highly rotatory lactides. Various samples were examined polarimetrically until a specimen showing a fairly high activity was obtained. The syrup finally used showed α_{5461} (200 mm) + 20·6°. An examination of this by the sodium salt method of Patterson and Forsyth (28) indicated that about 75% of the syrup was d-lactic acid.

This/

This lactic acid syrup was resolved by crystallisation of first the zinc and then the zinc ammonium salts as described by Patterson and Lawson (29). The finally purified crystalline zinc ammonium d-lactate showed α^{25}_{5461} (200mm) + 1·98° for 1·6 gms. in 20 cms. dilute ammonia solution. Ethyl d-lactate was obtained from the zinc ammonium salt by refluxing with ethyl alcohol and sulphuric acid for several hours (33). The pure product boiled at 55°/13mm and showed α^{19}_{5461} (100mm) =+12·73°. The bromination of this ester was carried out in chloroform solution by phosphorus pentabromide (32). The ethyl α - bromo-propionate thus obtained boiled at 49° - 51°/10 - 12 mm. and 57° - 58°/16 - 17 mm. and showed α^{21}_{5461} (100 mm)-57·38° and α^{21}_{5790} - 49·39°.

This ester is a colourless liquid when pure but rapidly becomes yellow even in subdued artificial light. The vapour of the liquid causes great irritation to the eyes.

Photographic examination for evidence of circular dichroism.

As used for the previous work with caryophyllene nitrosite, the component parts of the Fresnel triprism were cemented together by Canada Balsam. For work in the ultra violet the absorption due to the balsam had to be avoided and to overcome this difficulty the Canada Balsam/

Balsam was removed and the faces of the component prisms put into optical contact by Messrs. Adam Hilger. A Nickel spark was used as source of ultra violet light since the number of lines at 2800 A.U. assist the examination.

Except for the modifications rendered necessary by the introduction of the Fresnel triprism for the two contiguous beams of circular light the procedure adopted was that generally employed for absorption spectrophotography in the ultra violet and the apparatus employed is illustrated in Figure 2 below.

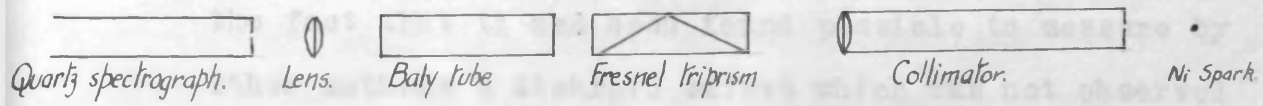
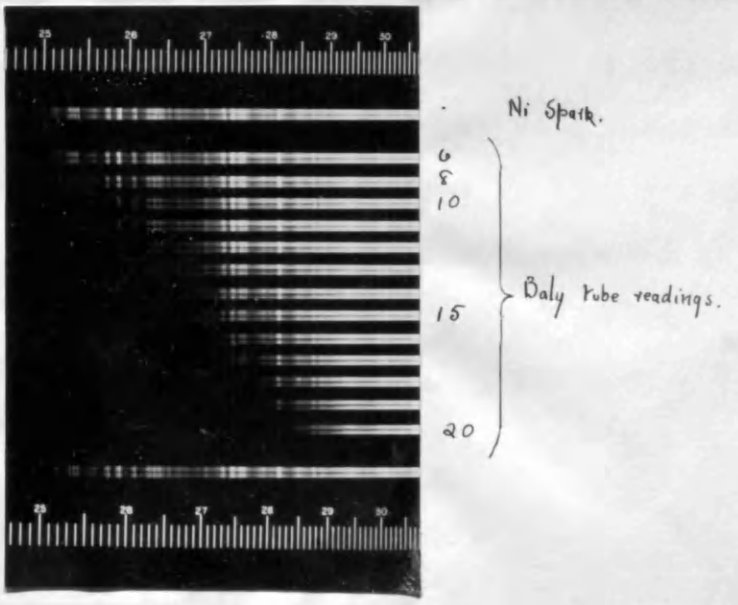


Fig. 2.



The print on foregoing page shows the absorption due to a 0·22% solution of ethyl ∝-bromopropionate in alcohol. The absorption for the one form of circular light appears in the upper of each pair of exposures whilst the lower shows the absorption for the other form. It will be seen that no difference of absorption is apparent for the two forms of light at the wave length (about 2800 A.U.) for which it might be expected even although the great dispersion in this spectral region by the type of apparatus employed assists the sensitivity. Later publications by Kuhn (14) showed that the circular dichroism was indeed very small, but the fact that it had been found possible to measure by other methods a dichroic effect which was not observed by the above apparatus indicated that whilst good as a direct approach to the problem, the method is not sufficiently refined for the observation of small effects.

SECTION 3.

Improved Methods and Apparatus for Determination of Rotation Dispersion, Circular Dichroism and Absorption.

It was mentioned previously that the magnitude of the circular dichroic effect may be expressed as the angle which characterises the ellipticity of the light emerging from the solution, but that older methods for the determination of this quantity were not entirely satisfactory. Great progress in this field was rendered possible by the publication by Bruhat (2) of a suggested apparatus for the measurement of ellipticity with standard optical instruments. The great advantage of this method lies in the fact that by means of an attachment to an ordinary polarimeter, quantitative measurements of rotation and circular dichroism can be made thoughout the visible spectrum with practically the ease and simplicity of ordinary rotation dispersion observations. Moreover with slight modification a similar method has been employed by Kuhn for continuing the measurements far into the ultra violet (18). The theory and suggested form of apparatus is here briefly summarised from Bruhat's publications (2, 3) before giving an account of the final methods found to give very satisfactory results.

The/

The Elliptical Vibration.

The form of an elliptical vibration is defined by the relationship $\frac{b}{a}$ of minor to major axis. This relationship (the ellipticity) is characterised by the angle χ whose absolute value, less than 45°, is defined by $|\tan \chi| = \frac{b}{a}$ It is convenient to consider this angle positive for right ellipses, and negative for left ellipses. When the minor axis b is equal to zero, the vibration is rectilinear and the ellipticity zero. When the minor axis is equal to the major axis the vibration is circular, its ellipticity is +45° for a right circular vibration and -45° for a left.

The effect of the Quarter Wave Plate.

It can be shown that a rectilinear vibration, after traversing a quarter wave plate, yields an elliptical vibration whose axes coincide with those of the plate, and the ellipticity of this ellipse is equal to the angle between the incident vibration and the slow axis of the quarter wave ... ... 1.

and conversely,

if an elliptical vibration fall on a quarter wave plate so that the axes of the ellipse coincide with those of the plate, the emergent vibration is rectilinear and the angle between the slow axis of the quarter wave and the emergent rectilinear vibration is equal to the ellipticity of the ellipse ... ... 2.

It can be further shown that for the more general case of an elliptical vibration striking a quarter wave, where the axes of vibration and quarter wave do not coincide, that, provided the angles representing azimuth of axes (α) and ellipticity (β) of incident vibration are small, the ellipticity of the emergent vibration (β') is equal to the angle between the major axis of the incident vibration and slow axis of quarter wave ($\beta' - \alpha$) and angle (α') between major axis of emergent vibration and slow axis of quarter wave is equal to the ellipticity of the incident vibration. ($\alpha' = \beta$)... ... ... 3.

Application to experimental procedure.

For a simple case where there is no rotation at the point where the dichroism is to be measured (e.g. at the head of the band) there may be employed an apparatus as shown below:

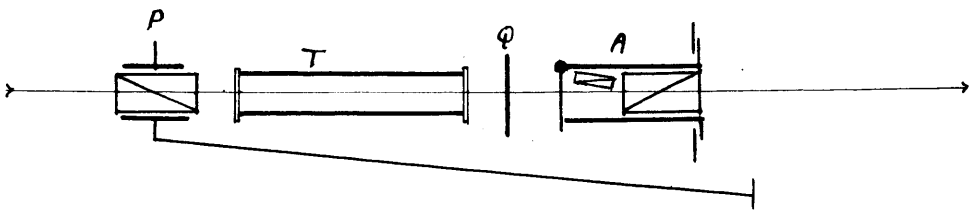


Fig. 3.

Before the insertion of the tube T and quarter wave Q the analyser A is set at zero for the light through the polariser P. Thereafter the quarter wave Q is introduced, with its slow axis approximately parallel to the vibration from P and its orientation adjusted until there/

there is once more equality of illumination in the fields seen by the observer; the slow axis of Q is then parallel to the vibration furnished by P and indicated by A.

On the introduction of the tube T containing the circularly dichroic solution with zero rotation, the emergent vibration from T is elliptical; the major axis in plane of incident vibration. The vibration incident on the quarter wave Q is therefore an ellipse with its axes coinciding with those of the quarter wave and hence by (2) page 13 the emergent vibration is rectilinear, the angle between the emergent vibration and the slow axis of Q being equal in magnitude to the ellipticity of the incident vibration. This angle is read by setting the analyser A to equal illumination and the measurement of dichroism in this simple case therefore becomes the same as the measurement of ordinary rotation, with the same degree of accuracy.

Extension to Solutions exhibiting Rotation as well as dichroism.

In order to extend this method to solutions showing both rotation and dichroism it is only necessary to compensate first for the rotation of the solution by turning the polariser P. The emergent light from tube T is then elliptical with its axes corresponding to those of Q, T.

The/

The drawback to this form of procedure is that both A and P should be mounted on graduated circles, P giving the rotation and the dichroism. Since, however, the solution is isotropic the procedure can be modified by interchange of light source and observer, first setting P and then instead of rotating A turning both Q and P at the same rate in the same sense. By examination of the diagrammatic representation of this method it will be seen that it can be carried out with an ordinary polarimeter, provided there is introduced after the polarising prism a quarter wave plate on a graduated circle capable of rotation in the plane of mounting and of removal and re-introduction in the same orientation.

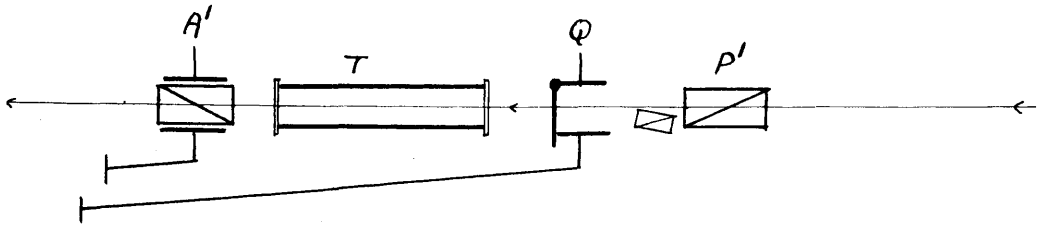


Fig. 4.

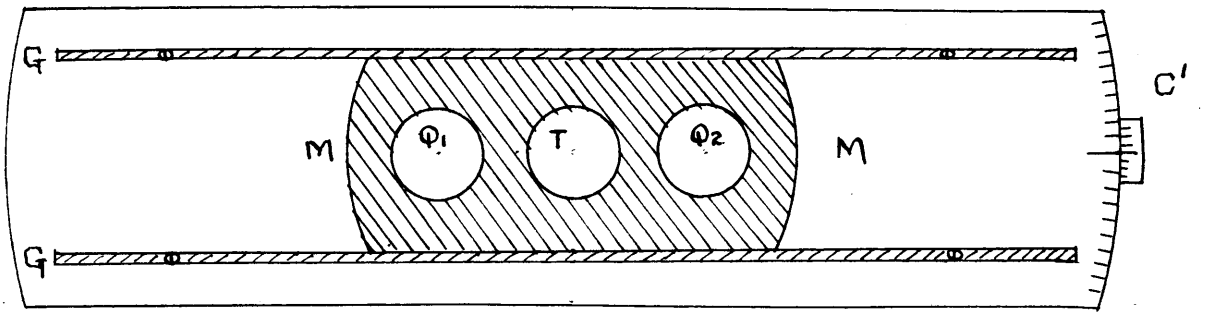


Fig. 5.

The type of mounting for the Quarter Wave introduced just after the polarising prism is illustrated in Fig. 5. M M is a slide which runs along the grooves G G and in which the three holes Q_1, T, Q_2 are made as shown. In the two outside spaces are placed mica plates, quarter wave for yellow and blue light, respectively, two such plates being sufficiently accurate for the whole spectral range and much more convenient than a series of plates, each accurately quarter wave for individual colours. The centre space is left blank. The whole system pivots around the centre and the amount of rotation is read on the graduated circle at C' . By this means one or other of the plates can be introduced in the path of the light ray and removed without disturbing the orientation of the system.

By modification of these suggestions to suit individual requirements and by the introduction of a suitable/

suitable light source and monochrometer it was found possible to arrange the apparatus described below, features of which are its construction employing standard optical instruments and its utilisation for readings of rotation and ellipticity throughout the entire visible spectrum.

*A Spectropolarimeter was formed by combining a Hilger polarimeter with a Hilger constant deviation spectroscope. Two symmetrical slits were fitted to the spectroscope, that next the polarimeter having a lateral adjustment whilst the polarising system of the polarimeter was turned through 90° so as to suit the vertical field necessary for the spectrometer. As a light source, good throughout the spectrum, but particularly useful for readings far into the red, a 1000 c.p. Pointolite lamp was found most 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.

*The necessary mechanical additions and alterations to the apparatus were very efficiently carried out by Messrs. McCulloch in the workshop of the Chemistry Department of this University.

The quarter wave plate for the ellipticity measurements mounted on the special holder described above was introduced immediately after the polarising system. At first the rotation of the plate was read by a vernier scale as recommended by Bruhat (3), but due to the construction of the Hilger instrument, the scale had to be situated some distance from the observer on the side next the light source and the inconvenience of reading was intensified when a thermostat was necessary for the observation tube. The ellipticities under consideration do not exceed a few degrees, and it was found to be a great advantage to control the rotation of the quarter wave 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. or 2·5 cm. glass tube with cemented end pieces. The end pieces must be specially tested for strain and a small correction for the ellipticity made when necessary. Ordinary polarimeter tubes with ends held in position by metal screw caps are quite unsuitable for this type of work. To avoid the use of glass windows in the thermostat, the ends of the tube were held in brass sleeves

which/

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 (27).

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 quarter wave 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 quarter wave plate removed, and a determination of the rotation made in the usual way. The quarter wave 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 quarter wave 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/

The absorption measurements were made with a Hilger-Nutting photometer. 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 for the absorption measurements. $\mathrm{Log}\,(I_o/I)$ is read directly from the photometer scale.
(I_o = incident intensity, I = emergent intensity).

