THE COTTON EFFECT AS EXHIBITED BY SOME NITRO COMPOUNDS

with an additional paper on the photochemical oxidation of some pseudo nitrols.

A Thesis submitted to the University of
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by

ROY R. GORDON, M.A., B.Sc.

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THE MEASUREMENT OF OPTICAL ROTATORY POWER AND CIRCULAR DICHROISM IN THE ULTRA VIOLET WITH SPECIAL REFERENCE TO THE COTTON EFFECT.

PART I. HISTORICAL INTRODUCTION.

In two papers published in the "Memoires de la Société d'Arceuil" in 1809, Malus described how, by reflection from water, a beam of light could acquire all the properties of one of the beams produced by the double refraction of Iceland Spar i.e. how light could be "polarised" by reflection. He also showed that a plane polarised ray may be considered as the resultant of two rays polarised in rectangular planes. Thus when a ray of light is reflected at the polarising angle of 52° 45' from the surface of water, it is split up into two rays which are polarised parallel and perpendicular respectively to the plane of incidence.

These experiments were extended by Fresnel to the case of reflection at internal surfaces i.e. total reflection. It was then discovered that plane polarised light when totally reflected, was partially "depolarised". This depolarised light, however, was not a mixture of ordinary light and plane polarised light but was shown to be the resultant of two plane polarised rays one in the plane of incidence, the other perpendicular to it and differing in phase by 1/8th of a wave length when the plane of the incident ray makes an angle of 45° with the plane of incidence. After two reflections the light is completely depolarised but may be made plane polarised again by two further reflections. To this "completely depolarised light", Fresnel gave the name "circularly polarised light" since the resultant of two such plane polarised rays is a circular helix.

During the time that Fresnel was carrying out the above researches, Biot discovered that the plane of polarisation of a ray was rotated when it traversed a thin plate of quartz cut perpendicular to the axis. This rotation, he found, varied with the thickness of quartz traversed and also with the wave length of light employed. He also found that certain organic liquids and also solids when in solution possessed this property.

Fresnel showed that a ray of plane polarised light travelling along the axis of quartz is split up into two circularly polarised rays which travel with unequal velocities and hence may be separated by oblique incidence on an optically active medium such as quartz. He succeeded in separating these two components by using a tri-prism, two of the prisms being of right quartz and the third of left quartz. In a thin plate of quartz, where the two rays are not separated, they will recombine on re-emergence to form a plane polarised ray whose plane of polarisation makes an angle with that of the incident ray. This angle depends on the pitch of the helix, i.e. the wave length and also on the thickness of quartz traversed, the difference in the distance travelled by the two components being proportional to this.

In this way optical rotation was shown to be circular double refraction.

When ordinary refraction is plotted on a wave length basis in the absence of an absorption band, it is found to increase regularly with decreasing wave length.

If, however, an absorption band is present the dispersion curve no longer increases regularly with decreasing wave length but rises to a maximum on one side of the band, falls to zero in the middle of the band (or at least shows a point of inflection), reaches a minimum value and finally increases again. Since optical rotation is a difference between two circular refractions it was suggested that a similar effect might be shown by the curve of rotary dispersion in the neighbourhood of an absorption band.

THE COTTON EFFECT.

The effect just described was realised in the case of potassium chromium tartrate by Cotton(1) whose diagram is reproduced below

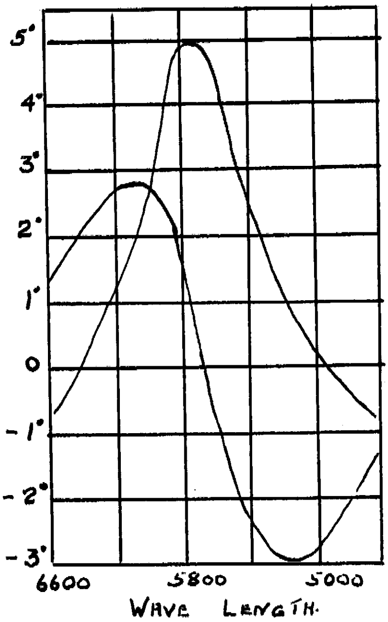


Fig. I.

The anomaly here is in the visible region.

In the case of circular double refraction in the region of absorption another effect makes its appearance in the shape of the dichroism. Biot had observed that certain crystals had the property of absorbing the ordinary and extra-ordinary plane polarised rays to different extents. This phenomenon was called DICHROISM. Bearing in mind the close similarity between the double refraction of ordinary light and the circular double refraction of an optically active medium it was soon suggested that a similar effect might be found for these two circular components. This was first observed by Haidinger(2) in the case of amethyst quartz. The term Circular Dichroism is applied to this effect.

In 1895, Cotton demonstrated the existence of circular dichroism in optically active absorbing solutions of copper ammonium tartrate. His method here was to pass two circularly polarised rays one right, the other left, produced by two quarter wave plates placed side by side, through two tubes containing the solution. The two beams were of unequal intensity after passing through the solution showing that they were absorbed to different extents.

It can be shown quite easily (for further discussion see pages on Measurement of Circular Dichroism) that the effect on the emergent ray of absorbing one circular component more than the other, is to render it elliptically polarised, the major axis of the ellipse being equal to the sum of the amplitudes of the circular components, while the minor axis is equal to their difference. Instead, therefore, of measuring directly the difference of absorption for right and left circular light, the ellipticity may be taken as its measure. By plotting ellipticity against wave length it is seen that it rises to a maximum at the maximum of absorption, which in turn coincides with the point of inflection of the rotatory dispersion curve.

The anisotropy factor.

By dividing the ellipticity by the absorption at the same wave length, we obtain a factor, commonly denoted by the symbol g, and called the anisotropy or dissymmetry factor, which may be taken as a measure of the optically active behaviour of the band. Both effects are shown diagrammatically below (Figs. II, A and B).

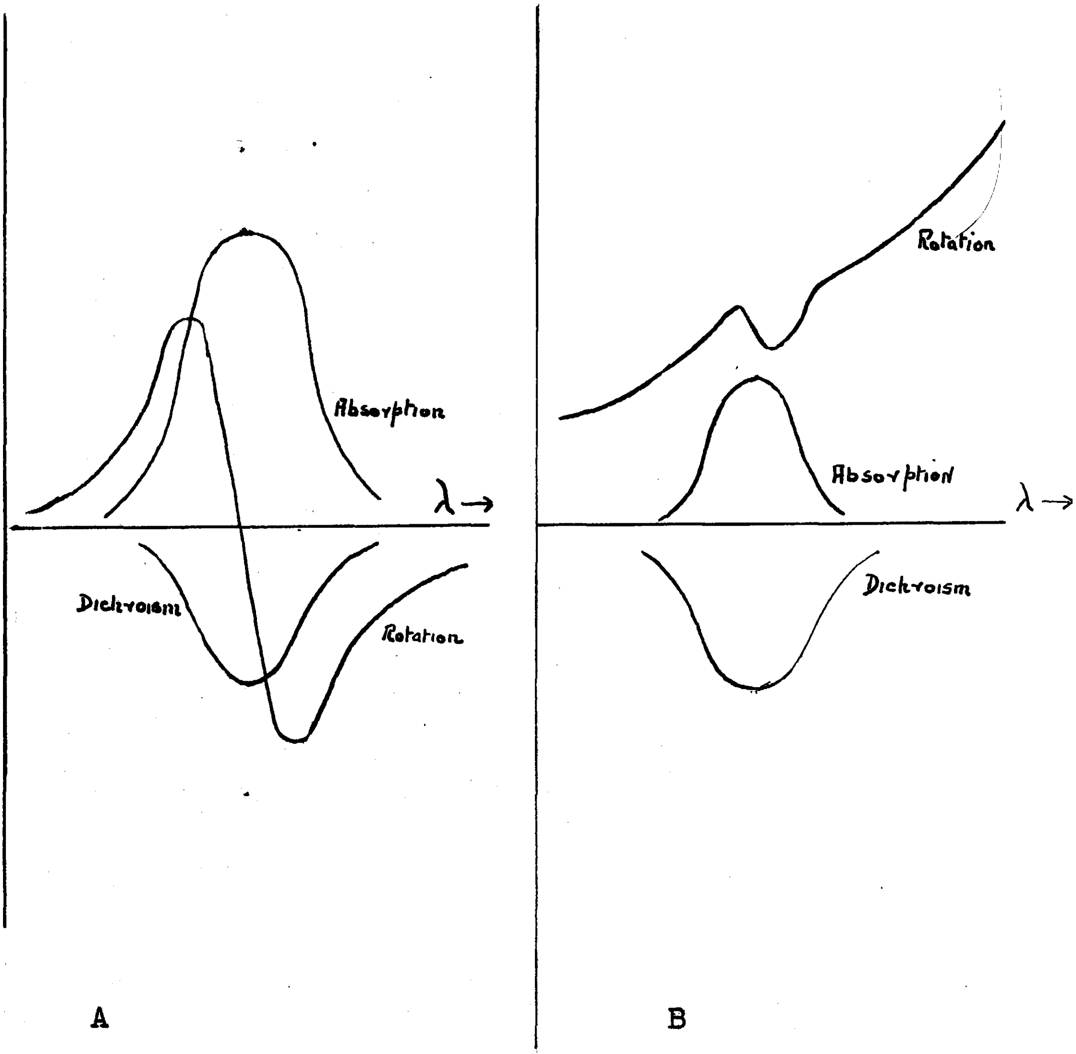
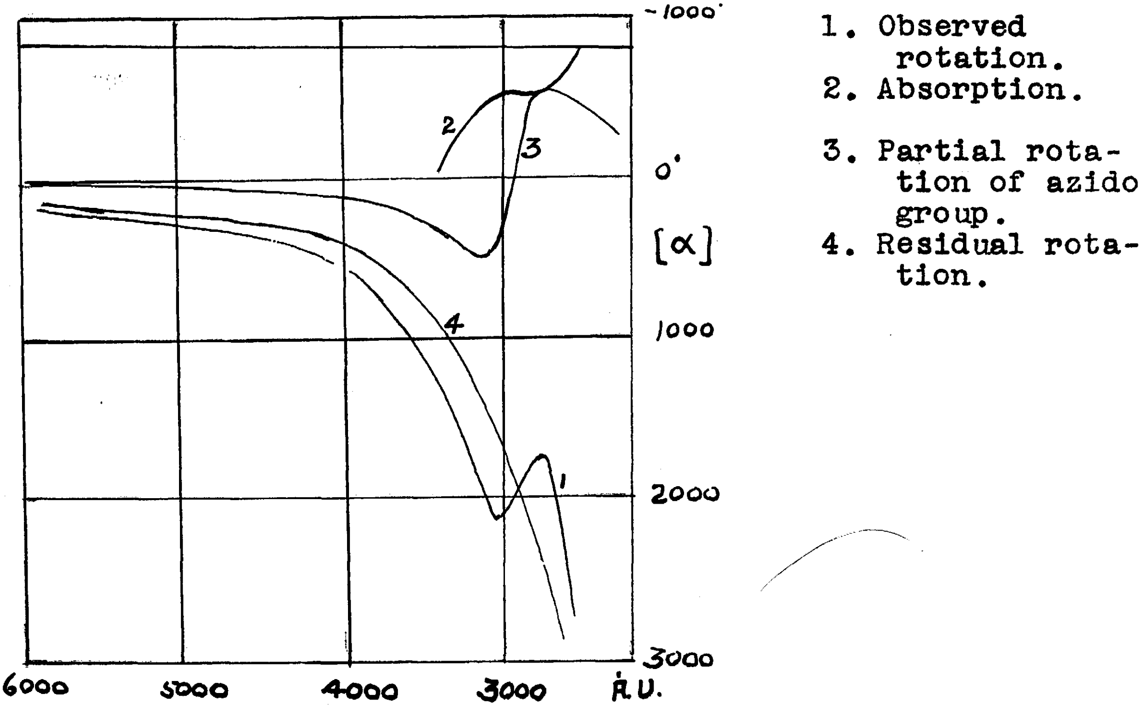