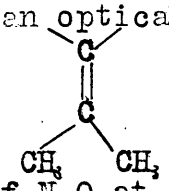
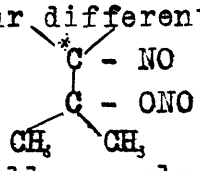
By means of this apparatus there were obtained the results described in the subsequent sections.

Section 4.

Results of Measurements for Caryophyllene Nitrosite. $C_{15}H_{24}N_2O_3$

The circular dichroism and rotation dispersion of this substance had been previously examined by Mitchell with the methods outlined in the Section on ethyl α - bromopropionate, but it was considered of value to study these effects in a new solvent by means of the apparatus of Section 3, and to obtain quantitative measurements for absorption and ellipticity in a form suitable for the theoretical treatment in a later section.

Preparation.

Caryophyllene is an optically active sesquiterpene containing the grouping  and the nitrosite is formed by the addition of N_2O_3 at the double bond, and since one of the carbon atoms is then joined to four different groups it becomes asymmetric as indicated.  The existing optical activity in the caryophyllene molecule appears to be sufficient to cause the exclusive formation of the dextrorotatory nitrosite.

The/

The method employed was essentially that of Kremers and Schreiner (12), the addition in small quantities of glacial acetic acid to a well cooled mixture of caryophyllene, saturated sodium nitrite solution, and petroleum ether, which leads to the liberation of the nitrous anhydride and its absorption by the caryophyllene. As the compound formed is light sensitive, the preparation was carried out in a dark room, using only a small blue light for illumination. Recrystallisation from alcohol, aqueous acetone, and several times from acetone in the dark was required to give the pure deep blue crystals melting sharply at 115° when quickly heated.

Observations.

By means of the apparatus described in Section 3 the observations shown in the accompanying table were obtained for a solution containing ·009 mol./litre of the nitrosite in toluene, taken at 19°C. A 6 cm. tube was used for rotations and ellipticities until the absorption became too great, when a 2.5 cm. tube was employed. The results for rotation and ellipticity are recorded as molecular quantities. The mean of a considerable number of rapid determinations was found to be the best method of obtaining reliable readings for the difficult but important observations from 6200 A.U.

to/

to 6900 A.U., where in addition to the decreasing sensitivity of the eye for matching of colours there is added the disturbing influence of the elliptical light, which renders fine setting of the analyser scale very difficult.

The absorption was examined in 10 cm. cells, and recorded as the molecular extinction coefficient $\varkappa$ defined by $I = I_0 10^{-\varkappa cd}$ (d in cm. c in mols. per litre).

In assessing the importance of an absorption band, both for asymmetric photochemistry and for its contribution to the optical rotatory power of the molecule, the quantity of significance is referred to by Bruhat (3 page 249) as the "relative difference of absorption" for left and right circularly polarised light and by Kuhn (14, 15) as the "anisotropy factor". With a view to its employment later in the theoretical section, the quantity defined by Kuhn is calculated wherever possible for the results of measurements. This anisotropy factor "g" is defined as $g = \frac{\varepsilon_l - \varepsilon_r}{\varepsilon}$ where $\varepsilon_l, \varepsilon_r, \varepsilon$, are respectively the absorption coefficients for left and right circularly polarised light, and ordinary light, but in practice it is generally determined by measurements of ellipticity and ordinary absorption. Under the present conditions, when observations made with the same solution are reduced for the same length of solution under the same conditions the anisotropy factor becomes/

becomes equal to $\frac{4\tau \times 0{\cdot}4343}{\text{Log.}I_o/I}$ where τ is observed ellipticity in radians.(18).

This quantity was calculated for the results obtained with caryophyllene nitrosite and is shown in the last column of the table on sheet 25 (a). It will be seen that it is remarkably constant inside the absorption band, in accordance with the predictions of Kuhn's theory (Section 7). The general form of the rotation dispersion curve is that usually associated with the appearance of circular dichroism inside an absorption band, as indicated in Figure 1 of the introduction. A discussion of the full significance of the curves and the calculation of the rotations from the absorption and ellipticity data, is given in Section 7.

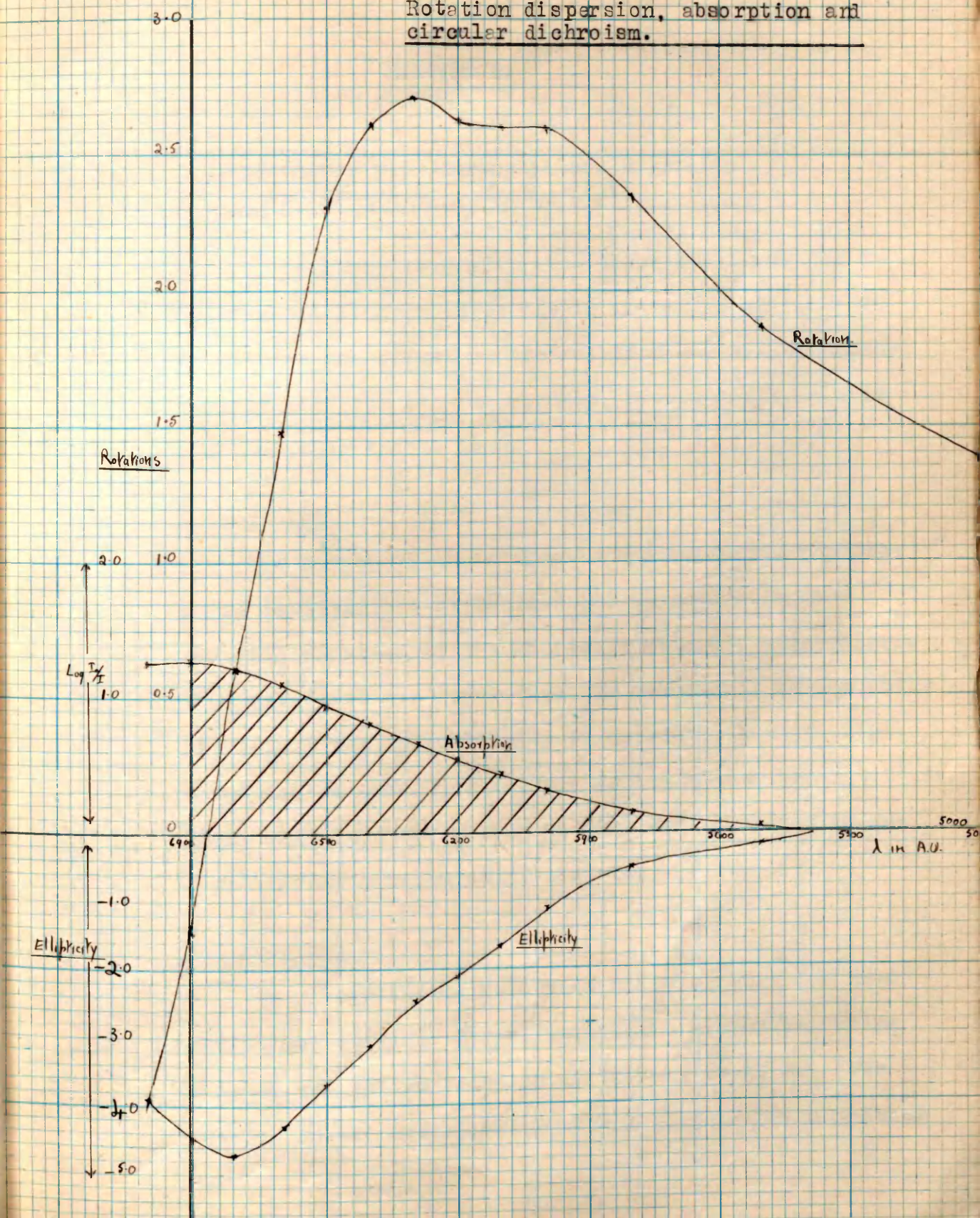
ROTATION DISPERSION AND CIRCULAR DICHROISM OF CARYOPHYLLENE NITROSITE.

In this Table the results for rotation, circular dichroism, and absorption are given as observed values of rotation, ellipticity (in degrees), and Log I_o/I for a 6 cm. tube, under which circumstances the anisotropy factor "g" in the last column is equal to $\frac{4 \times \cdot 4343 \times \cdot 01745 \times \text{ellipticity}}{\text{Log } I_o/I}$. The table containing the results recorded as molecular quantities is placed for convenience in Section 7 (page 61).

λ. Å.U.	Rotation	Ellipticity	Log I_o/I	Anisotropy Factor g
6900	− 0·98°	− 3·85°	1·25	− ·09
6800	− 0·36	− 4·52	1·28	− ·11
6700	+ 0·62	− 4·76	1·25	− ·12
6600	+ 1·48	− 4·30	1·11	− ·12
6500	+ 2·30	− 3·68	·92	− ·12
6400	+ 2·61	− 3·19	·82	− ·12
6300	+ 2·71	− 2·55	·67	− ·12
6200	+ 2·63	− 2·15	·54	− ·12
6100	+ 2·62	− 1·66	·43	− ·12
6000	+ 2·60	− 1·16	·30	− ·12
5800	+ 2·35	− ·56	·15	− ·11
5500	+ 1·87	− ·13	·04	− ·09
5000	+ 1·38	-	-	-

CARYOPHYLLENE NITROSITE

Rotation dispersion, absorption and circular dichroism.



Section 5.

Experiments with β Caryophyllene Nitrosite Hydrochloride $C_{15}H_{25}N_2O_3Cl$.

In caryophyllene nitrosite there still remains an unsaturated linkage (6). It is therefore of interest to observe the effect on the rotation and allied phenomena of addition of, for example, hydrochloric acid to the remaining double bond.

Preparation.

The caryophyllene nitrosite hydrochloride was prepared as described by Deussen (6) by saturating an ethereal solution of the nitrosite with dry hydrochloric acid gas. It was found that the ether must be perfectly dry before any hydrochloride is obtained, but if this condition is satisfied the yields are almost quantitative. Light blue crystals melting at 139° were obtained by recrystallisation from ethyl acetate.

Observations.

The observations were made under exactly the same conditions as those for caryophyllene nitrosite, using a 0·008 mol./litre solution in toluene at 19° C. The results on the accompanying sheets show the same general form/

form as for the nitrosite but the rotation effects are much smaller, in agreement with the new anisotropy factor, which is again constant but much smaller than for the nitrosite.

It is interesting to note that whilst the absorption is practically the same, the effect of the band on the rotation dispersion is obviously greatly reduced. This indicates that although the nitroso group, with its absorption maximum at 6800 A.U. is chiefly responsible for the rotatory effects in that region of the spectrum, the rest of the molecule influences the rotatory contribution of the band to such an extent that reduction of the unsaturation in other parts of the molecule results in reduction of the anomalous rotatory effects inside the absorption band. The quantitative relationship between the reduction in the anisotropy factor and the decreased rotation is again discussed in Section 7.

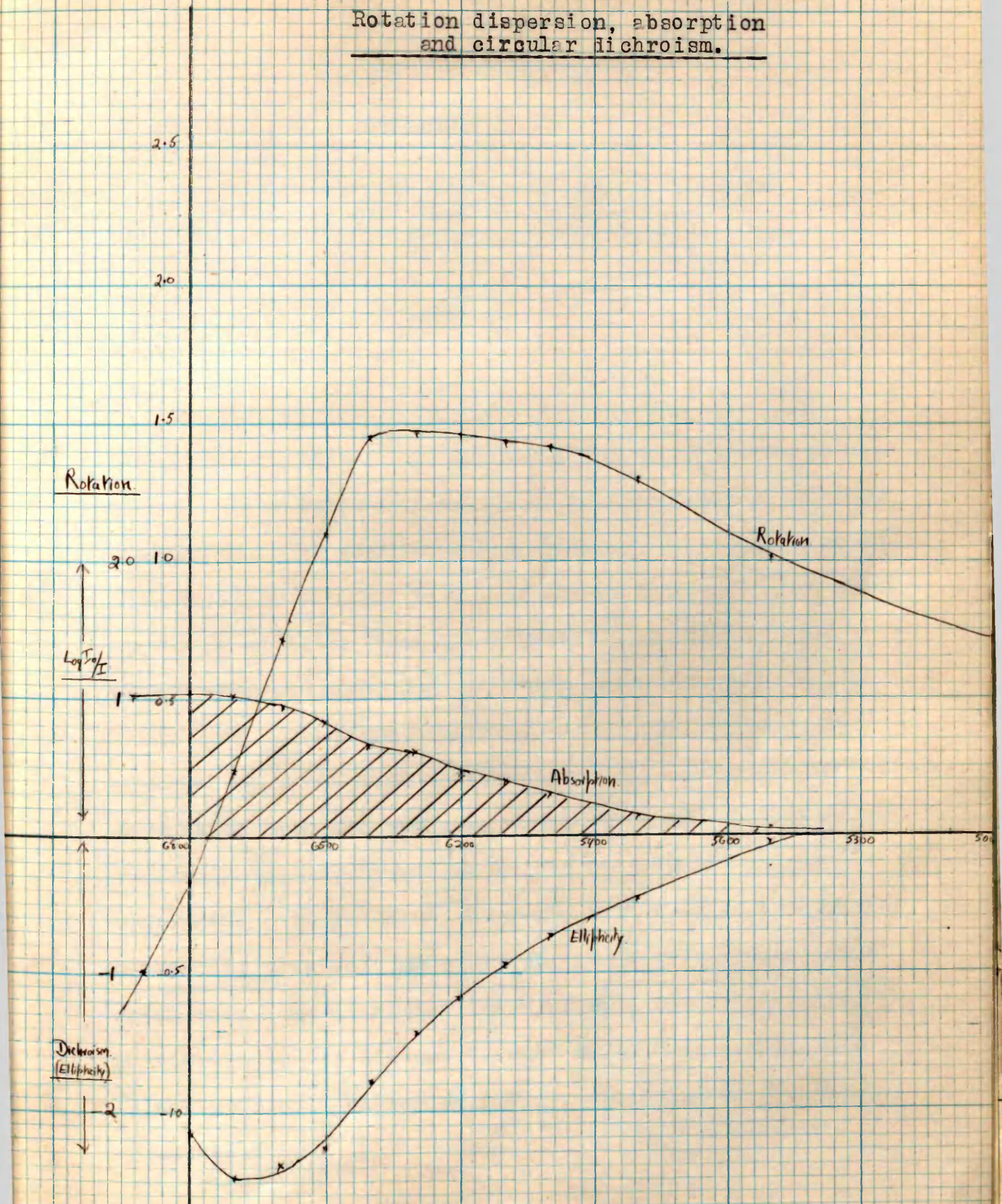
ROTATION DISPERSION AND CIRCULAR DICHROISM OF CARYOPHYLLENE NITROSITE HYDROCHLORIDE.

In this Table the results for rotation, circular dichroism, and absorption are given as observed values of rotation, ellipticity (in degrees), and Log I_o/I for a 6 cm. tube, under which circumstances the anisotropy factor "g" in the last column is equal to $\frac{4 \times \cdot 4343 \times \cdot 0174 5 \times \text{ellipticity}}{\text{Log } I_o/I}$.
The table containing the results recorded as molecular quantities is placed for convenience in Section 7 (page 62).

λ Å.U.	Rotation	Ellipticity	Log I_o/I	Anisotropy factor g
6900	− 0·48°	-	1·04	—
6800	− 0·17	− 2·16°	1·08	− ·06
6700	+ 0·24	− 2·47	1·04	− ·07
6600	+ 0·72	− 2·38	·97	− ·07
6500	+ 1·10	− 2·26	·83	− ·08
6400	+ 1·45	−1·79	·68	− ·08
6300	+ 1·47	−1·41	·61	− ·07
6200	+ 1·46	−1·18	·49	− ·07
6100	+1·44	− ·94	·40	− ·07
6000	+1·42	− ·71	·30	− ·07
5800	1·30	− ·47	·15	− ·09
5500	1·01	− ·04	·06	− ·02
5000	0·72	-	-	

CARYOPHYLLENE NITROSITE HYDROCHLORIDE

Rotation dispersion, absorption and circular dichroism.



Section 6

The Development of Absorption and Circular Dichroism with Rise of Temperature.

A Nitrosites

In view of the interesting results with the caryophyllene derivatives it was thought that extension of the work to other optically active nitrosites might be equally productive. As regards the possibility of preparation of a crystalline product in a pure optically active form those appearing suitable were the nitrosites of phellandrene, zingiberene and bornylene. Since these are white solids which give colourless solutions at room temperature, it appeared at first that they would not be so any use in connection with the study of anomalous rotation dispersion phenomena due to absorption in the red by blue coloured compounds. It is known, however, that nitroso compounds frequently give colourless solutions at room temperatures which turn blue at higher temperatures, the colour being attributed to the dissociation of white double molecules into blue single molecules (30). Solutions of the three nitrosites/

nitrosites indicated above were found to behave in this way, but those of phellandrene and zingiberene were unstable towards heat and therefore unsuitable for quantitative work. The bornylene nitrosite was not affected to any great extent provided the heating was not too prolonged. The results obtained with the compound fully justified the long and at times not very pleasant series of organic reactions necessary to prepare this substance.

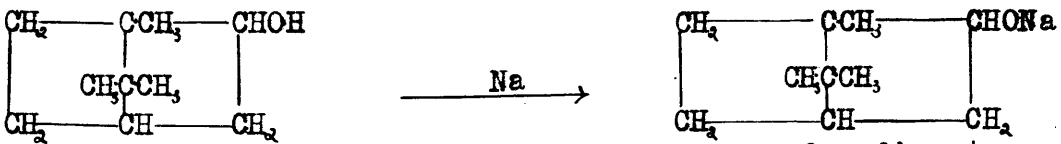
Preparation of optically active Bornylene Nitrosite from l-borneol.

This preparation comprises three distinct stages -

1. Preparation of Methyl bornyl xanthogenate from borneol.
2. Decomposition of xanthogenate to form bornylene and purification of bornylene.
3. Preparation of nitrosite.

---

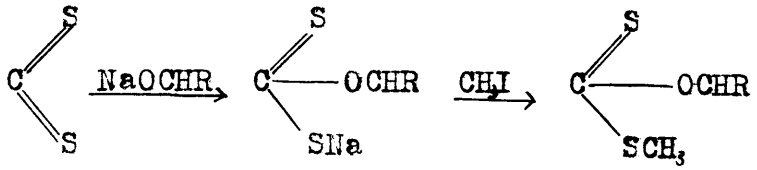
1. This is the first stage of Tschugaef's method for the preparation of an unsaturated hydrocarbon from the corresponding alcohol (31). The course of the experiment may be represented thus, -



This is conducted by gradual additions of sodium to a boiling solution of the borneol in toluene.

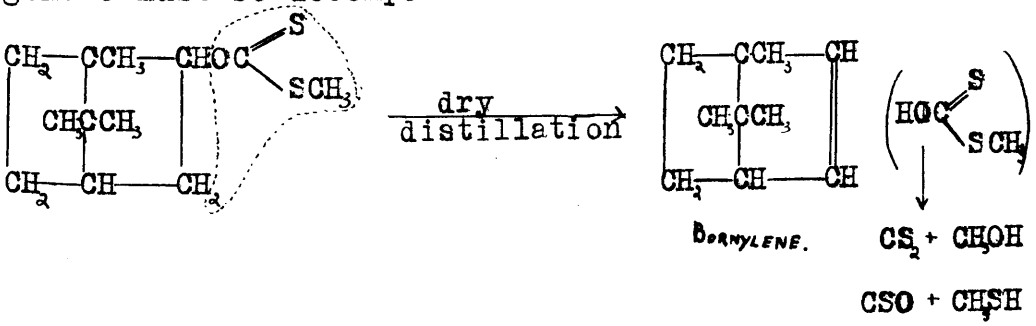
Methyl bornyl xanthogenate is prepared by addition of excess/

excess of carbon disulphide and introduction of the methyl group in the usual way by action of methyl iodide. Writing the sodium salt as NaOCHR this stage may be represented as



As first obtained the methyl bornyl xanthogenate was a dirty yellowish product melting at 52° but after several recrystallisations from alcohol pure white crystals melting at 56° - 57° were formed.

2. The decomposition of the xanthogenate by dry distillation with formation of bornylene is the most uncertain as well as disagreeable part of the process. Theoretically the high temperature (170° - 220°) necessary for the decomposition presents the problem of possible racemisation and in practice the extraordinary volatility of the bornylene itself restricts the use of reduced pressure to lower the decomposition temperature. In addition the most intolerable smells of the by-products at this stage constitute a problem of their own when large quantities of the xanthogenate must be decomposed.



The apparatus illustrated below was ultimately found to give satisfactory yields with a minimum of discomfort.

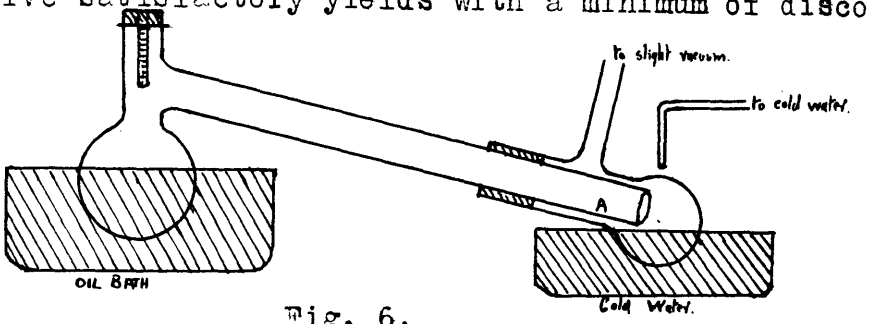


Fig. 6.

Both flasks are made of pyrex glass and an important feature is the very wide side arm of the distillation flask. From the first distillation of the xanthogenate a viscous liquid was obtained, but on redistillation this yielded a solid product, which in turn was distilled over sodium until pure (four to six distillations). The pyrex flask with the very wide pyrex side arm was particularly suitable for these distillations, as part of the side arm could be heated and the lower part cooled so as to obtain a large part of the solid at A in diagram. At these later distillations most of the solid came over between 130° - 140° and this bornylene had a pungent but not unpleasant smell. The final purification of the bornylene to remove traces of other terpene compounds by selective oxidation was carried out as described by Henderson and Heilbron (8).

3. The preparation of the Nitrosite.

At first attempts were made to prepare the nitrosite

by/

by the methods employed for other terpenes such as caryophyllene, but these were quite unsuccessful and ultimately the preparation adopted was exactly that of Henderson and Heilbron (8), using 50 gms. bornylene at a time. After frequent recrystallisations from acetone pure white crystals of bornylene nitrosite melting at 163° were obtained.

The borneol used as starting material showed $[\alpha]^{19}_{5790}$ -37·9° (c = 11·52 in alcohol) and the bornylene obtained gave $[\alpha]^{19}_{5790}$ +22·8° (c = 7·63 in light petroleum).

Observations.

As already mentioned the solutions of the bornylene nitrosite at ordinary temperatures are quite colourless but on warming become blue. It was decided to take a series of observations at different temperatures to see if this alteration in the solution was accompanied by any abnormal effects on the optical properties. Measurements were therefore made for a toluene solution of bornylene nitrosite at different temperatures. The very interesting result was obtained that along with the development of the absorption band in the red giving rise to the blue colour there was a corresponding development of circular dichroism with a pronounced effect on the rotation dispersion curve.

The results for temperature at 14° and 63° are shown in the accompanying table and graph (Sheets 32(a) and 32(b)).

Observations/

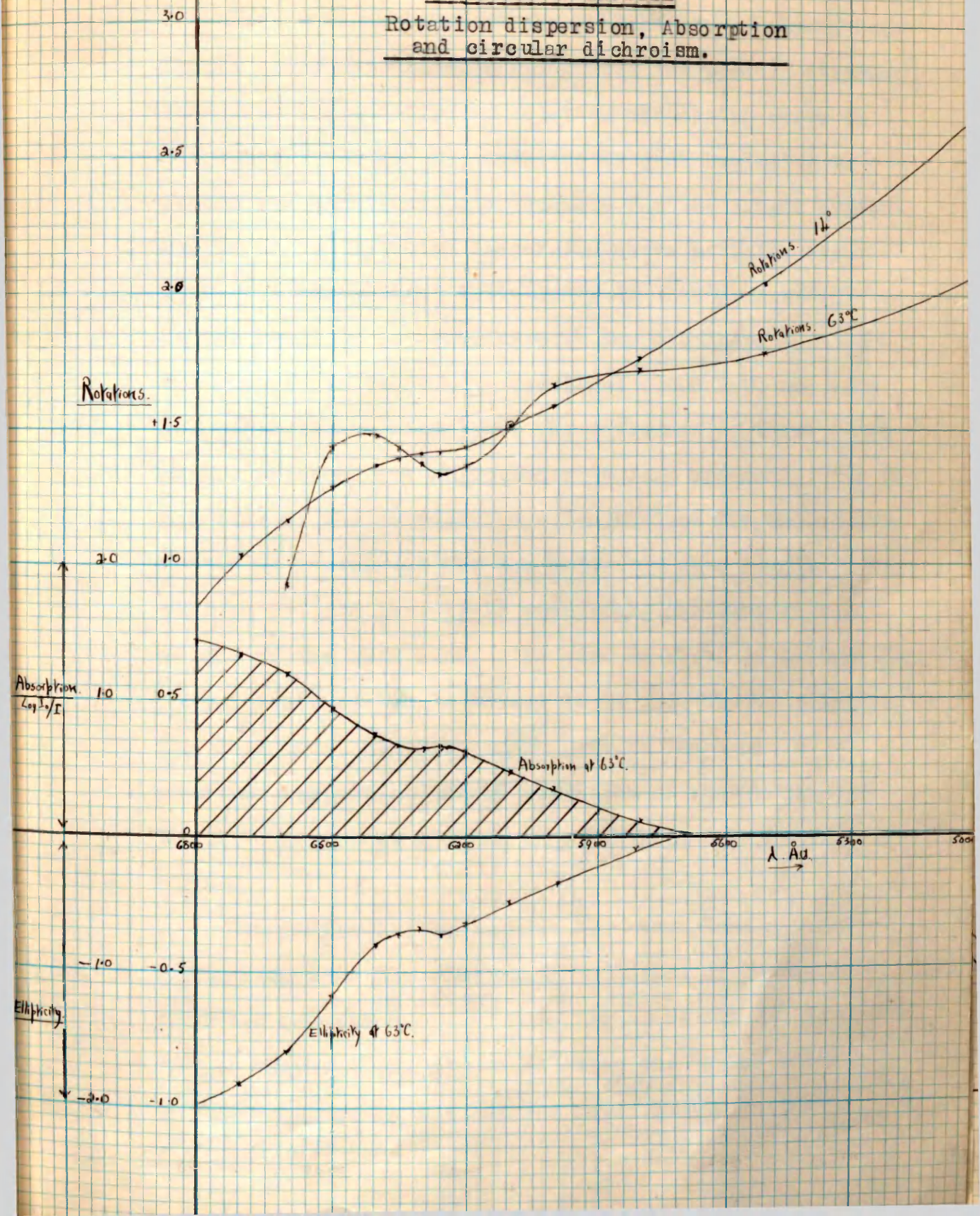
ROTATION DISPERSION AND CIRCULAR DICHROISM OF BORNYLENE NITROSITE.

Wave-length, A.U.	Temp. 14° Rotation	Temperature 63°			Anisotropy factor
		Rotation	Ellipticity	Log I_0/I	
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	-	-	-

An additional absorption reading taken at 6800 A.U. gave a value for log I_0/I of 1.44.

BORNYLENE NITROSITE

Rotation dispersion, Absorption and circular dichroism.



Observations taken at intermediate temperatures confirmed these measurements and showed the gradual alteration from the one type of rotation dispersion curve to the other. At 14° the solution is just beginning to absorb red light and this accounts for the slight irregularity in the rotation dispersion curve at this temperature. A very slight ellipticity is also present but it is too small to be measured with any accuracy. At 63° two absorption bands have developed (6800 A.U. and 6250 A.U. approximate heads) and the influence of these bands on the rotation and ellipticity is very apparent. As in the case of the caryophyllene derivatives the anisotropy factor is calculated for the different wave length. It will be noticed that it is remarkably constant in the middle of the weak band. As will be shown in Section 7, on the basis of Kuhn's theory it is possible to estimate the individual contributions of these two bands to the rotation dispersion and by summation of these contributions to arrive at a curve of similar form to that observed.