FIG. II.

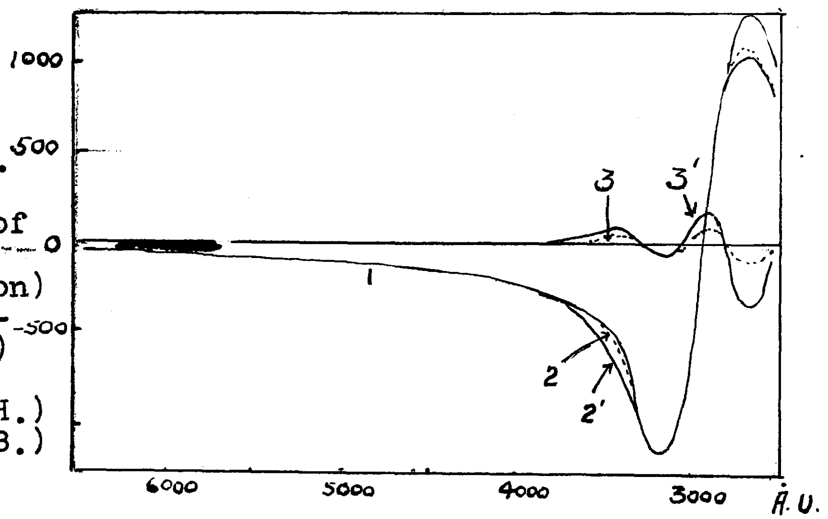
Fig. IIA shows the simplest case, Fig. IIB shows the case where the Cotton Effect is superimposed on a normal dispersion curve.

Examples of both forms of these curves are given in the literature. The diagrams shown below are those of Kuhn (figs. III and V) and of Lowry (fig. 14).



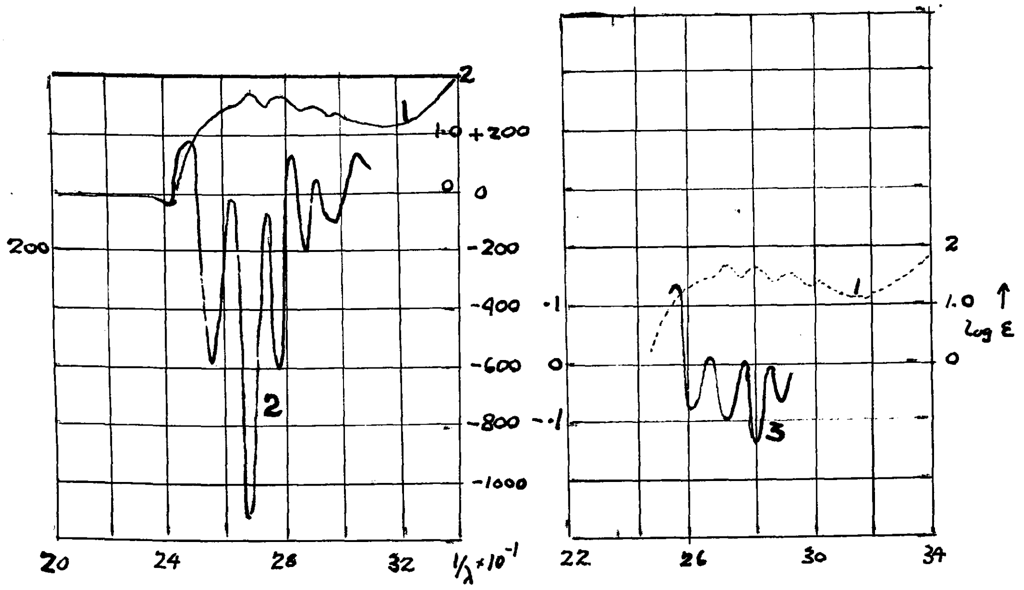
Absorption and Anomalous Rotation Dispersion of α- azido propionic Dimethylamide. (3)

FIG. III.



1. Observed Rotation.
2. Partial Rotation of CHO. (Lowry & Hudson)
2' - - - - (Kuhn & Braun)
3. Residual Rotation (L. & H.)
3' - - (K. & B.)

Tetra-acetyl μ arabinose (4) (FIG. IV.)



1. Absorption.
2. Molecular Rotation of methylcyclohexyl carbinol nitrite.
3. Circular Dichroism.

FIG. V.

Methylcyclohexyl carbinol nitrite (5)

Mathematical representation of the dispersion curve.

Biot had observed that rotation increased with decrease wave length of light employed. For several of the substances studied he found that the curve could be represented by an equation of the form $\alpha = \frac{k}{\lambda^2}$ where α = rotation and λ the wave length. This equation was only approximately true and held for wave lengths far removed from an absorption band.

Drude(6) extended Clark Maxwell's electro magnetic theory to the case of optically active media assuming that the vibrating particles in the medium travelled in short helices instead of in straight lines as in ordinary refraction. It has since been shown that his mathematical treatment did not correspond to his model and that such a model would not give rise to optical rotation. His mathematical treatment, however, led to an equation of the form $[\alpha] = \Sigma \frac{k_n}{\lambda^2 - \lambda_n^2}$ This has been applied extensively by Lowry to rotary dispersion and give satisfactory results except close to an absorption band where, from the form of the equation, the rotation would become infinite.

Natanson and later Kuhn(7) have attempted to find an expression which would represent the form of the curve of dispersion within an absorption band. To do this they have assumed that within the band, the rotation does not become infinite owing to the presence of frictional forces. These forces will be proportional to the velocity of the particles and will therefore be proportional to their distance from the head of the absorption band where the forced vibrations would be largest. These authors therefore take the friction term to be of the nature of a frequency.