The difficulty throughout the bornylene nitrosite measurements is the disturbing influence of the undissociated molecules. The rotation curve for 63° is really composed of (a) the retation due to the undissociated molecules and (b) the rotation due to the dissociated/

dissociated molecules which give the colour to the solution and are responsible for the abnormal rotation effects. As the exact amount of the dissociation was not known, all the observations were taken in a 6 cm. tube under the same conditions, and are recorded as such. 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 A.U. at the higher temperature.

A paper embodying the results of this section with a description of the apparatus was recently published in the Journal of the Chemical Society (26).

B. Nitrosochlorides.

Extension of the caryophyllene work might also be considered from the aspect of the influence of groupings associated with the nitroso group. In the nitrosites, for example, the addition to the double bond consists of a nitroso grouping and a nitro grouping. It may be asked if the replacement of the nitro grouping by another group would cause any great alteration of the effects inside/

inside the absorption band which is characteristic of the nitroso group. The obvious course is to prepare a specimen of optically active caryophyllene nitrosochloride and examine its optical properties in the red. Unfortunately the terpene nitrosochlorides as a class are difficult to obtain in a pure homogeneous form and in particular this is true of caryophyllene. The yields of the crude nitrosochloride obtained in the initial stages of the preparation are very small. Moreover this crude product is chiefly composed of the inactive α caryophyllene nitrosochloride, and contains only small amounts of the active β caryophyllene compound together with a corresponding small amount of another active substance of rotation opposite to that of the nitrosochloride (7). These latter two substances are very difficult to separate and naturally exercise an enormous influence on the rotatory power of one another. A large amount of expensive material is required to obtain even a very small quantity of the final active βcaryophyllene nitrosochloride (7), and the heavy expense of a complete study of this compound would only be justified by exceptional results. It was thought that it might be possible however to prepare from a reasonable amount of starting material a sufficiently pure specimen of βcaryophyllene nitrosochloride to obtain some indication of the magnitude of the dichroic effect, if any.

Preparation/

Preparation.

The nitrosochloride was prepared as described by Deussen (7), when he showed that the caryophyllene nitrosochloride described by Wallach (35) was not homogeneous but consisted of three substances. This crude nitrosochloride was obtained by the gradual addition of a saturated solution of hydrochloric acid in ethyl alcohol to a well cooled mixture of caryophyllene, ethyl acetate, alcohol, and amyl nitrite. The preparation must be done in small quantities. The best results were obtained with quantities of the order of 10 ccs. of each of the starting material and fifteen simultaneous preparations gave a yield of 5 to 6 gms. crude nitrosochloride, and several series of such simultaneous preparations were run until the total yield was 50 gms.

By repeated extraction with a 10% solution of ethyl acetate in alcohol about three grams of the mixture of the β caryophyllene nitrosochloride and the other substance were obtained. The subsequent separation of these two compounds consists essentially of fractional crystallisation from ethyl acetate and alcohol mixtures, but as Deussen remarks in his description of the preparation these two compounds stick stubbornly to one another. Large quantities would be required for a complete separation but it was found possible to purify the β caryophyllene nitrosochloride from the other compound of opposite rotation sufficiently/

sufficiently for it to show a definite laevo rotation.

Observations.

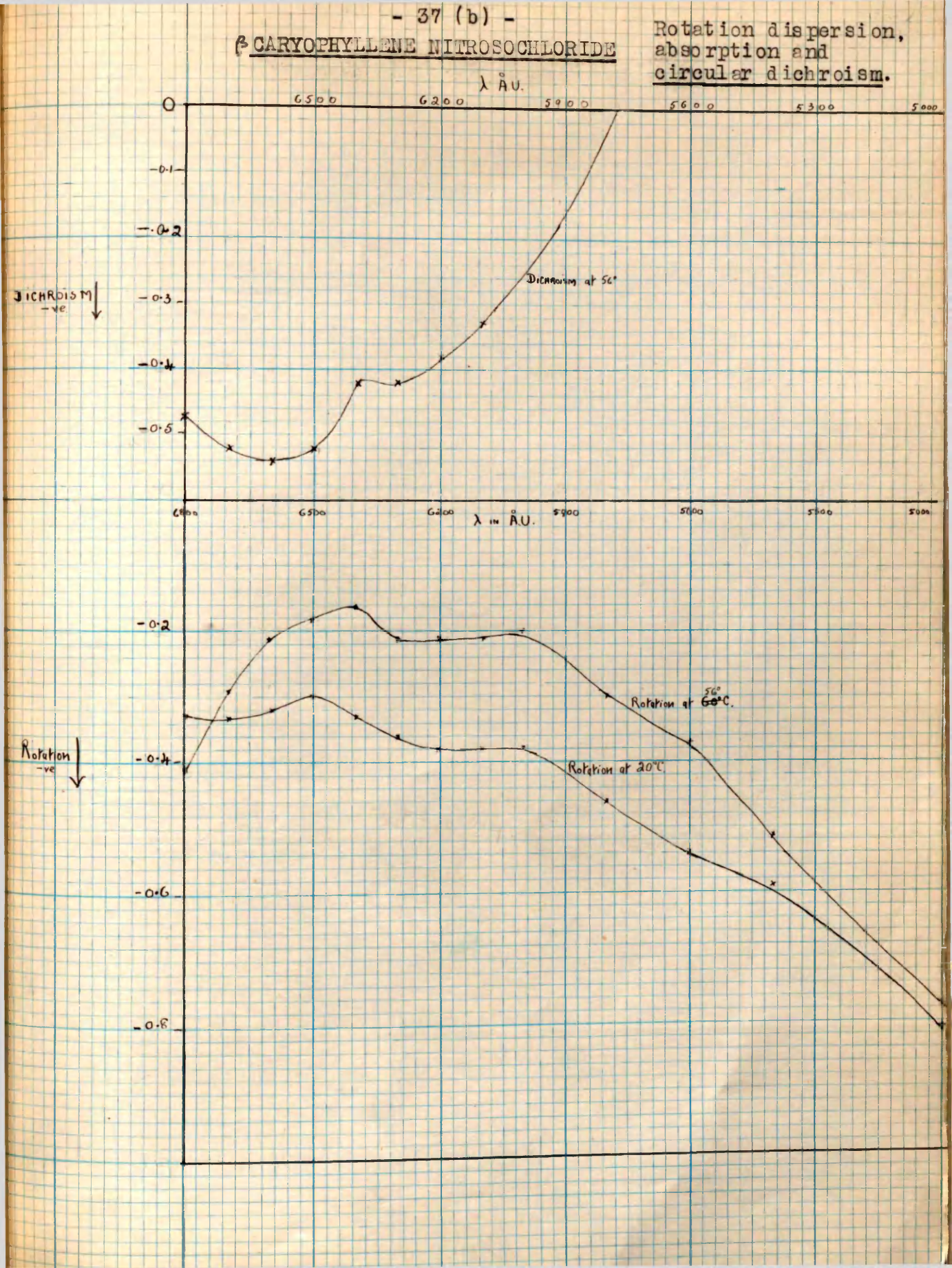
Like bornylene nitrosite, caryophyllene nitrosochloride is a white substance dissolving to give colourless solutions at room temperatures, but on warming these solutions turn blue. It was found that in this case the colour change was more pronounced in ethyl acetate solution than in toluene, but even at its best the depth of colour was slight. Observations were made at 20° and 56° for a solution of 0.193 gms. β caryophyllene nitrosochloride (M.Pt.144°-146°) in 5 ccs. ethyl acetate solution. The readings at the higher temperature were taken as rapidly as possible in view of the volatility of the solvent and the instability of the compound at these higher temperatures. It will be seen from the results overleaf that there is undoubtedly a dichroic effect at 56° and there are irregularities in the curve very similar to those seen in the bornylene nitrosite results. At 6900 A.U. the negative rotation has grown larger, whilst at 6500 - 6000 A.U. the observed laevo rotation has greatly decreased. This is in accordance with the rotation contribution of the nitroso group to be expected at these wavelengths from the results with the previous compounds. Owing to the instability of the compound and the slight colour density, as well as solvent and purification problems, a quantitative series of measurements for determination of the anisotropy factor was not attempted, but definite evidence is shown in the results given that the nitroso group may exhibit circular dichroism inside its characteristic absorption band, even when it is associated with some other than the nitro group.

β Caryophyllene Nitrosochloride

Wave Length A.U.	Rotation at 20°	Rotation at 56°	Ellipticity at 56°
6800	-0.33°	-0.41°	-0.47°
6700	-0.33	-0.29	-0.52
6600	-0.32	-0.21	-0.54
6500	-0.30	-0.18	-0.52
6400	-0.33	-0.16	-0.42
6300	-0.36	-0.21	-0.42
6200	-0.38	-0.21	-0.38
6100	-0.38	-0.21	-0.33
6000	-0.38	-0.20	
5800	-0.46	-0.30	
5600	-0.54	-0.37	
5400	-0.59	-0.51	
5000	-0.81	-0.77	

β CARYOPHYLLENE NITROSOCHLORIDE

Rotation dispersion, absorption and circular dichroism.



Section 7.

Discussion of Results with reference to Theory of Werner Kuhn.

The Drude theory was the first systematic attempt to formulate mathematical expressions for the measurements associated with the appearance of optical activity in certain substances, and is certainly the classical theory; but it has been criticised both on its fundamental assumptions and for its weaknesses inside the absorption band (11). It is contended that the conception of spiral electronic paths scarcely represents the true state of matters inside the molecule, and the simple form of the expression for the variation of rotation with wavelength becomes discontinuous inside the absorption band. Amongst later theories which sought to remedy such defects that due to Born achieved a firmer basis by the hypothesis that optical activity is due to the mutual coupling of vibrators inside the molecule but the treatment was cumbersome and the simplicity of the final Drude formulation was entirely lost. Kuhn adopted the Bornian basis but clarified

the treatment by means of a very simple model and has provided an expression for the course of rotation which while very complex inside the absorption band does represent the form of the curve and at greater distance from the absorption band reduces to the simple Drude expression (13, 14). In addition there is derived for the first time a clear connection between the intensity of the absorption, the circular dichroism and the rotatory power of the band.

The simplified model employed by Kuhn in his first theoretical treatment may be represented as follows:

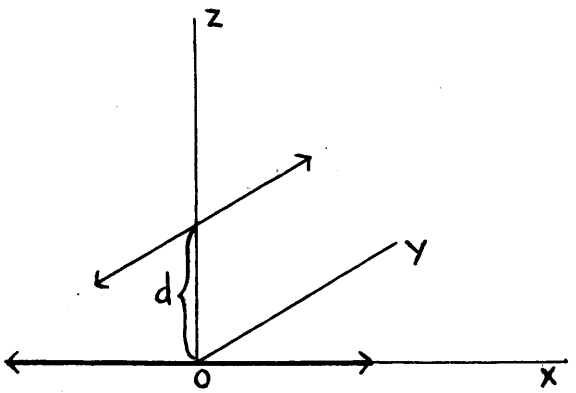


Fig. 7.

A particle of given charge and mass is lodged in the zero point of the coordination system x, y, z. It is elastically bound to its position of rest and has the property of motion only in the direction of the x - axis. A second particle of given charge and mass different to first particle is lodged at the point z = d. It also is elastically bound to its position of/

of rest and can move only in the direction of the y - axis.

Equations can be formulated for the motion of these two particles both when coupling is absent and when it is present. The analysis shows that optical activity does not appear if the vibrations are uncoupled. For the introduction of optical activity coupling between the particles, as well as a finite (in relation to the incident wavelength) interval is necessary. Such a model with coupled resonators exhibits different relations of the characteristic frequencies for left and right circular light, resulting in the circular double refraction characteristic of optical activity. Rotatory power is thus traced back to a dependence on the rotatory sense of the light, of the work which a circular wave does on the system. Kuhn extends the relations deduced from consideration of this simple model to the general case of any number of coupled resonators and by this means obtains formulae which represent the course of rotation both inside and outside the absorption band. There is deduced a quantitative relation between rotatory power, absorption, and ellipticity and in this connection it is shown that the relative difference $\frac{\varepsilon_e - \varepsilon_i}{\varepsilon}$ of the absorption coefficients for left and right circular light in a band/

band of uniform source is proportioned to $\frac{1}{\lambda}$ therefore of constant sign and in a small band practically constant. ($\varepsilon_\ell, \varepsilon_r, \varepsilon$, extinction coefficients for left and right circular light and ordinary light respectively). The dichroism however ($\varepsilon_\ell - \varepsilon_r$) changes its sign in different absorption regions so that the algebraic sum is zero.

This quantity g Kuhn denotes as the "anisotropy factor" and it is of great value in assessing the relative importance of different absorption bands. It can be determined either by direct measurement of the individual extinction coefficients, or by determination of the circular dichroism and ordinary absorption as described in previous Sections (page 24).

The quantitative mathematical treatment of the considerations above yields the following equation for the contribution of a definite absorption band to the optical rotation of the molecule. [(14) page 290.]

$$\varphi = \frac{1}{2\sqrt{\pi}} \frac{\nu}{\nu_0} g_0 \varepsilon_{max} \left[e^{-\frac{(\nu_0-\nu)^2}{\Theta^2}} \int_0^{\frac{\nu_0-\nu}{\Theta}} e^{x^2} dx - e^{-\frac{(\nu_0+\nu)^2}{\Theta^2}} \int_0^{\frac{\nu_0+\nu}{\Theta}} e^{x^2} dx \right] \quad \ldots\ldots (1)$$

φ = rotation per cm. at frequency ν
ν_0 = absorption frequency.
ε_{max} = maximum extinction coefficient ($I = I\, e^{-\varepsilon d}$)
g_0 = anisotropy factor at middle point of band.
Θ = distribution parameter

The distribution parameter Θ determines the half value interval ν' in which $\nu' = \Theta 1.6651$.
The half value interval ν' is frequency interval between points in spectrum for which the absorption is half the maximum absorption.

An integral of the type $e^{-c^2}\int_0^c e^{x^2}dx$ for large values of C reduces to $\frac{1}{2C}$ hence the expression (1) for large values of $\frac{\nu_0-\nu}{\Theta}$ and $\frac{\nu_0+\nu}{\Theta}$ (i.e. when ν is far from ν_0, the frequency considered far from the absorption frequency) reduces to the simple Drude form as shown.

$$\varphi = \frac{1}{2\sqrt{\pi}}\,\frac{\nu}{\nu_0}\,g_0\,\varepsilon_{max}\left[\frac{\Theta}{2(\nu_0-\nu}\;-\;\frac{\Theta}{2(\nu_0+\nu)}\right]$$

$$= \frac{1}{2\sqrt{\pi}}\,\frac{\Theta}{\nu_0}\,g_0\,\varepsilon_{max}\,\frac{\nu^2}{\nu_0^2-\nu^2} \qquad = \text{Constant}\;\frac{1}{\lambda^2-\lambda_0^2}$$

Since also $\frac{\nu_0-\nu}{\Theta}$ is in practice a large number, the dependence of the rotation on the frequency is controlled by the first factor inside the bracket, i.e.,

$$e^{-\left(\frac{\nu_0-\nu}{\Theta}\right)^2}\int_0^{\frac{\nu_0-\nu}{\Theta}} e^{x^2}dx$$

When this is graphed we obtain a rotation curve of the type shown in Figure 1 (Page 2). ((14) page 291).