From these assumptions, applied to a rather specialised model of linear vibrators, Kuhn has evolved a semi empirical equation for the partial rotation due to a group. This has been found to give good agreement with the experimental curve in many cases. His equation is given below.

$$[M] = \frac{100}{2\pi} \cdot \frac{(\varepsilon_2 - \varepsilon_1)_{max}}{\log_{10} e} \cdot \frac{\nu}{\nu_0} \left[e^{-\left(\frac{\nu_0-\nu}{\theta}\right)^2} \int_0^{\frac{\nu_0-\nu}{\theta}} e^{x^2} dx - \frac{\theta}{2(\nu_0+\nu)} \right]$$

Calculated curves showing the application of the equation are given in Figs. III-V.

This equation cannot be expected to give perfect results because of the specialised nature of the model on which it is based. In this Kuhn(8) assumes two linear vibrators which can vibrate only at right angles to one another. He does not attempt to say in what part of the molecule these are situated nor does he say anything about their dimensions or the nature of the coupling force by which they are connected. The remainder of the framework of the molecule is neglected. This must have some effect, however, which is not included in the formula given above, so that it must be regarded as being of the nature of an approximation to the truth.

Recently a further advance has been made in the physico-mathematical treatment of optical activity by Born(9) who also starts from the conception of vibrating electric doublets. The equation he derives, however, is rather complicated and cannot be applied to the region of absorption. A mathematical treatment of this is at present impossible.

From an examination of the curves shown in the above diagrams it will be seen that an absorption band may have a very marked effect on the rotation as observed in the visible. Indeed in some cases (Fig.IV) the whole of the rotation in the visible may be due to an absorption band lying in the near ultra violet. A study of the Cotton Effect is therefore important in determining the form of the rotatory dispersion curves of a series of compounds since, from the vicinial rule of Kuhn and Freudenberg(10), the form of the partial rotation curve due to a chromophoric group, does not change greatly for small changes in the other constituents. The effect has already been studied in a number of cases by Kuhn and Lowry(11) and their co-workers. The groups studied so far are given in the bibliography, the nitro group being added to the number by this thesis.

It will be seen from the formula of the pseudo-nitrols that these compounds contain two accessible absorption bands one due to the NO group and the other to the NO_2 group. From a study of the Cotton Effect due to these groups, some information may be obtained as to the form of the curve of rotatory-dispersion of these compounds.

Since the ellipticity is of opposite sign for the two optically active forms, it is clear that the two forms must have different absorption coefficients for right and left light. This fact will be seen to be of great importance when we come to discuss asymmetric photochemical action.

ASYMMETRIC PHOTOCHEMICAL ACTION.

By Beer's law, only that light which is absorbed can cause photochemical action. In the region of a Cotton Effect one circular component is absorbed more than the other, and, from this, it will be seen that it should be possible, by irradiating a racemic mixture with one form of circular light, of wave length corresponding to the maximum of ellipticity, i.e. maximum of difference in absorption, to obtain a preferential decomposition of one of the optical antipodes. This. by leaving an excess of the other component, will cause optical activity to appear from a racemic mixture.

Many unsuccessful attempts were made to realise this experimentally, among these being the attempt to produce an optically active compound by the bromination of cinnamic acid(12), presumably with light of the wave length of the absorption due to the double bond since we can hardly have two activated forms of the bromine atom.

In recent years quite a number of successful cases have been recorded. First, we have the case of ethyl α - bromopropionate(13) due to Kuhn. This was irradiated with light of 2800 A.U. and developed a rotation of 0.05. The same author(14) also had the example of the dimethylamide of a-azidopropionic acid where a rotation of - 1.04 in a 1dm. tube after being decomposed to 37% by light of wave length 3200 - 2800 A.U. In the visible region of the spectrum we have the case of humulene nitrosite(15). A 7% solution of this, when exposed to light of 6000-7800 A.U., developed a rotation of 0.21°.

At the same time there is the complementary problem of asymmetric synthesis. If one form of circular light favours the formation of one antipode then we should expect the production of rotation. Karagunis and Drikos(16) have done this, using solutions of the triphenyl radicals, chlorinating these preferentially under the influence of light of wave length 5890 and 4358 A.U. Following the rotation during the course of the reaction, they found that it rose to a maximum of 0.07° after 80 mins., illumination falling thereafter. A similar result was obtained using the other kind of circular light. They were unable, however, to decide whether the rotation developed was due to the halogenide formed, or whether it was due to the radical left over since these have been obtained in the optically active condition. A method whereby this question might be decided would be to examine the rotatory dispersion. If the rotation is due to the radical then there would be a Cotton Effect in the region of absorption, due to the radical, while if the rotation is due to the halogenide, then the Cotton Effect will be in the halogen band.

Still other results have been noted recently, in the shape of the bromination of trinitro stilbene(17). The rotations here were exceedingly small, being of the order of 0.04° and do not appear to be associated with any absorption band.

Since it had already been shown that the nitroso group was associated with a Cotton Effect(18) and was capable, given suitable conditions, of yielding positive results in asymmetric decomposition, it seemed desirable to examine other compounds containing this group.

The choice of compounds for this line of research is subject to certain limitations. For purposes of purification and ease in handling, the substance should be a solid. It must be optically active and exist also in the inactive condition. Also it must be capable of being decomposed photochemically to give inactive products since the laws governing optically mixtures are not known.

With these limitations in mind, the psuedo nitrols appeared to be suitable and their photochemical behaviour was examined.

PART II. THE MEASUREMENT OF OPTICAL ROTATORY POWER IN THE ULTRA VIOLET.

In section I the production of plane polarised light by reflection was described. The general method, however, is to use a polarising prism. This depends on the power of double refraction possessed by most crystals. Two methods are in use for the production of plane polarised light from this. The first is to use a thickness of crystal great enough to cause a separation of the two rays, so that one may be stopped by a screen. The second method is to cause one of the rays to be totally reflected, leaving the other unchanged. In the measurement of rotation in the visible the latter method is used, while in ultra violet polarimetry, the first method is employed.

A polarimeter consists in essence of a polariser which produces a plane polarised ray by either of the above methods and an analyser which consists of a similar arrangement of prisms. As the analyser is rotated, the intensity of the field varies from a maximum to absolute darkness in the case where the principal planes of the analyser and polariser are at right angles to one another.

If two prisms are in such a position of extinction and an optically active medium is introduced between them, then the field will not remain dark and the analyser will require to be moved through an angle to restore this condition.

This is the angle of rotation and, when divided by the length of active medium traversed and by its density, the result is called the Specific Rotatory Power of the substance.

In practice it is not found to be sufficiently accurate to use this position of absolute extinction which, to the eye, appears to extend over a considerable angle. To overcome this difficulty, a device called the half shadow is introduced. This consists, in the case of totally reflecting prisms, of a second smaller prism placed behind the polariser and covering part of the field. The principal axis of the second prism is inclined at a small angle to that of the main prism. When the field is viewed through both prisms it will not have uniform intensity unless the principal axis of the analyser bisects the angle between the two prisms constituting the polariser. This small angle is called the half shadow angle. An apparatus of this design, due to Lippich, but with a triple field is used extensively in visual polarimetry.

Since the angle of rotation varies with the wave length of light used, it is necessary to use a monochromator, either in the form of coloured filters or by using a constant deviation spectroscope. This latter is the most suitable for work on rotatory dispersion and, in visual work, the spectroscope is put between the light source and the polarimeter. In ultra violet polarimetry, on the other hand, the spectroscope comes after the polarimeter since there, the whole spectrum is photographed,and the wave length of the extinction point, is found from this.

ULTRA VIOLET POLARIMETRY.

For the measurement of optical rotatory power in the ultra violet, the optical parts of the instrument must be constructed of quartz or calcite. The use of quartz, by reason of its optical activity, introduces complications which will be dealt with later. All Canada balsam, which is used in visual polarimeters to cement the two halves of the polariser together, must be eliminated since the balsam does not transmit light below 3400 A.U..

The first measurements to be made in the ultra violet were those of Soret and Sarasin (19), who determined the rotatory power of quartz down to 2143 using a modification of Foucault's method, the dark band being made to coincide with known lines of the cadmium spectrum and their position observed by focussing the rays on a fluorescent screen. This method, however, is not very accurate, owing to the fact that the bands had not got sharp edges, so that they could not be set accurately on the cross wires.

The type of instrument used for the measurement of rotation in the visible, may be adapted for use in the ultra violet by observing the conditions mentioned above and recording the results photographically.

Quartz has the advantage over calcite, that it will allow of rotations being measured down to 1850 A.U., whereas

Iceland Spar. of a thickness of 4 cms. transmits only to 2400 A.U. A polarimeter, in which all the optical parts are of quartz or fluorspar, has been constructed by W. Kuhn(20) and a similar instrument has been employed for the work in this thesis. The general layout of this instrument is shown in the diagram below.

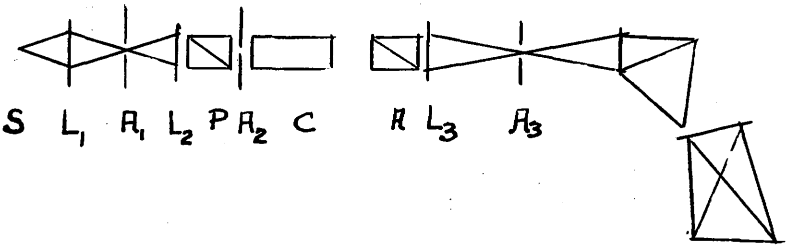


FIG. VI.

S	Fe arc as light source
L_1	Plano convex quartz lens
A_1	Brass plate with pinhole
L_2	Convex lens
P	Polariser
A_2	Screen
C	Cell containing solution
A	Analyser
L_3	Quartz-fluorite achromatic doublet
A_3	Screen.

The Prisms.

These are Rochon prisms as illustrated in the sketch below, the lines representing the optic axis.

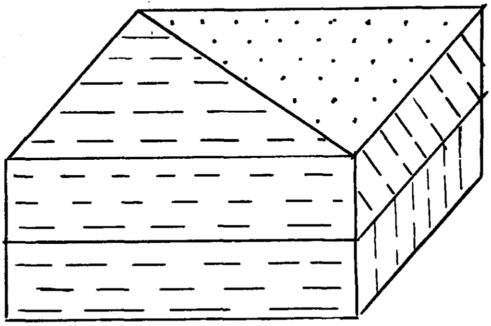


FIG. VII.

The two halves of each prism are composed one of right and the other of left quartz, the two left pieces being cut from the same block, so that they are exactly equivalent to one another, and similarly for the right hand pieces. In order to obtain the half shadow device, the polarising prism is split horizontally, each half ground away by $2\frac{1}{2}$ and then cemented together again, thus forming a fixed half shadow of 5°.

In that half of the prism nearest to the light source, the light must run parallel to the optic axis, while, in the second part, it runs perpendicular to it. Since it is obliquely incident on the second part, there is a separation of the ordinary and extra ordinary rays formed when a ray travels through quartz perpendicular to the optic axis. The ordinary ray is undeviated, while the extra ordinary ray is deviated towards the face. AB using a prism of 4 cm. length and 2 x 2 cm. aperture, a separation of 5 mm. is obtained after a distance of 27 cm. The extraordinary ray is cut off before reaching the active solution, either by using a screen or by using a brass cell of such a size that only the ordinary ray is allowed to enter. By this means, any interference between the two rays due to internal reflection, may be prevented.

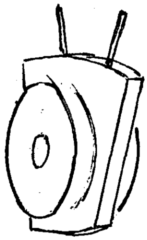
The analyser consists of a simple Rochon prism arranged so that that part in which the axis is parallel to the direction of propagation, is nearest to the spectograph. The incident ray, which is now plane polarised, has its intensity reduced by an amount depending on the angle which its plane makes with the axis of the first part of the analyser. Once again, two rays are formed. These travel undeviated until they reach the oblique separating surface, where they are separated, the ordinary ray again passing on unchanged. If the analyser is not placed as described, the incident ray, which has already been rotated by passage through the solution, will be still further rotated each wave length by a different amount before reaching the surface of separation, or that part of the prism which reduces the intensity. The effect of this will be that a single direction of the second part will not reduce the intensity of all incident wave lengths equally, since these make varying angles with the axis. No extinction would be obtained in that case. After the intensity has been reduced, the amount of rotation produced does not matter, since it does not affect the photographic plate. The separation of the two rays in this case amounts to 6 mm. after a distance of 37.8 cm.

THE LIGHT SOURCE.

At first a nickel spark was used but was abandoned owing to its small intensity requiring such long exposures, that the plates were fogged. More than this, the light source was not steady enough, and in addition, was very noisy. An iron arc running at 3 amps. was tried next. This cut down the exposures but still was not steady enough; the flickering leading to a lack of distinction in the dividing line and giving rise to a black line on each side of it. To obviate this, a brass screen with a hole of 1 mm. was placed as shown at A_1 in Fig. VI. This was a slight improvement, though it did not remove the trouble. A smaller hole was no improvement. A concave mirror of nickel was placed behind the light source, so that the light was brought to a focus on the pinhole. A silver mirror could not be used for this purpose, because there is a region of low reflective power in the ultra violet. This concave mirror was only a limited success and finally a quartz plano convex lens of focus 1·5" was used. The difficulty of keeping the point of light from this focussed steadily on the pinhole, was finally overcome by running a large electromagnet in series with the arc, as recommended by Houston in his "Treatise on Light", p. 250.

THE CELL.

The first cell to be used was one of five cms. with quartz ends. These were presumably matched but on examination, were found to have a considerable resultant rotation even in the visible. The equivalent thickness of quartz to cause this rotation was calculated and a correction curve was drawn from the data given by Lowry(21). This proved to be a most unsatisfactory arrangement, for, in most cases, the rotation due to the tube exceeded that due to the substance. under examination. Moreover, the ends were found to possess considerable ellipticity, so that they were useless for the measurement of circular dichroism. In addition to this, the cell was found to be too long for work anywhere near an absorption band. A smaller cell of brass was therefore constructed as shown in the sketch below



This cell is 0.99 cm. long, and is equipped with two ends of fused silica free from strain. These were obtained from The Thermal Syndicate and have been used throughout the present work. The two ends are screwed on and the cell filled by means of the two small holes in the top, which are then stoppered with two small brass plugs. This prevents any loss by evaporation during the course of a number of readings, the time for this sometimes occupying a full day.

General arrangement and adjustment.

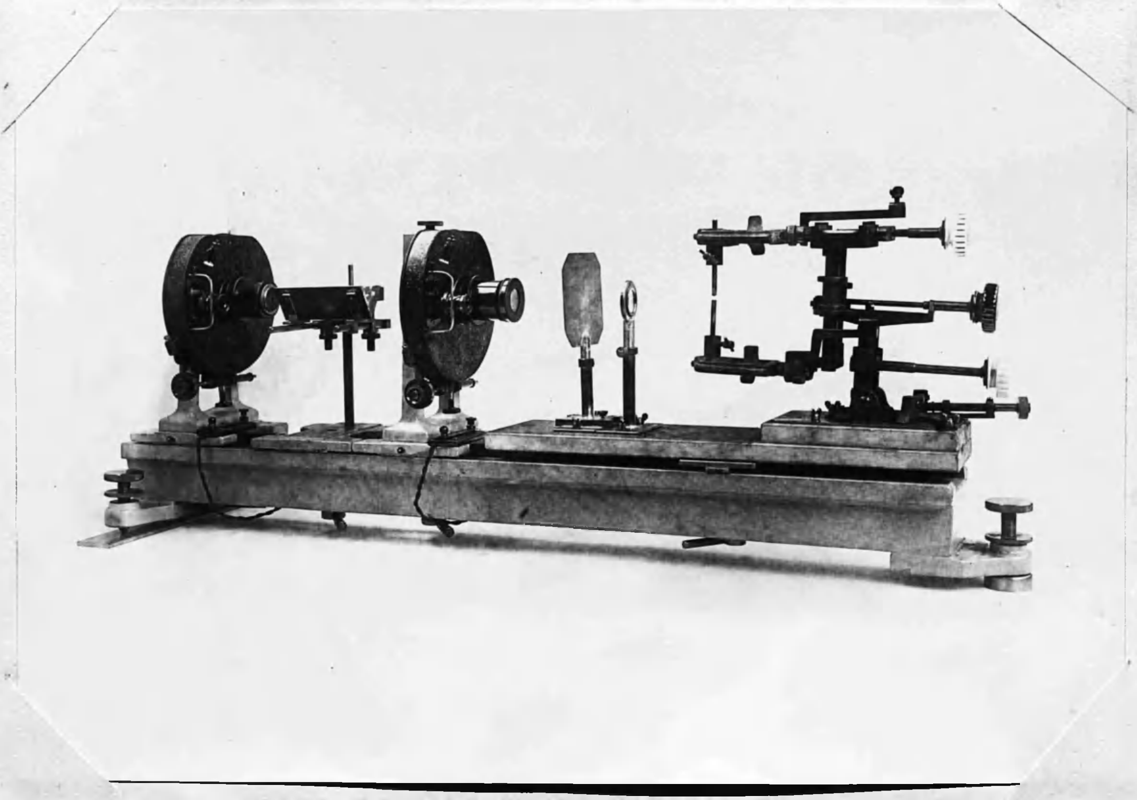
The polariser and analyser are mounted independently on a heavy cast iron optical bench, with two levelling screws at the front and one at the back. In order to get the polariser and analyser into the correct position with respect to one another and to the spectograph, the front of the polarimeter was mounted on two iron plates sliding over one another. By pulling the polarimeter, using the single screw as centre, the light could be focussed on the slit of a constant deviation spectroscope placed at exactly the same distance from the polarimeter as the slit of the spectograph. By this means, an enlarged image of the dividing line was obtained, and, by moving the polariser and analyser, the optimum position of these could be found visually. Only slight corrections were necessary after this, to obtain the positions for photographic work.

This same arrangement with the constant deviation spectroscope was also employed to ensure that the levelling of the prisms was correct. By focussing the dividing line on the cross wires in the eyepiece, and rotating the polariser through 180°, any displacement of the dividing line could easily be seen. The polarising prism is held in place in a cork-lined holder, by means of three pairs of screws. By adjusting these the dividing line was obtained, so that it remained unaltered in level after being turned through 180°.