As given in (1) the formula is not suitable for application to experimental data.

The following substitutions are made:

The following substitutions are made: [(14) page 293.]

Mol. rot. $[M] = \frac{100\varphi}{C}$ where C is concentration in gm. mol. per litre

$$\varkappa_{max} = \frac{\epsilon_{max}}{2{\cdot}303 \times C} \quad \text{where } \varkappa \text{ is defined by} \quad I = I_0 10^{-\varkappa cd}$$

(1) now becomes, -

$$[M] = \frac{100 \times 2{\cdot}303 \times \nu}{2\sqrt{\pi} \times \nu_0} g_0 \varkappa_{max} \left[e^{-\left(\frac{\nu_0-\nu}{\theta}\right)^2} \int_0^{\frac{\nu_0-\nu}{\theta}} e^{x^2} dx - e^{-\left(\frac{\nu_0+\nu}{\theta}\right)^2} \int_0^{\frac{\nu_0+\nu}{\theta}} e^{x^2} dx \right] \quad \ldots (2)$$

The expression inside the bracket attains a maximum (for $\nu_0 - \nu = 0{\cdot}9\,\theta$) of 0·541. If $[\phi]$ is value of $[M]$ at this point ν_ϕ

$$[\phi] = \frac{100 \times 2{\cdot}303 \times \nu_\phi}{2\sqrt{\pi} \times \nu_0} g_0 \varkappa_{max}\, 0{\cdot}541$$

$$[\phi] = \frac{100}{2{\cdot}85} g_0 \varkappa_{max} \quad \ldots (3)$$

Insertion of the value for g_0 from (3) into (2) gives

$$[M] = \frac{[\phi]}{0{\cdot}541} \frac{\nu}{\nu_\phi} \left[e^{-\left(\frac{\nu_0-\nu}{\theta}\right)^2} \int_0^{\frac{\nu_0-\nu}{\theta}} e^{x^2} dx - e^{-\left(\frac{\nu_0+\nu}{\theta}\right)^2} \int_0^{\frac{\nu_0+\nu}{\theta}} e^{x^2} dx \right] \quad (4)$$

In practice, for the last term of expression inside the bracket $\frac{\nu_0+\nu}{\theta}$ is large and the integral may be set equal to $\frac{\theta}{2(\nu_0+\nu)}$, a small term which is practically constant throughout the absorption band.

On/

On making this substitution there is obtained the final form of the equation given by Kuhn as that from which his curves are calculated. (Actually the final form given in one of the original theoretical papers [(14), page 294] is incorrect, due to a misprint which appears corrected some time later (23), page 60.)

$$[M] = \frac{[\phi]}{0{\cdot}541} \frac{\nu}{\nu_\phi} \left[e^{\left(\frac{\nu_0-\nu}{\Theta}\right)^2} \int_0^{\frac{\nu_0-\nu}{\Theta}} e^{x^2} dx - \frac{\Theta}{2(\nu_0+\nu)} \right] \quad \text{.....(5)}$$

It is regrettable that whilst curves in abundance are to be found in the publications by Kuhn, tables of data are not given and doubt is left as to the method by which he evaluated the integral. At some distance from the seat of absorption Kuhn indicates that the limiting value may be used and he hints at a series for the other positions, but at no time does he give the full specimen calculation which would clarify the whole treatment and application to experimental data. In this connection it is of interest that only very recently a publication in a French journal containing calculations with respect to Kuhn's theory was followed by a report of an amended calculation after communication with Kuhn. (36, 37).

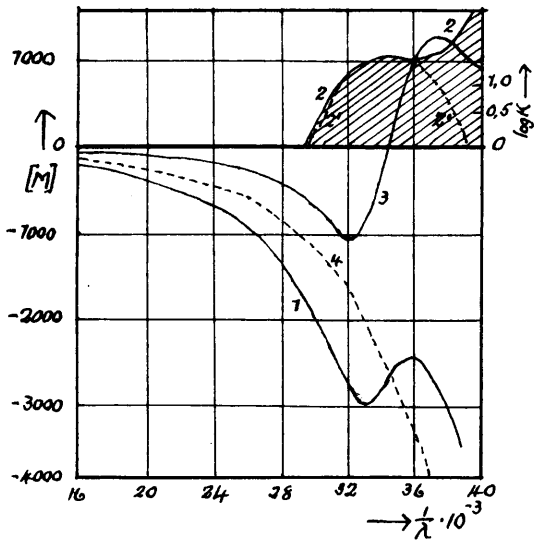


Fig. 7.

This diagram is reproduced from Z. physikal Chemie. B. 8. (1930), page 296, and shows the results obtained by Kuhn and Braun for a solution of azidopropionic acid dimethylamide in ether.

Curve 1 shows the observed molecular rotation.

2 shows the observed absorption.

2' shows the calculated absorption.

3 shows the calculated rotation contribution of the azide band.

4 shows the observed rotation minus the calculated rotation ("difference curve").

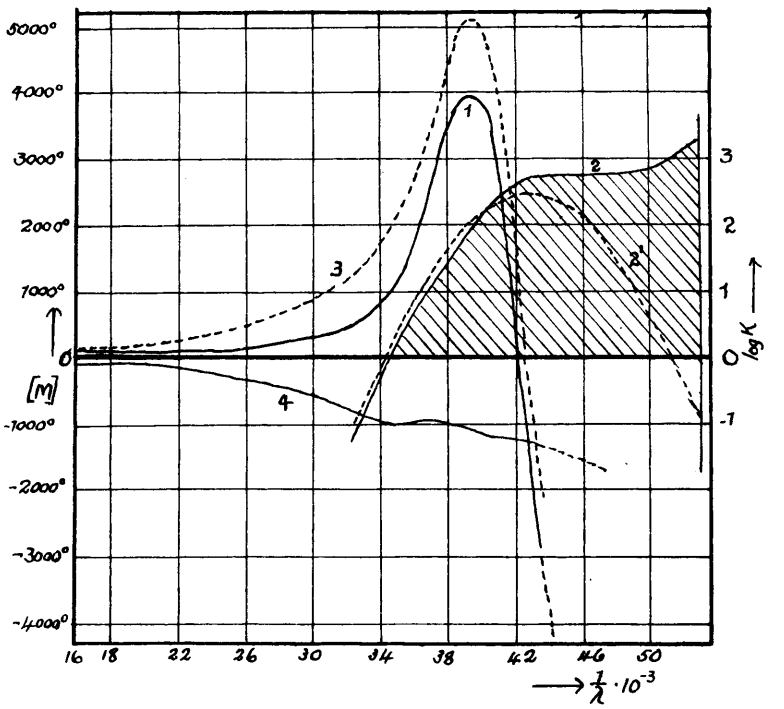


Fig. 8.

This diagram is reproduced from Z. physikal Chemie, B. 8. (1930), page 306, and shows the results obtained by Kuhn and Braun for a sulution of bromopropionic acid ethyl ester in hexane.

Curve 1 shows the observed molecular rotation.

2 shows the observed absorption.

2′ shows the calculated absorption of the bromide band.

3 shows the calculated rotation contribution of the bromide band.

4 shows the observed rotation minus the calculated rotation ("difference curve").

In his first attempt to formulate theoretical curves to show the rotation contribution of a given absorption band, Kuhn employs equation (5) page 44, assigning a numerical value to $[\phi]$. In many cases he later justified the value given to $[\phi]$ by measuring the anisotropy factor g at the head of the band, and the maximum molecular extinction coefficient which enables $[\phi]$ to be determined exactly by means of equation (3) page 43. In a recent paper (23) he definitely states that the curves were calculated using the value of $[\phi]$ obtained from anisotropy factor and extinction coefficient measurements.

By means he is able to show for various absorption bands what is termed the contribution to rotation of the band in question, and by subtraction of this from the observed values for the rotation, there is obtained a difference curve which represents the rotation contribution of the rest of the molecule.

In order to illustrate the type of results obtained the accompanying figures (pages 45, 46) are taken from the publication of Kuhn (14) pages 296 and 306). Figure 7 on page 45 shows the results with azidopropionic acid dimethylamide. Whilst the "observed curve" (1) shows a distinct anomaly, the "difference curve" (4) obtained by subtraction of the "azido curve" (3) shows

no/

no such anomaly, thereby indicating that by means of (3) the rotation contribution of the azido band (λ_o = 2900 A.U.) can be represented.

For the curves in Figure 8, page 46, we have a similar type of reasoning. The contribution of the bromo band of α-bromopropionic ester is calculated and subtracted from the observed rotation giving the different curve (4), which this time still shows a slight anomaly, but very little when compared to curve (1).

It will be noticed that the absorption due to the band is represented by a calculated error curve of the type $\varkappa = \varkappa_{max}\, e^{-\left(\frac{\nu_o - \nu}{\Theta}\right)^2}$ where Θ is the constant defining the half value interval ν' as in the calculation for rotation (page 41). In later examples Kuhn arrives at rotation curves by summation of the individual contribution of several small overlapping bands; in one case he has four such bands with the same anisotropy factor (19).

By suitable mathematical manipulation of several curves from the expression (5) with different values of the constant $[\phi]$ and absorption frequency ν_o, it would probably be quite possible to smooth out the anomalies in any given example of a typical "Cotton effect" rotation curve, and in this respect the Kuhn theory lends/

lends itself to doubtful extension. The exact significance of the final "difference curve" which Kuhn interprets as the "rotation due to the rest of the molecule", is a little obscure and as yet no definite check on its final form can be obtained. If the minor absorption curves necessary for the smoothing of any minor anomalies are entirely masked by the main band then the justification for their introduction is only to be found by the final result that the difference curve is smooth. So far as the theory attempts to formulate curves for rotation dispersion its value will be considerably greater when the actual rotation to be observed can be obtained from the equation derived.

Nevertheless the theory does represent an advance in that it renders possible the calculation of the form of the curve to be expected as the rotatory contribution of a given band, on the basis of measurements for circular dichroism and ordinary absorption. In the work described in previous Sections it was found possible in many cases to evaluate g. It is therefore of interest to see if by utilisation of the considerations outlined in the Kuhn theory, it might be possible to formulate curves of the type obtained in the compounds studied.

I_+,

It has already been suggested that the anomalies in the red region of the rotation dispersion curves studied are due to the nitroso group. This can be confirmed by the form of the difference curve obtained on subtraction of the "nitroso curve" from the observed curve for the rotation dispersion of the compounds. If the "difference curve" so obtained shows no irregularities then it can be concluded that the abnormal optical effects in the red are due to the nitroso band.

The case of bornylene nitrosite is of particular interest since with the appearance of two absorption bands in the red, there is the simultaneous development of circular dichroism and a complete alteration in the form of the observed rotation curve. It is necessary first of all to distinguish the absorption contributions of the two overlapping bands. This can be done by Kuhn's method of representing each individual absorption contribution by means of a curve of the type $\alpha = \alpha_{max} e^{-\left(\frac{\lambda-\lambda_0}{\theta}\right)^2}$ where $\theta = \frac{\lambda'}{1.6651}$, λ' in this case being the wave length interval between points in the spectrum for which the absorption is half its maximum value. When a complete observed absorption curve is not available, as in the case of bornylene nitrosite, where readings could not be obtained beyond 6900 A.U., λ' may be assessed by observing the distance of the one half value position from the head of the band and doubling this to give λ'. Unfortunately in the case of bornylene nitrosite the exact location of the half value position for the main band cannot be accurately gauged due to the disturbing influence of the secondary band, and measurements are not/

not available on the long wave side where this secondary would not interfere. Similarly the secondary band constants are obscured by the main band effects. Several combinations of curves were tried until there were obtained those shown graphically on sheet 60(a) and the calculated values for which appear on sheet 60. It will be seen that the curve obtained by the sum of the values for the two calculated curves shows quite good agreement with the observed curve.

By means of the values for θ and λ_o obtained from these curves, along with the anisotropy factor g_o at the head of each band and the maximum extinction coefficient the contribution of each band to optical rotation may be calculated by means of equations on pages 42 to 44. In the case of bornylene nitrosite the dissociation effects make it impossible to calculate the molecular rotation and extinction coefficients. In this case the necessary alterations in the constant were made and into equation (2) were inserted the value for g_o and Log I_o/I and the values of α, the rotation for a 6 cm. tube for different wave lengths, were calculated. In the form given by Kuhn the equation gives the rotations in radians and the factor 57.30 was therefore/

therefore introduced to bring the result to degrees. The equation used for calculating bornylene nitrosite (Main Band) therefore became

$$\left[\begin{array}{l}\lambda_o = 6800, \quad g_o = 0.040, \text{ max. } \log I_o/I = 1.44 \\ \theta = 365\end{array}\right]$$

$$\alpha = \frac{2.303 \times 6800 \times 0{\cdot}040 \times 1.44 \times 57{\cdot}30}{2\sqrt{\pi} \times \lambda}\left[e^{-\left(\frac{\lambda-6800}{365}\right)^2}\int_0^{\frac{\lambda-6800}{365}} e^{x^2}dx - \frac{365}{2(\lambda+6800)}\right]$$

$$= \frac{14570}{\lambda}\left[e^{-\left(\frac{\lambda-6800}{365}\right)^2}\int_0^{\frac{\lambda-6800}{365}} e^{x^2}dx - \frac{365}{2(\lambda+6800)}\right]$$

In order to evaluate the integral of the type $e^{-C^2}\int_0^C e^{x^2}dx$ inside the bracket, a series was employed until $C = 2$ when the value $\frac{1}{2C}$ was used. [c.f.(14) page 290-291].

The series used was

$$\frac{1}{\sqrt{2}}\left[\sqrt{2}C - \frac{(\sqrt{2}C)^3}{1.3} + \frac{(\sqrt{2}C)^5}{1.3.5} - \frac{(\sqrt{2}C)^7}{1.3.5.7} + \ldots\ldots - \frac{(\sqrt{2}C)^{15}}{1.3.5.7\ldots.15} + \right]$$

It was found necessary to take the series as far as the term in C^{15} for some of the values of C near 2 before the next term could be neglected.