The same process was repeated for the analyser.

The photograph resulting from this instrument consists of the iron arc spectrum divided along its length by a thin white line. The zero was first fixed visually, using the arrangement described above. It was found, however, that the zero so obtained did not hold for photographic work, differing from the value finally obtained for this by about 0.5°. The photographic zero was fixed by taking a number of positions of the analyser round the position found visually. These readings differed by 0.02°, so that the zero could be fixed to within 0.015°. The zero is that position of the analyser at which the two halves of the spectrum have the same intensity all the way along. At other positions the top half is either darker or lighter than the lower half. When an optically active medium is placed between the polariser and analyser, the resulting photograph shows a change over from dark on the upper, to dark on the lower half, or vice versa, one wave length only being extinguished, i.e., matching in both halves. The case just described would hold only for a dispersion curve passing through zero, but the same effect would be obtained rotating the analyser through a small angle and finding the wave length which is unaltered. The angle would then be the rotation of the substance for that wave length. By repeating this procedure for various angles a complete dispersion curve may be obtained. It should be noted that this procedure is the reverse of that employed in visual work in that here the rotation is first fixed and the wave length found corresponding to this.

Naturally the exposures required vary both with the amount of light transmitted by the solution and also with the part of the spectrum being examined A further factor is the type of plate used. After experiment, it was found that the



most satisfactory results were obtained using Ilford Iso-Zenith plates of H & D 650. With these the longest exposures required were 42 minutes with 2-2 dinitro camphane. Some experiment was also necessary to find the best developer to use with these plates. That finally used was a maximum contrast developer of 50 gms. each of hydroquinone, sodium bisulphite and potassium bromide in two litres of water. For use equal quantities of this solution and a solution of 90 gms. caustic soda in two litres of water are taken, the time of development being about 1 minute.

Trial of the instrument with camphor.

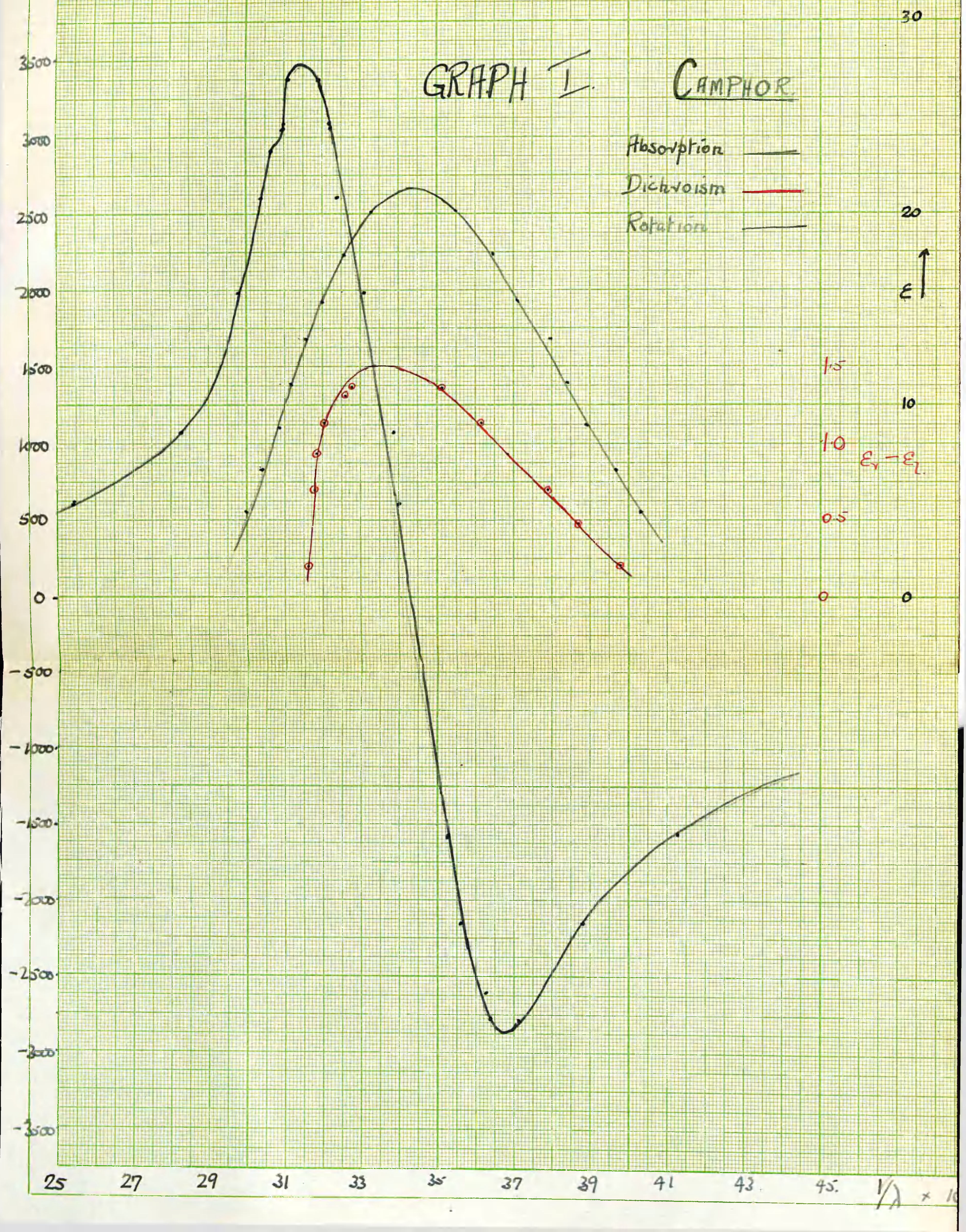
The instrument having been adjusted it was now necessary to try it out on some substance whose rotation in the ultra violet was known. For this purpose camphor, whose rotation has been studied by Lowry and Gore,(22) was chosen. The results, using a 1% solution in Hexane, are given in Table I and illustrated in graph I. The rotation rises to a large positive maximum of M =3500° at =3200, thereafter falls to zero at 2950, rising after this to a negative maximum of M =3000° at 2720 A.U. These results agree closely with those recorded by the above authors, i.e., M =3950° at 3200 A U, zero at 3020 and negative maximum of 3300° at 2720 A U for a solution in cyclohexane. For camphor vapour(23) the following results are recorded :-

Maximum M =3040° at λ =3200, zero at 3020 A U and
minimum M =2830° at λ =2800.

TABLE I

ROTATORY DISPERSION OF CAMPHOR 1% soln. in hexane

ROTATION α	MOL ROT $[M]$	$1/\lambda \times 10^{-1}$	
+ 2.2	+ 3377	31.12	31.95
+ 2.1	+ 3100	31.00	32.20
+ 2.0	+ 3068	30.95	32.20
+ 1.9	+ 2915	30.70	32.22
+ 1.7	+ 2607	30.40	32.40
+ 1.3	+ 1992	29.80	33.05
+ 0.7	+ 1073	28.48	33.40
+ 0.4	+ 614	25.39	-
- 1.0	-1535	-	41.30
- 1.4	- 2148	35.60	38.80
- 1.8	- 2760	36.40	37.10

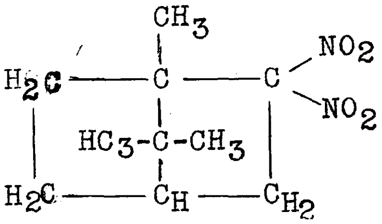

GRAPH I
CAMPHOR
Absorption
Dichroism
Rotation
3500
3000
2500
2000
1500
1000
500
0
-500
-1000
-1500
-2000
-2500
-3000
-3500
30
20
10
0
ε
1.5
1.0
0.5
0
ε_r − ε_l
25
27
29
31
33
35
37
39
41
43
45
1/λ ×

The graph also shows a small irregularity near the positive maximum. This small "step-in" has been noted by other workers(24) and is said to be due to the fact that the absorption band in camphor is composite. A further evidence of this is to be seen in the fact that the curve is not symmetrical, the positive peak being much narrower than the negative one. These facts are further supported by the observation that the circular dichroism is situated chiefly on the long wave side of the absorption band.

From these results it was concluded that the instrument was correctly adjusted as far as rotation was concerned at least.

Rotatory Dispersion of 2-2 dinitrocamphane.

The problem under examination was to find the contribution, if any, due to the nitro group in an optically active compound. To avoid the labour and expense of a lengthy resolution a nitro compound was sought which would be optically active naturally. Such a substance was found in the oxidation product of camphor pseudo-nitrol. This was prepared by allowing the nitrol to stand exposed to light and oxygen for 14 days on a porous plate. As described in another section of this thesis, the product formed was shown to be 2-2 dinitro camphane which has the structural formula :-



For purposes of rotation this was recrystallised six times from alcohol-water solution.