By/

By these means the rotation curves representing the individual contribution of the two bands at 6800 and 6200 A.U. were calculated. They are represented graphically on sheets (60, b+d) and the calculated values are shown on page, 60. On summation of these there is obtained the curve shown on sheets (60, b+d) Itwill be seen that the two maxima and the trough of the calculated summation curve and observed curve agree very well. The difference curve obtained by subtracting calculated from observed values is very similar to that obtained at 14°. It must be remembered that this difference curve here represents not only "the rotation of the rest of the molecule" in this red region but also the rotation due to the undissociated molecules. In addition the anisotropy factor for the band at 6800Å is somewhat indefinite due to the difficulty of observation at that wave length and a variation of this would assist in smoothing out the slight irregularity still existing in the difference curve. In view of all the disturbing influences there is a good agreement between the form of the calculated and observed curves and this is reflected by the comparative smoothness of the difference curve.

βCaryophyllene Nitrosite and βCaryophyllene Nitrosite Hydrochloride.

In these compounds it at first appeared that, unlike the bornylene nitrosite, the absorption due to the nitroso group consisted of one uniform band with its head at 6800 A.U. Curves for the rotation dispersion formulated on this basis however would not give the very definite negative value at 6800 A.U., nor such a pronounced flattening effect at λ 6000 - 6400Å.u, the flattening being very noticeable in the case of the hydrochloride. In addition there is the rapid rise of the anisotropy factor to a constancy over a very long range. All these considerations, in addition to the bornylene results, suggested that the absorption for the nitrosite and the nitrosite hydrochloride might again be due to the summation of two bands, the secondary band in this case being completely masked by the main band. (c.f. (19) where four overlapping bands had a constant anisotropy factor).

Again measurements beyond 6900Å.u were not available and/

and no definite half value position could be established. By successive trials, however, it was found possible to formulate the curves shown on sheet (61(b)) where it will be seen that the absorption for both compounds can be very accurately represented as the sum of two overlapping bands. In both compounds the main constants for the band are the same but for the hydrochloride the secondary band is relatively more intense. The effect of this is seen when the calculated curves for rotation are drawn, since in the summation the relatively greater effect of the secondary band in the hydrochloride causes a greater flattening at 6000 - 6400Å, although the generally lower rotation for the hydrochloride also enhances the flattening.

The calculation of the rotation curves was on the lines indicated for the bornylene compound except that in this case it was possible to calculate molecular rotation. It is interesting to note how the much lower anisotropy factor for the caryophyllene nitrosite hydrochloride indicates immediately the much lower contribution of the band to the molecular rotation/

rotation, even although the maximum molecular extinction coefficients are almost the same.

The calculated curves for these compounds (sheets 61, 62, (b & c)) when compared to the observed curves give every justification for the belief that the rotation anomaly - and indeed almost the entire rotation - in the red is due to the nitroso absorption. The difference curve is very similar for both compounds, although as might be expected, it is higher for the nitrosite than for the hydrochloride.

There is still a slight anomaly in the difference curve but it is very slight and only its regularity makes it of importance. This small anomaly may be explained by the assumption of minor absorption bands completely masked by the larger bands. It will be noticed also that in one of the examples from Kuhn's work given on page 46 a slight anomaly still remains.

The foregoing represents an attempt to employ absorption and ellipticity measurements (giving the values of g and α) to formulate graphs for the contribution to rotation of given absorption bands on the/

the lines of the very recent work of Werner Kuhn. Difficulties in the form of disturbing factors such as dissociation in the case of bornylene nitrosite, the absence of complete absorption data due to the difficulty of continuing measurements beyond 7000 A.U. and the general difficulty of optical measurements in the extreme red, cannot be entirely eliminated, but even with these it is plain that the form of rotation dispersion curves inside absorption bands can be accounted for on the lines of the Kuhn theory.

Criticism may be directed at the justification for calculating an absorption curve always as if it were of the form $\varkappa = \varkappa_{max} e^{-c^2}$ and at the somewhat vague significance of the results obtained for the "difference curve". In this latter connection studies of groups of closely related compounds can do much to confirm the explanations advanced by Kuhn on the basis of electronic distribution. In addition there is in practice the tedious nature of the calculations necessary to evaluate an expression for the rotation which at best is only an approximation.

A/

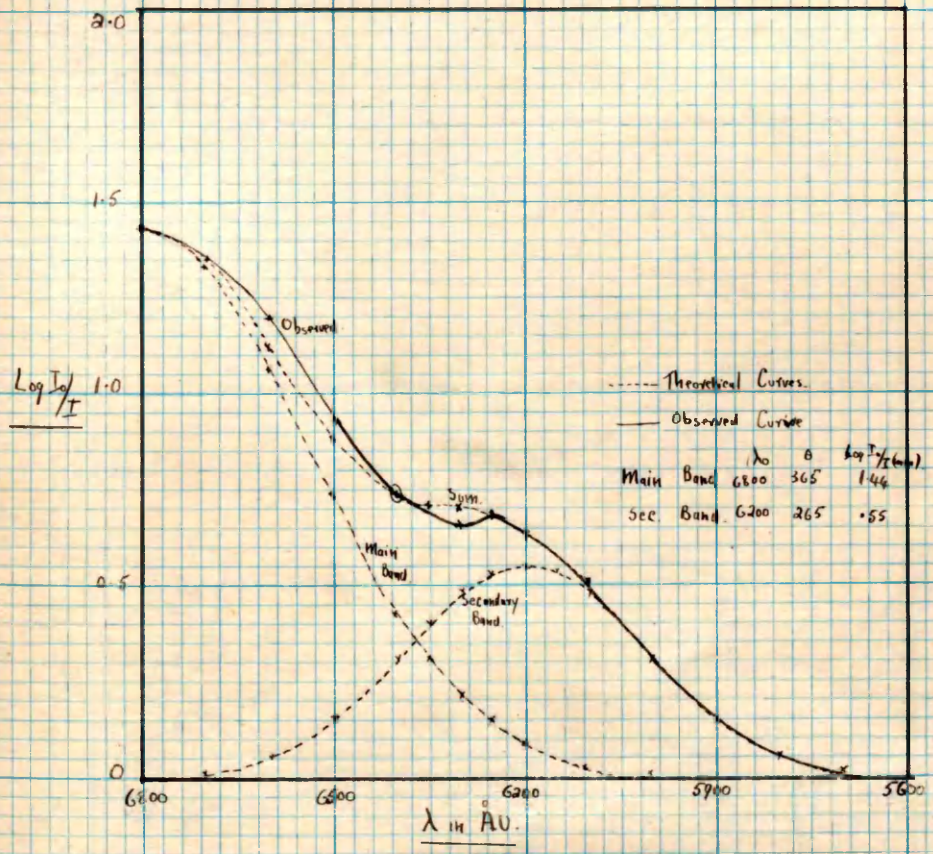
A valuable feature is the introduction of the expression $\frac{\varepsilon_a - \varepsilon_r}{\varepsilon}$ for the "anisotropy factor", since this gives a quantitative significance to the rotatory contribution of different absorption bands, and is moreover capable of extension to include other influences such as solvent effect.

ROTATION AND ABSORPTION FOR BORNYLENE NITROSITE

	Rotations for 6 cm. tube					Absorption (log I_o/I) for 6 cm. tube.			
	Calculated		A	B	B - A	Calculated			
$\lambda_{A.U.}$	Main Band	Sec. Band	Sum	Observed	Diff.	Main Band	Sec. Band	Sum	Observed
6900	-·52°	-·10°	-·62°	-	-	-	-	-	-
6800	+·03	-·13	-·10	-	-	1·44	-	1·44	1·44
6700	+·54	-·15	+·39	+0·38°	-·01°	1·34	·02	1·36	1·35
6600	+·97	-·22	+·75	+0·93	+·18	1·07	·06	1·13	1·20
6500	+1·14	-·31	+·81	+1·44	+·63	·74	·15	·89	·94
6400	+1·16	-·32	+·84	+1·48	+·64	·43	·31	·74	·74
6350	-	-	-	-	-	·31	·40	·71	·69
6300	+1·00	-·21	+·79	+1·39	+·60	·22	·48	·70	·65
6250	-	-	-	-	-	·15	·53	·68	·68
6200	+·77	0	+·77	+1·36	+·59	·09	·55	·64	·63
6100	+·59	+·22	+·81	+1·52	+·71	·03	·48	·51	·49
6000	+·52	+·35	+·87	+1·66	+·79	·01	·31	·32	·33
5800	+·43	+·25	+·68	+1·72	+1·04	-	·06	·06	·10
5500	+·34	+·13	+·47	+1·79	+1·32	-	-	-	-
5000	+·29	+·09	+·38	+2·08	+1·70	-	-	-	-

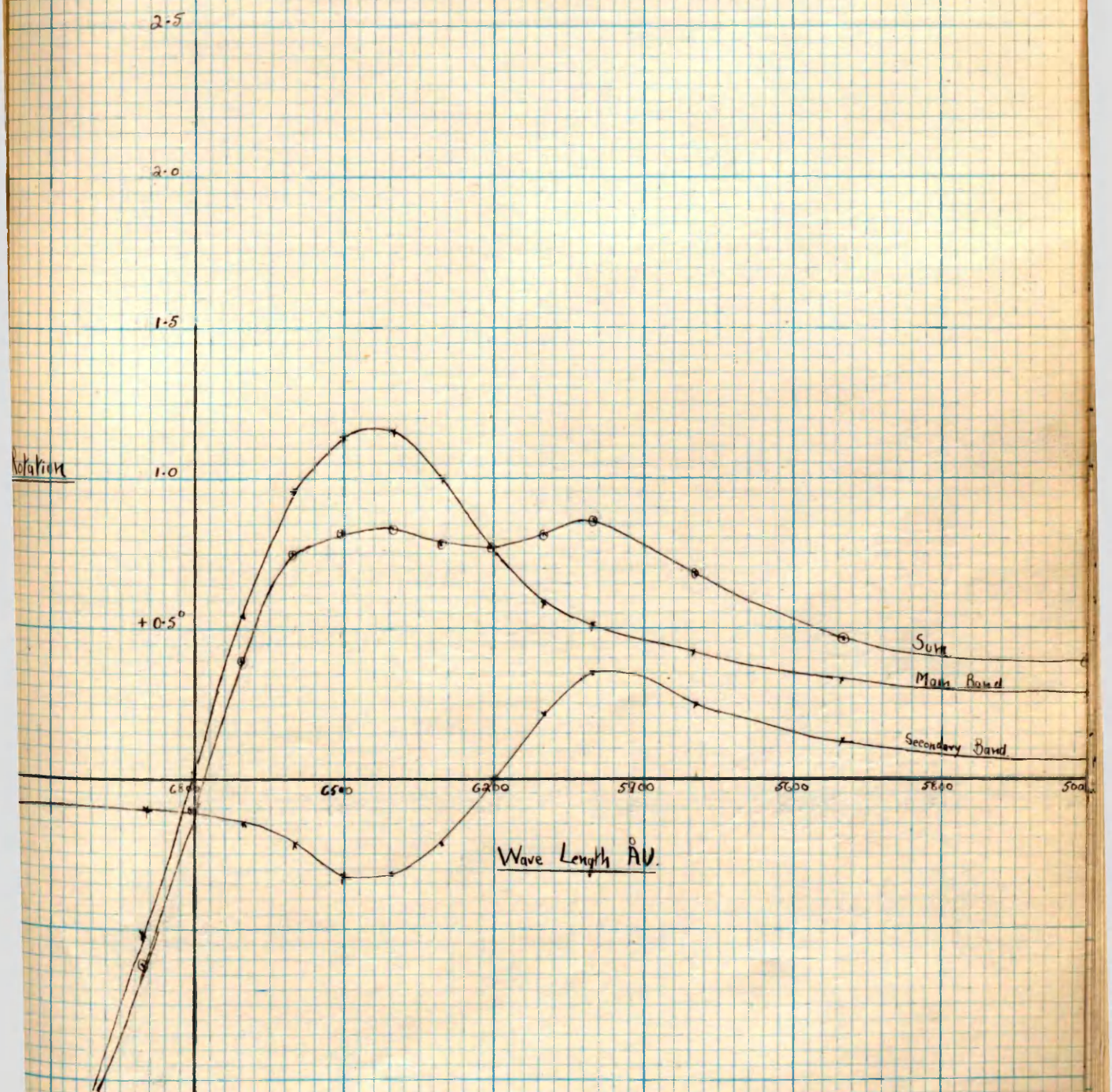
BORNYLENE NITROSITE

Individual and combined contributions to Absorption of two bands in red region comprising the "Nitroso Absorption".