The rotatory dispersion was first studied in the visible, using an ordinary spectro polarimeter consisting of a Hilger constant deviation spectroscope and a Lippich polarimeter, with a 1000 c.p. Pointolite lamp as light source. The results of this are shown in Table 2 and graph 2, from which it will be seen that the rotation rises rapidly towards the ultra violet.

For work in the ultra violet region various concentrations had to be used, depending on the absorption at the point under examination. These solutions varied from 1.25% to 0.156%, alcohol being used throughout as solvent. In all cases the length of tube used was 0.99 cm. and the temperature room temperature of 17°C. The exposures required also varied from 2 minutes for the zero up to a maximum of 45 minutes, using Iso-Zenith 650 plates.

The results are given in Table 3 and illustrated on graphs 3-5. From this it is obvious that the rotation is anomalous, rising to a negative maximum of $[\alpha]$ =2640° at a wave length of 3030 A.U. Thereafter the rotation falls steeply to zero at a wave length of 2770. Beyond this the rotation is positive, but cannot be followed very far owing to the large amount of general absorption.

From data obtained from the circular dichroism and absorption curves, a calculated curve for the partial rotation due to the NO_2 group has been drawn using Lowry and Hudson's(25)

TABLE 2

ROTATORY DISPERSION OF 2-2 DINITROCAMPHANE IN VISIBLE

conc. 2.073 gms./100c.c. EtOH

λ	ROTATION	SPEC ROT
6800	− 0.92	− 74.0
6700	− 0.97	− 78.0
6600	− 0.99	− 79.6
6500	− 1.03	− 82.8
6400	− 1.06	− 85.2
6300	− 1.11	− 89.2
6200	− 1.14	− 91.6
6100	− 1.15	− 92.5
6000	− 1.17	− 94.1
5900	− 1.23	− 98.8
5800	− 1.32	− 105.
5700	− 1.38	− 110.9
5600	− 1.43	− 114.9
5200	− 1.66	− 133.5
5000	− 1.83	− 147.1

GRAPH 2.

Rotatory Dispersion of
2 2 Dinitrocamphane in
the visible

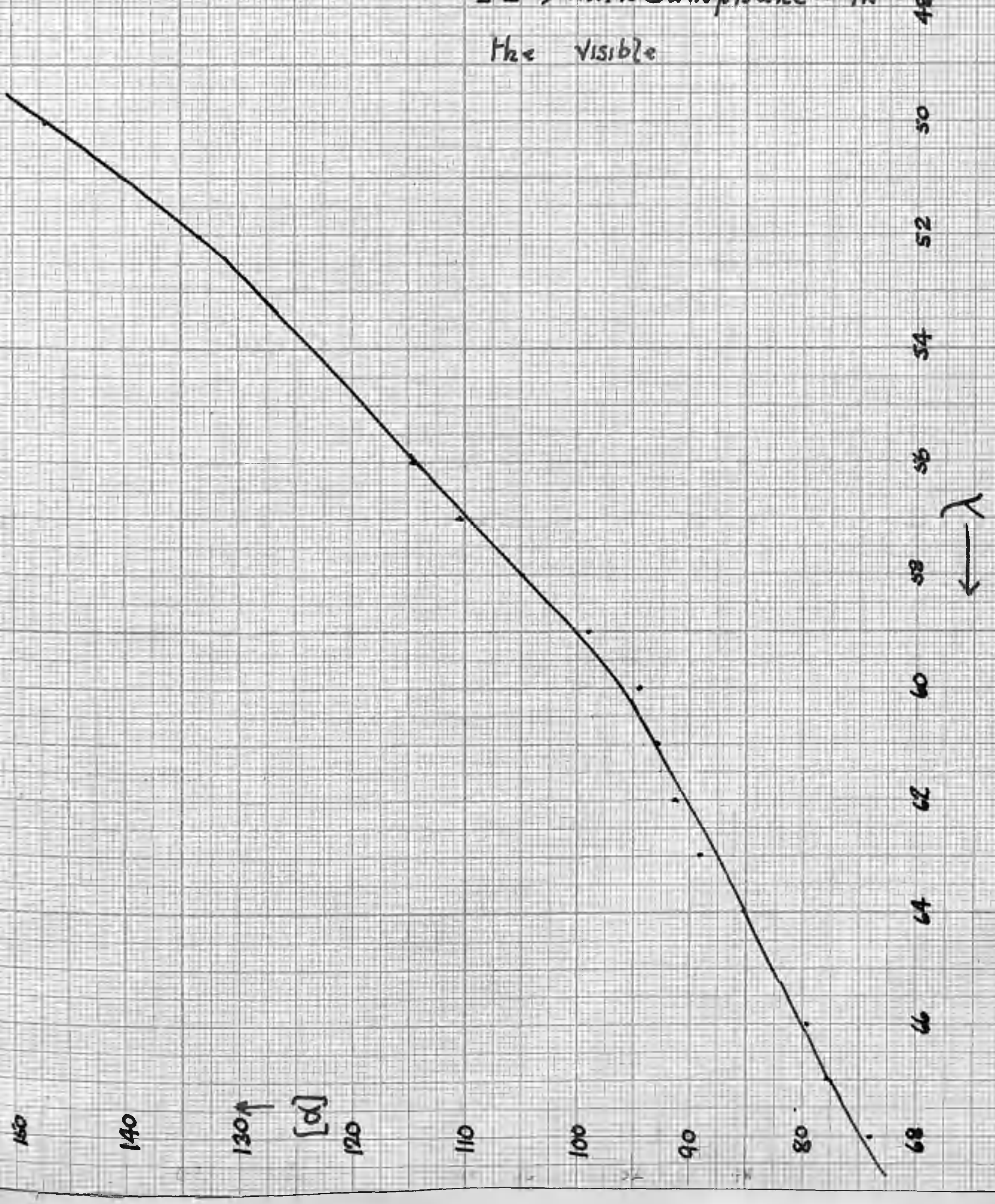


TABLE 3

ROTATORY DISPERSION OF 2-2 DINITROCAMPHANE IN ULTRA VIOLET

0.156 gms./100 c.c.

λ	ROT	SPEC ROT
2980	-0.4	-2590
2946	-0.35	-2267
2912	-0.25	-1619
2869	-0.20	-1295
2833	-0.15	-971.4
2804	-0.10	-647.6
2762	0.00	0
2706	0.10	647.6
2679	0.15	971.4
2644	0.20	1295
2618	0.25	1619

0.625 gms/ 100 c.c.

λ	ROT	SPEC ROT
3720	-0.5	-808.1
3558	-0.6	-971.4
3350	-0.7	-1132
3248	-0.8	-1295
3222	-0.9	-1454

conc. 0.312 gms/100 c.c.

λ	ROT	SPEC ROT
3193	-0.5	-1619
3126	-0.7	-2267
3047	-0.8	-2590

TABLE 4

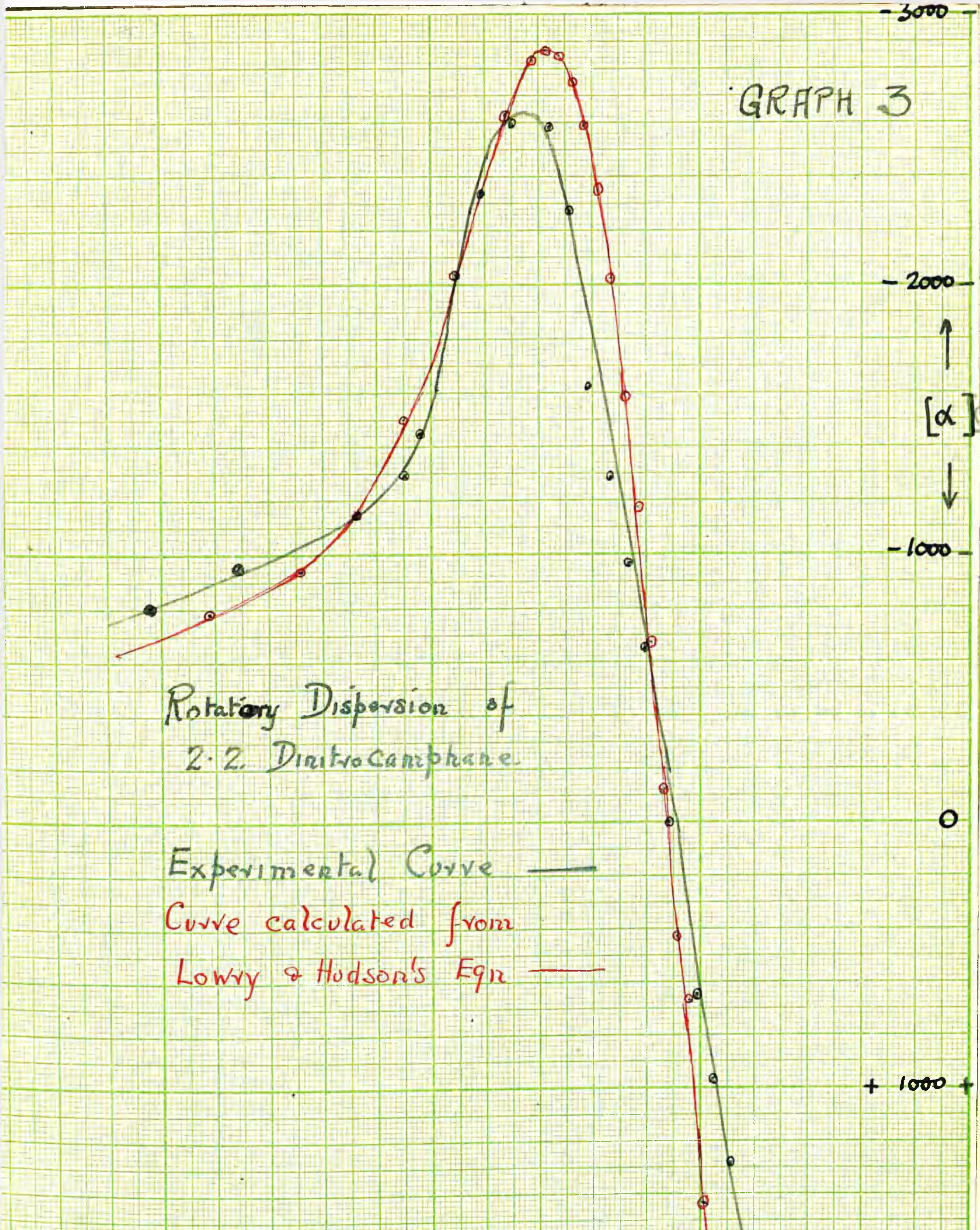
CALCULATION OF ROTATION FROM LOWRY & HUDSON'S EQUATION

I λ	II c	III $e^{-c^2}\int_0^c e^{x^2}dx$	IV $\frac{\theta}{2(\lambda+\lambda_0)}$	V III + IV	VI $[\alpha]$
5650	12.0	.0417	.01427	.05597	-151.
5170	10.0	.0500	.01513	.06513	-192.
4690	8.0	.0625	.01610	.0786	-255.5
4210	6.0	.0833	.01721	.1005	-363.8
3850	4.5	.1111	.01814	.1292	-512.6
3610	3.5	.1429	.01883	.1617	-682.7
3442	2.8	.1936	.01934	.2129	-942.3
3346	2.4	.2353	.01964	.2549	-1161.
3250	2.0	.3013	.01995	.3212	-1506.
3154	1.6	.4000	.02023	.4202	-2030.
3106	1.4	.4564	.02045	.4769	-2340.
3058	1.2	.5073	.02063	.5279	-2637.
3010	1.0	.5381	.02079	.5589	-2830.
2986	.9	.5407	.02087	.5616	-2867.
2962	.8	.5321	.02095	.5530	-2845.
2938	.7	.5105	.02105	.5315	-2757.
2914	.6	.4748	.02113	.4959	-2593.
2890	.5	.4244	.02122	.4456	-2351.

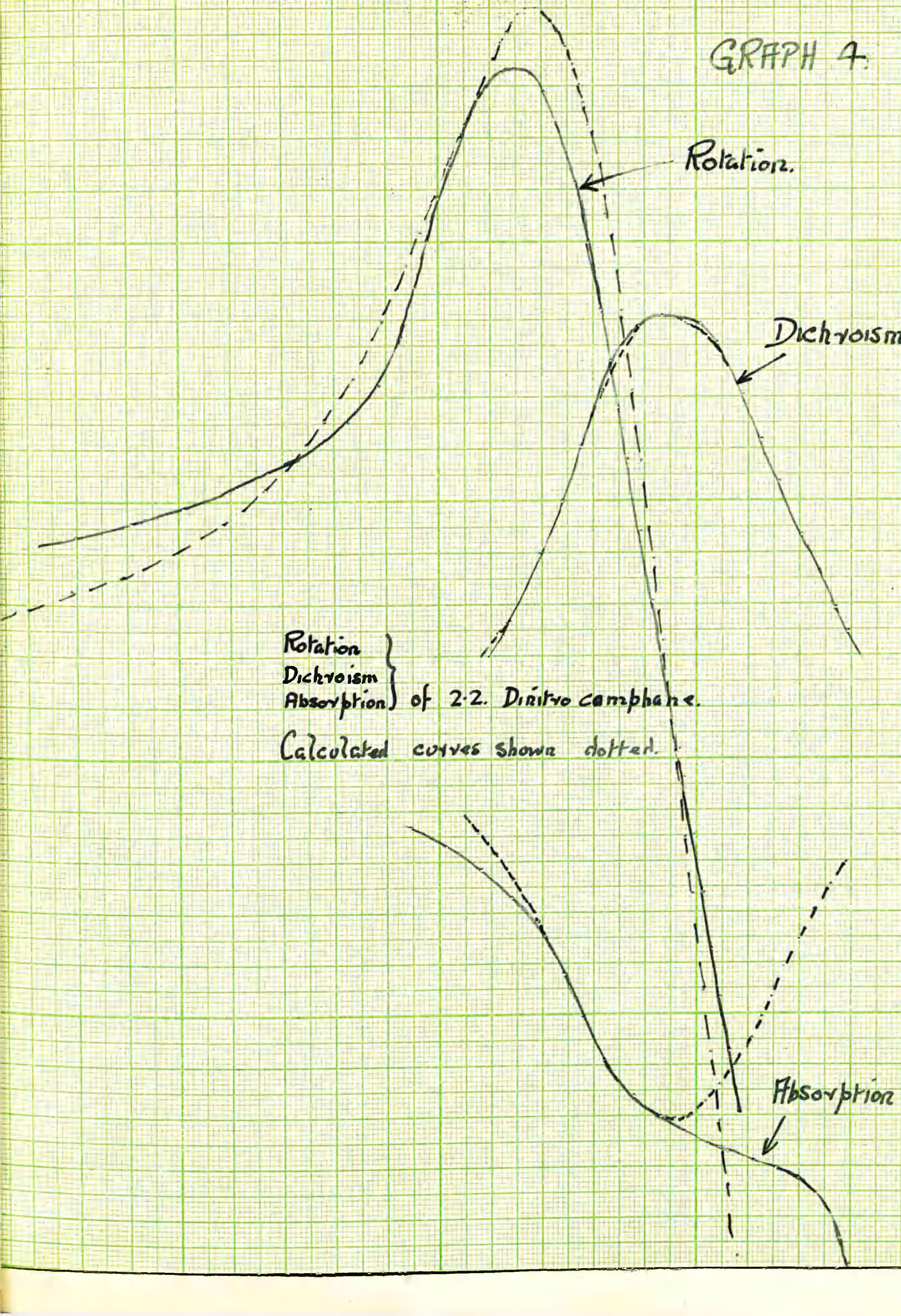
TABLE 4 (contd.)

I	II	III	IV	V	VI
2866	.4	.3594	.02132	.3807	-2024.
2842	.3	.2762	.02140	.2976	-1596.
2818	.2	.1946	.02150	.2161	-1169.
2794	.1	.0990	.02159	.1206	-657.9
2770	0	.0000	.02169	.02169	-119.3
2746	-.1	-. 0990	.02178	-.07722	427.0
2722	-.2	-.1946	.02187	.1727 -.~~2542~~	667.0
2698	-.3	-.2762	.02198	-.2542	1435.
2674	-.4	-.3594	.02207	-.3373	1923.
2650	-.5	-.4244	.02217	-.4022	2313.
2626	-.6	-.4748	.02227	-.4525	2626.
2602	-.7	-.5105	.02237	-.4881	2859.
2578	-.8	-.5321	.02247	-.5096	3012.
2554	-.9	-.5407	.02257	-.5181	3091.
2530	-1.0	-.5381	.02267	-.5154	3105.
2482	-1.2	-.5073	.02288	-.4844	2974.
2434	-1.4	-.4565	.02309	-.4334	2714.

GRAPH 3


Rotatory Dispersion of
2·2. Dinitrocamphane
Experimental Curve
Curve calculated from
Lowry & Hudson's Eqn
- 3000 -
- 2000 -
[α]
- 1000 -
0
+ 1000 +
+ 2000. +
3700
3200
← λ
2700

GRAPH 4.



Rotation
Dichroism
Absorption } of 2·2. Dinitro camphane.

Calculated curves shown dotted.

modification of Kuhn's equation,(26) in which they substitute wave lengths for frequencies and introduce an additional factor $\frac{\nu_0}{\nu}$ into the absorption equation as used by Kuhn.(26)

These equations are :-

Lowry and Hudson: $$\mathcal{E} = \mathcal{E}_{max}\, e^{-\left[\frac{\nu_0}{\nu} \cdot \frac{\nu_0 - \nu}{\theta}\right]^2}$$

Kuhn: $$\mathcal{E} = \mathcal{E}_{max}\, e^{-\left(\frac{\nu_0 - \nu}{\theta}\right)^2.}$$

$$[M] = \frac{[e]}{m} \frac{\lambda_\varphi}{\lambda} \left[e^{-\left(\frac{\lambda - \lambda_0}{\theta}\right)^2} \int_0^{\frac{\lambda - \lambda_0}{\theta}} e^{x^2} dx + \frac{\theta}{2(\lambda + \lambda_0)} \right]. \quad L \& H.$$

The calculated curve obtained from this is shown as red in graph 3. The method of calculation is as follows :-

Six columns are headed as shown in Table 4. Column 2 contains the values of C, i.e., $\frac{\lambda - \lambda_0}{\theta}$, for which the value of the integral $e^{-c^2} \int_0^c e^{x^2} dx$ is known, or may be obtained from the series. These values are contained in column 3. The maximum value of this integral occurs when C=0.9.