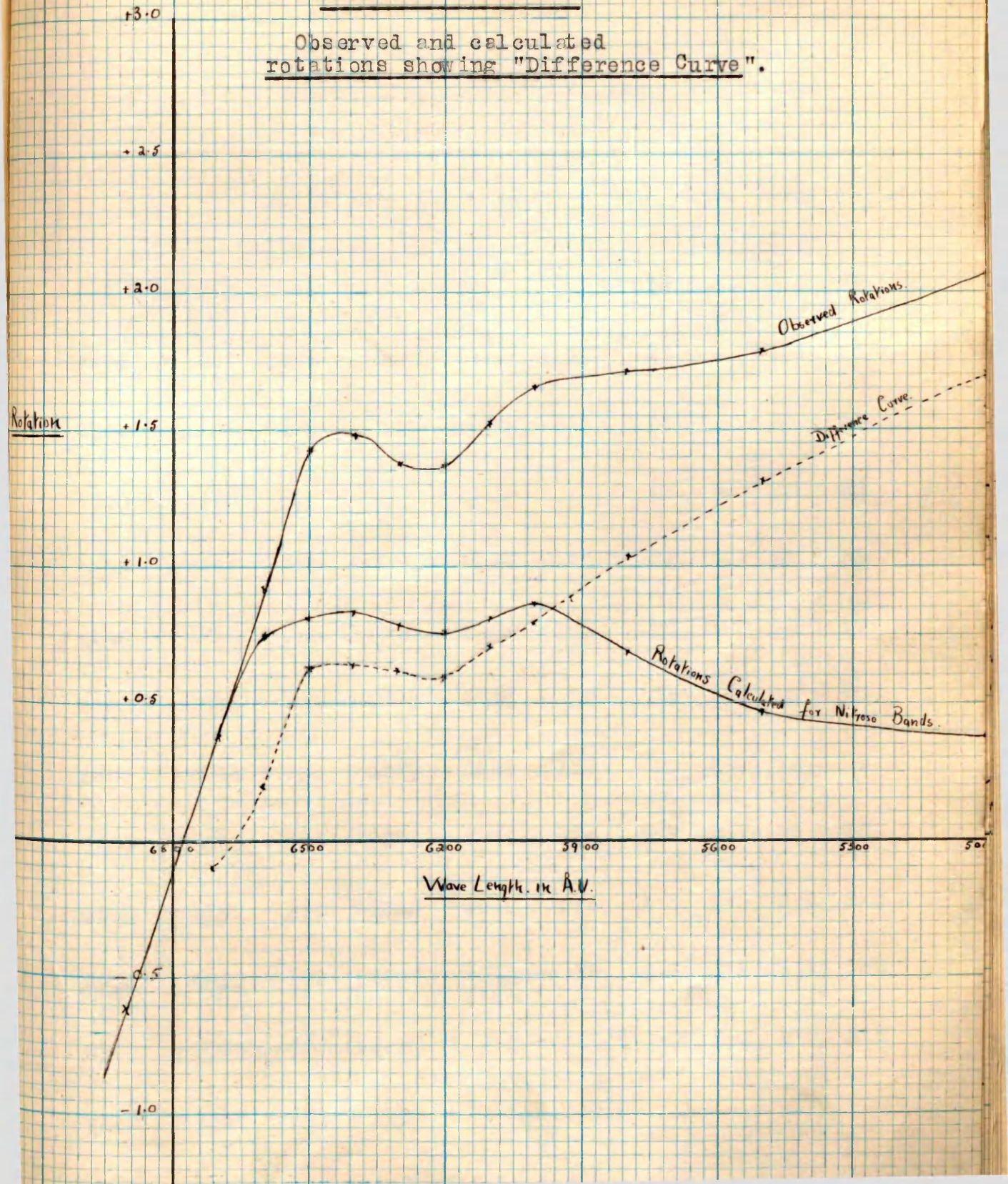
BORNYLENE NITROSITE

Individual and combined contributions to rotation of two bands in red region comprising the "Nitroso Absorption".



BORNYLENE NITROSITE

Observed and calculated rotations showing "Difference Curve".



ROTATION AND ABSORPTION FOR CARYOPHYLLENE NITROSITE.

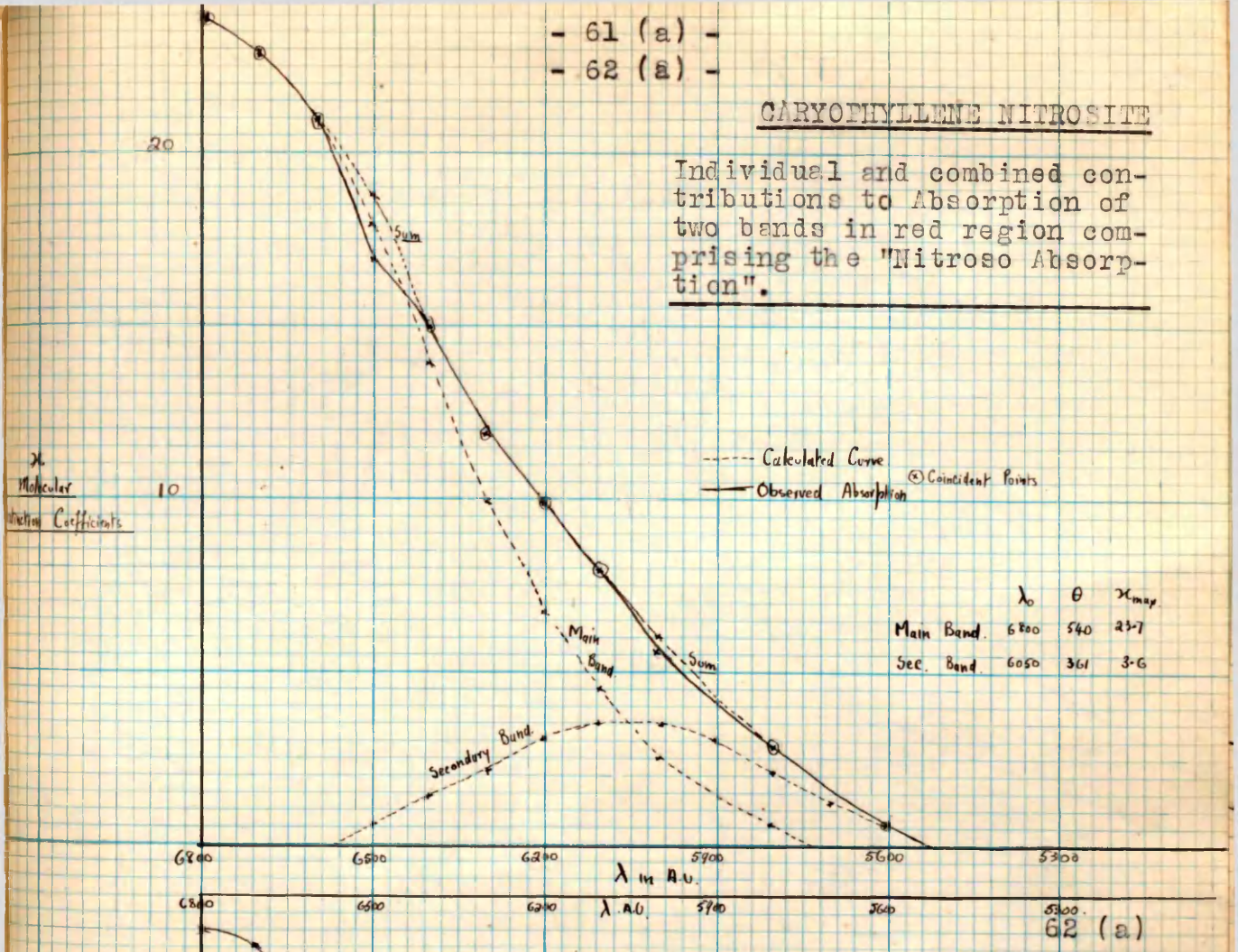
λ Å.U.	Rotations [M]					Mol. Ext. Coeffts. ε			
	Calculated		A	B	B-A	Calculated			
	Main Band	Sec. Band	Sum	Observed	Diff.	Main Band	Sec. Band	Sum	Observed
6900	-1570°	-292°	-1862°	-1815°	+ 47°	23	-	23	23
6800	0	-322	- 322	- 666	- 344	24	-	24	24
6700	+1609	-	-	+1149	-	23	-	23	23
6600	+3465	-575	+2890	+2740	-150	21	-	21	21
6500	+4790	-725	+4065	+4260	+195	18	0·7	19	17
6400	+5615	-795	+4820	+4830	+ 10	14	1·4	15	15
6300	+5944	-765	+5179	+5020	- 159	10	2·2	12	12
6200	+5860	-554	+5306	+4870	- 436	6·9	3·1	10	10
6100	+5560	-194	+5366	+4850	- 516	4·5	3·5	8·0	8·0
6000	+4635	+198	+4833	+4815	- 18	2·6	3·5	6·1	5·6
5800	+3095	+833	+3928	+4350	+ 432	0·7	2·2	2·9	2·8
5500	+2455	+671	+3126	+3465	+ 339				
5000	+1870	+306	+2176	+2555	+ 379				

ROTATION AND ABSORPTION FOR CARYOPHYLLENE NITROSITE HYDROCHLORIDE.

λ A.U.	Rotations [M] Calculated Main Band	Calculated Sec. Band	A Sum.	B Observed	B - A Diff.	Mol. Ext. Coeffts. $\varkappa$ Calculated Main Band	Calculated Sec. Band	Calculated Sum	Observed
6900	-920°	-190°	-1110°	-1000°	+110°	22	-	22	22
6800	0	-210	- 210	- 354	- 144	22·5	-	22·5	22·5
6700	+ 941	-	-	+ 500	-	22	-	22	22
6600	+2030	-374	+1656	+1500	- 156	20	-	20	20
6500	+2805	-472	+2333	+2290	- 43	17	·8	18	17
6400	+3290	-517	+2773	+3020	+ 247	13	1·5	14	14
6300	+3480	-498	+2982	+3065	+ 83	9·7	2·4	12	13
6200	+3435	-360	+3075	+3045	- 30	6·5	3·2	10	10
6100	+3260	-126	+3134	+3000	- 134	4·3	3·7	8·0	8·3
6000	+2710	+129	+2839	+2956	+117	2·5	3·7	6·2	6·2
5800	+1810	+542	+2352	+2708	+356	·7	2·4	3·1	3·1
5500	+1438	+436	+1874	+2105	+ 231	-	-	-	1·4
5000	+1094	+199	+1293	+1500	+ 207				

CARYOPHYLLENE NITROSITE

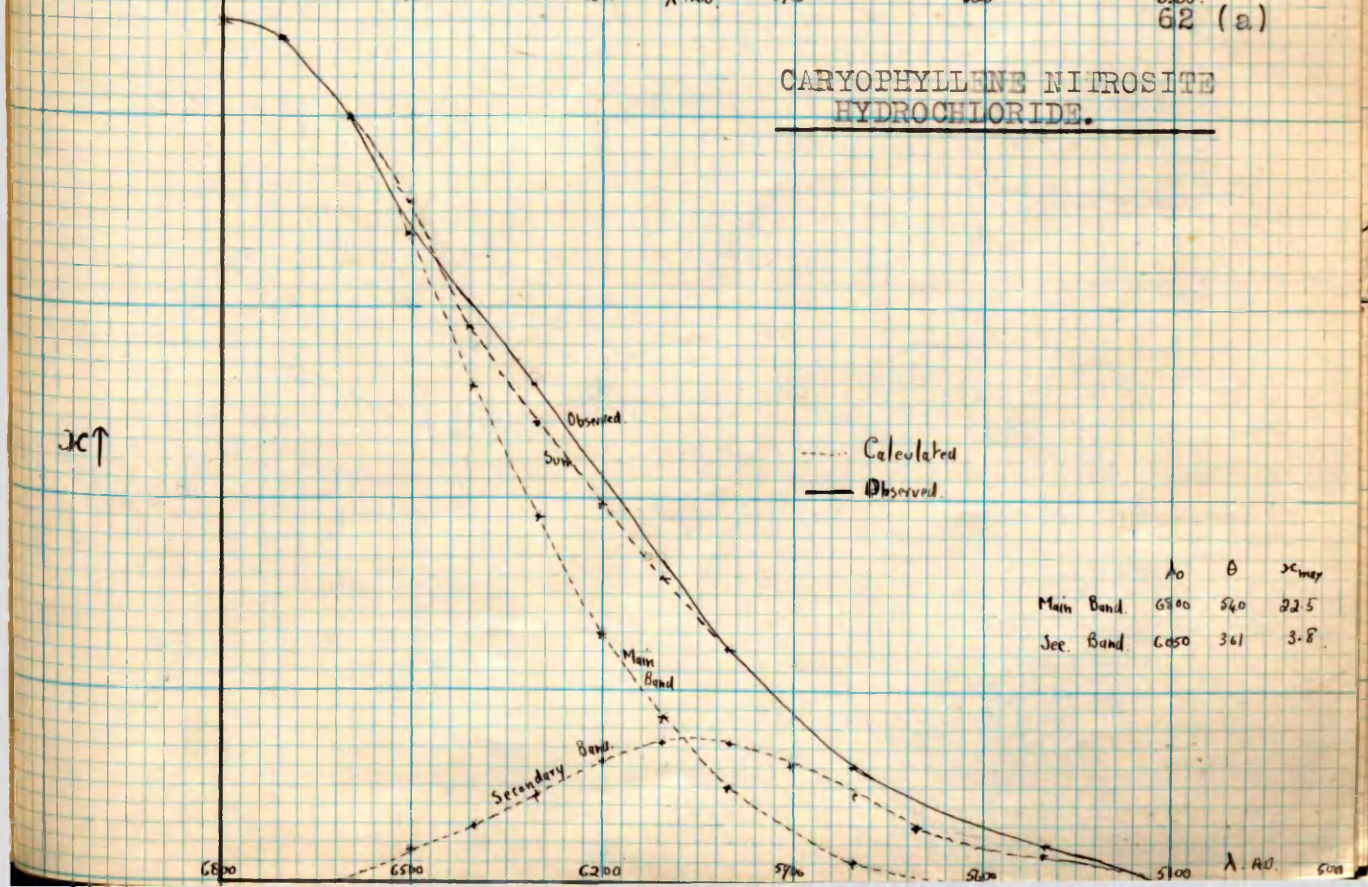
Individual and combined contributions to Absorption of two bands in red region comprising the "Nitroso Absorption".



	λ_0	θ	χ_{max}
Main Band.	6800	540	23·7
Sec. Band.	6050	361	3·6

62 (a)

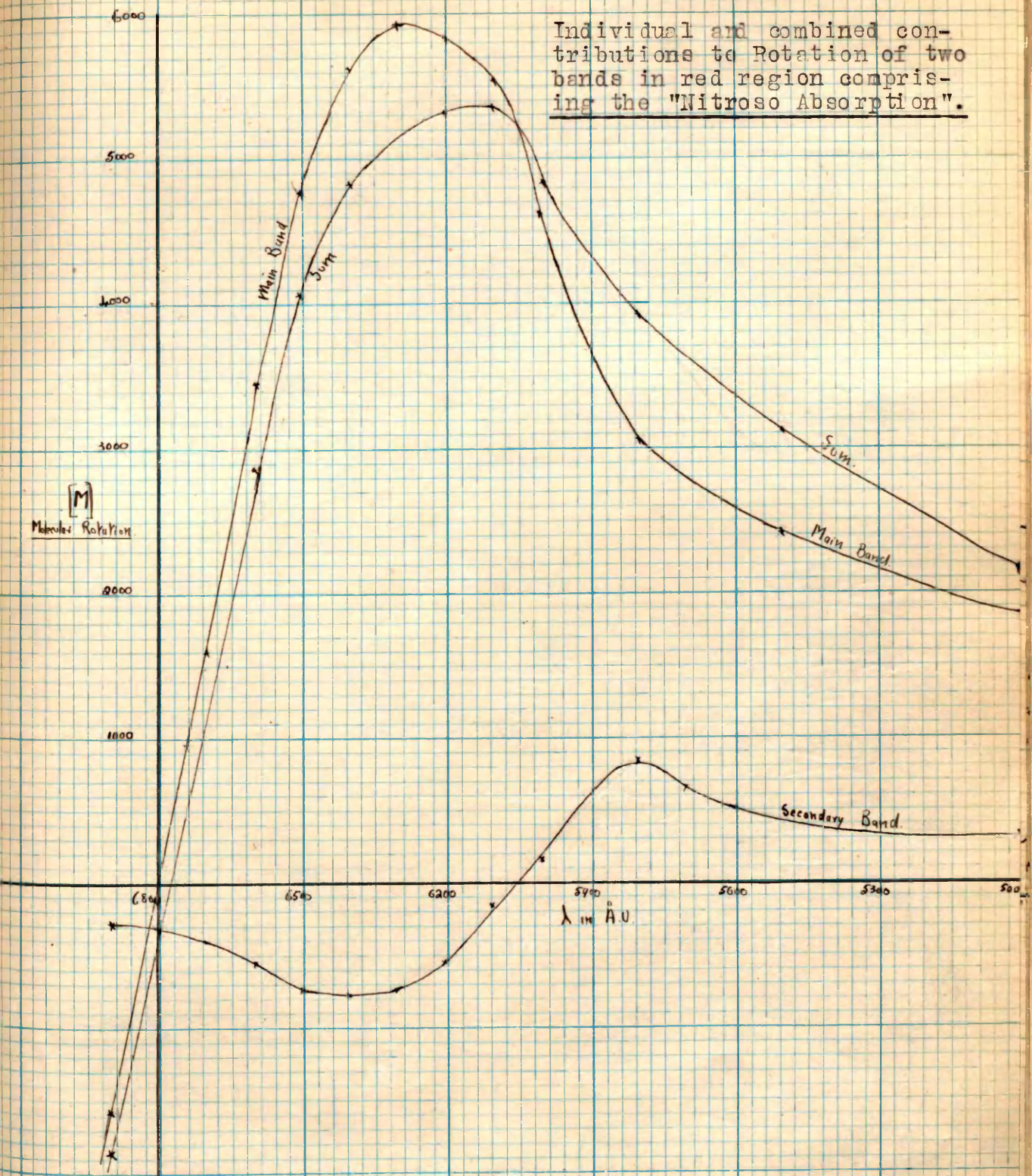
CARYOPHYLLENE NITROSITE HYDROCHLORIDE.



	λ_0	θ	χ_{max}
Main Band.	6800	540	22·5
Sec. Band.	6050	361	3·8

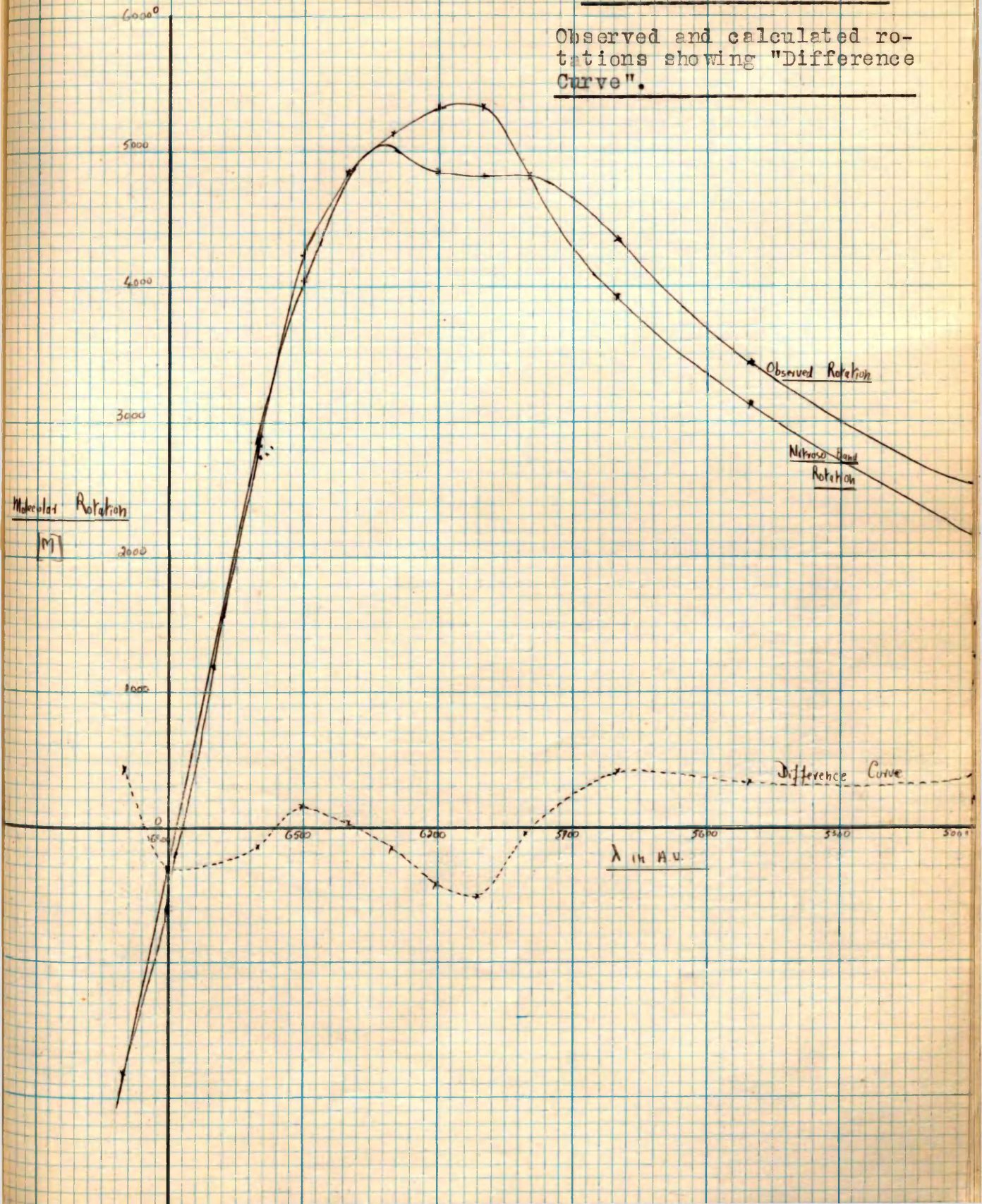
CARYOPHYLLENE NITROSITE

Individual and combined contributions to Rotation of two bands in red region comprising the "Nitroso Absorption".



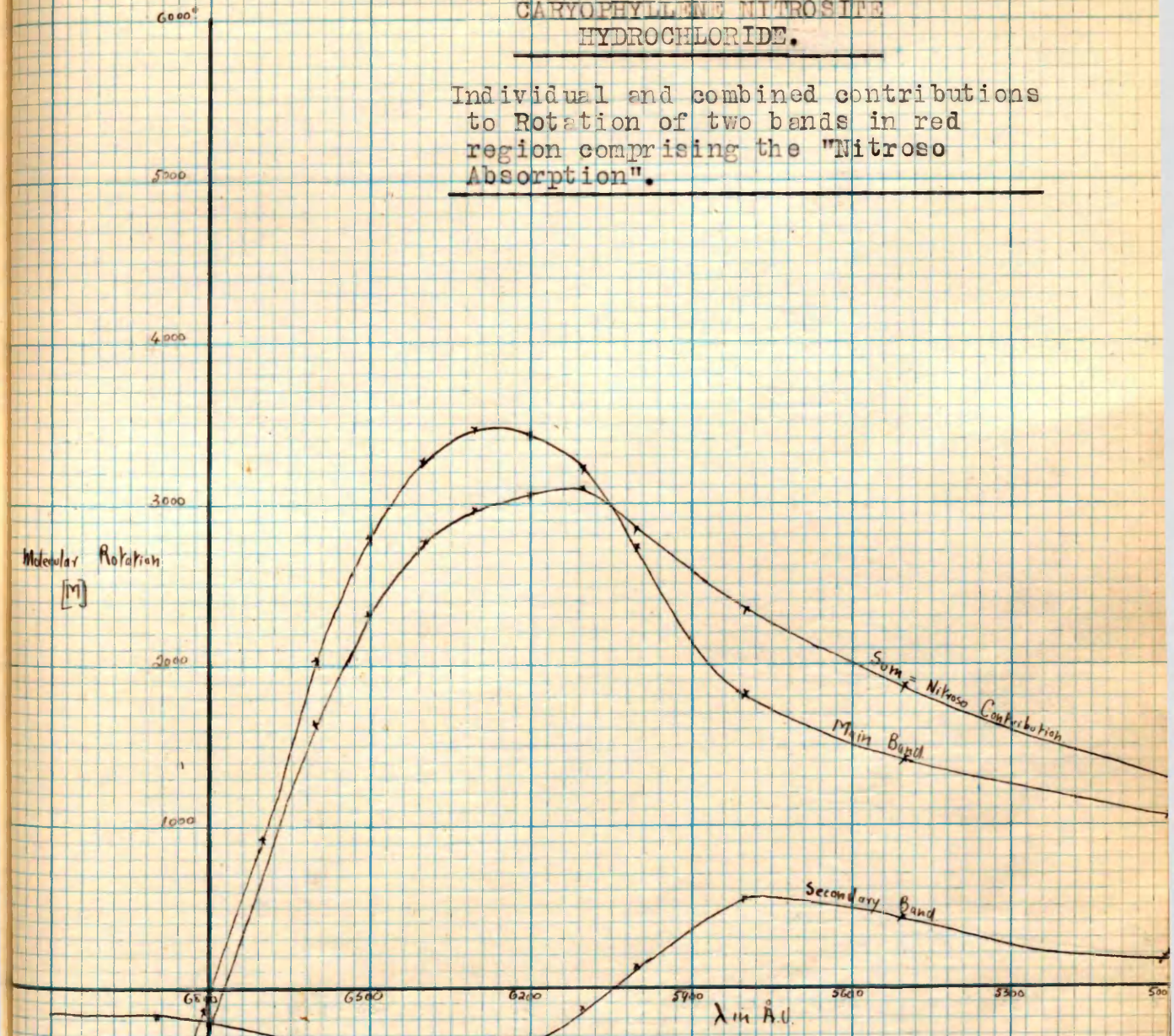
CARYOPHYLLENE NITROSITE

Observed and calculated rotations showing "Difference Curve".



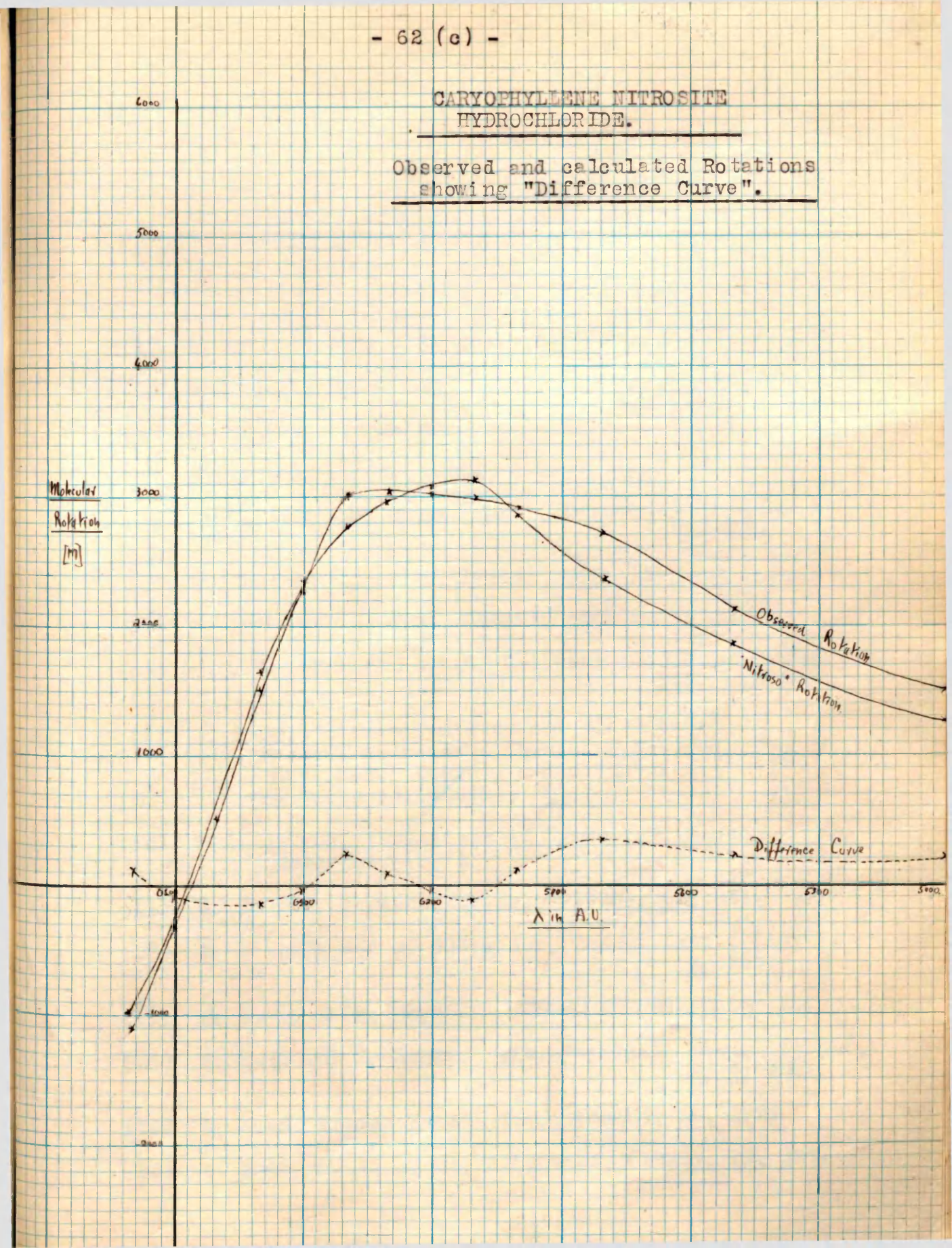
CARYOPHYLLENE NITROSITE HYDROCHLORIDE.

Individual and combined contributions to Rotation of two bands in red region comprising the "Nitroso Absorption".



CARYOPHYLLENE NITROSITE HYDROCHLORIDE.

Observed and calculated Rotations showing "Difference Curve".



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c.f. Kuhn (13) page 28.

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