Since λ'=1.6651 θ, where λ' is the half width of the band, or the wave length interval between those points at which the dichroism is half the maximum, and C= $\frac{\lambda - \lambda_0}{\theta} = \frac{(\lambda - \lambda_0)\ 1.6651}{\lambda'}$ the wave length of the maximum may be found: $\lambda = \lambda_0 + \frac{c\lambda'}{1.6651}$

In the present case we have: $\lambda_\varphi = 2770 + \frac{0.9 \times 400}{1.6651} = 2986$ A.U. This gives a wave length difference of 2986 - 2770 = 216 A.U. for an interval of 0.9 in C., i.e., an increment of 24 A.U. for each 0.1. Column 1 is now built up on this. Column 4 contains the values of $\frac{\theta}{2(\lambda+\lambda_0)}$, ($\lambda_0$ being the position of the head of the band) and in column 5 are given the values of the complete integral. The rotation may be calculated from the maximum value of the rotation obtained from $[\varphi] = -3723\left[\frac{(\varepsilon_l-\varepsilon_r)_{max}\lambda_0^2}{\lambda_\varphi}\right]$ The factor 3723 comes from $\frac{100}{-2\pi \log_{10} e}$ contained in the original equation. By multiplying the numbers in 5 by $\frac{[\varphi]\,\lambda_\varphi}{m.\,\lambda.}$ the other rotations may be found. The calculation of $[\varphi]$ may be omitted, however, and the rotations obtained directly from the original equation.

It will be seen from the graphs that the agreement between the calculated and experimental curves is close as regards the position of the maximum and zero of rotation. The absolute magnitudes, however, vary, so that when the calculated curve is subtracted from the observed curve, the resulting curve or crosses the zero line in several points. It is doubtful how much of this variation is due to experimental error and how much is due to the semi-empirical nature of the equation employed.

With respect to the first of these possibilities it should be noted that in the steep part of the curve following the maximum, a small difference in wave length makes a very large alteration in the size of the difference of specific rotation. A small experimental error would have a large effect in this region. Counteracting this is the fact that the instrument is very accurate in a part of the curve where the rotations change rapidly with wave length as they do in the region of absorption. In this part of the curve, using the concentrations stated above, the accuracy in reading the wave length of the point of extinction, which is all that is taken from the plate, is of the order of 15 A.U. Such a small difference in the steep part of the curve would half the difference between observed and calculated curves.

On the other hand, the instrument is not nearly so accurate in that region of the dispersion curve where the rotation changes only slowly with wave length. Here the error may be of the order of 25-60 A.U., again capable of almost halving the difference between calculated and observed curves. The accuracy here is also reduced by the fact that at the red end of the spectrum the wave length scale of the spectrograph is much less widely spaced than it is further into the ultra violet.

The curves have also been calculated using Kuhn's original equation, and also using Lowry and Hudson's modification of this on a frequency basis. These curves are shown in graph 5. The method of calculation is quite analogous to that described above. From these curves it appears that on a frequency basis Kuhn's equation fits better as regards position and size of the maximum and also on the short wave side of the maximum, but falls away too rapidly on the long wave side. On the other hand, Lowry and Hudson's equation, while it does not differ very greatly on the short wave side from Kuhn's, fits the experimental curve on the long wave side and hence appears to be better than the original equation. A similar behaviour in the difference curve has also been obtained by other workers, e.g., Lowry in the case of arabinose(27) where the difference curve crosses the zero axis in several places. From this it would appear that the variations in the difference curve in this example are also due in a great measure to the equation.

From the fact that the difference curve is practically zero it may be deduced that essentially the whole of the rotation of the substance, in the visible at least, is due to the presence of the nitro groups. This effect was more or less to be expected from the fact that if any substituent in this position is replaced by CH_2 the molecule is inactive, and also from the close proximity of the group to the visible region.

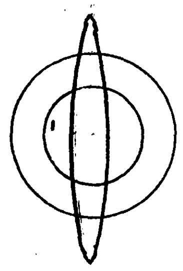
It is interesting to note that here it is difficult to suppose that the effect is due to induced dissymmetry in the sense in which it has been postulated by Lowry(28), for the CO group in camphor. There it was attributed to the presence of a semi polar double band which can become dissymetric when placed in an asymmetric field. In this it would be similar to the compounds of sulphur(29) which are of a pyramidal structure, one of the apices being occupied by a free valency. In the case of a polarisable group such induced dissymmetry may be possible, but it is difficult to see how this could take place in a 2-2 dinitrocamphane where we have two similar groups attached to carbon by single valency bonds, unless it were by a unsymmetrical arrangement of the linkages within the NO_2 groups themselves. There is the posibility that the nitro groups since they are placed in an unsymmetrical field are not exactly equivalent to one another. In this respect it might be interesting to compare the absorption spectra of the two mono nitro compounds.

Lowry's ideas on the origin of the optical rotatory power of camphor being due to the induced disymmetry of the CO group giving rise to a third asymmetric carbon, have been criticised recently by Kuhn(30) who maintains that before optical activity can make its appearance, two mutually interacting groups must be present in different parts of the molecule, which is in agreement with the general theory of Born. This, he holds, rules out the possibility of optical rotation being produced by a single electron as it would be in the case of a semi-polar bond. In addition to this the only cases known at present in which the optically active compound contains a semi-polar bond to carbon, are those of the aci forms of 2- nitro butane(31) and octane(32); in all other cases, a double bond to carbon is non-polar.

From such considerations it would appear that Lowry's theory of induced dissymmetry does not hold very well even for the cases where this might be possible and certainly not in the case of 2-2-dinitrocamphane where we have a clear example of what Kuhn terms vicinal action.i.e. the coupling of the vibrators with the frequency of the absorption band, with some other group within the molecule.

THE MEASUREMENT OF CIRCULAR DICHROISM.

Fresnel showed that a ray of plane polarised light, on entering an optically active medium, is split up into two circular components which travel with unequal velocities. Now, it can easily be seen from models or by consideration of the equations of wave motion, that if one of the circular components is absorbed more than the other, then the resulting emergent ray is elliptically polarised and cannot be extinguished by any position of the analyser. The ellipticity, i.e. the ratio of the minor to the major axis in the ellipse, is given by the difference and sum of the amplitudes of the two circular emergent rays. This is illustrated in the diagram. This phenomenon, which is exhibited by some absorption bands, is analogous to the unequal absorption of the ordinary and extra ordinary rays in certain crystals. The term Dichroism has already been applied to this and the name Circular Dichroism given to the corresponding effect in optically active media.



Methods exist by means of which elliptical light of a known ellipticity can be produced and the method of measuring the ellipticity produced by a solution, is to superimpose upon this a known ellipticity of opposite sign, so that the emergent light is plane polarised.

In the visible it is usual to use a quarter wave plate of mica, i.e. a plate of mica cut parallel to the axis and of such a thickness that the ordinary and extraordinary rays suffer a relative phase difference of $\frac{\lambda}{4}$ by transmission. If a plane polarised ray is incident, either perpendicular or parallel to the axis it emerges plane polarised, if incident at 45° it emerges circularly polarised and in any intermediate position, it is elliptically polarised. The tangent of the angle which the plane of the incident ray makes with the 'slow' axis of the plate may be taken as a measure of the ellipticity. A quarter wave plate is accurate only over a comparatively short range of wave lengths and, for this reason, is unsuited for use in ultra violet work where a large range of wave length is used. In this region therefore, a Fresnel rhomb is used introducing as it does only a third of the error in relative phase difference of that introduced by a quarter wave plate over the same range.

The Fresnel rhomb depends for its action on the fact that when a plane polarised ray is totally reflected, it is split up into two components which have a relative phase difference. This phase difference depends on the angle of incidence and the refractive index of the rhomb. To produce a phase difference of $\frac{\lambda}{4}$ the rhomb would require to have a refractive index greater than 2.4. This difficulty is overcome by using two internal reflections. Using an acute angle of $54^{\circ}37'$ as shown in the diagram, Fresnel obtained circularly

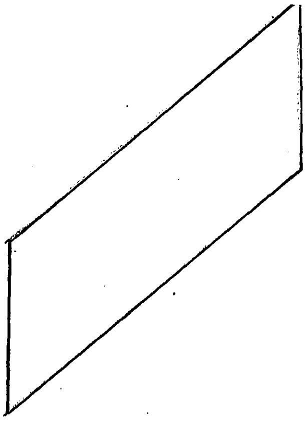


FIG. X.

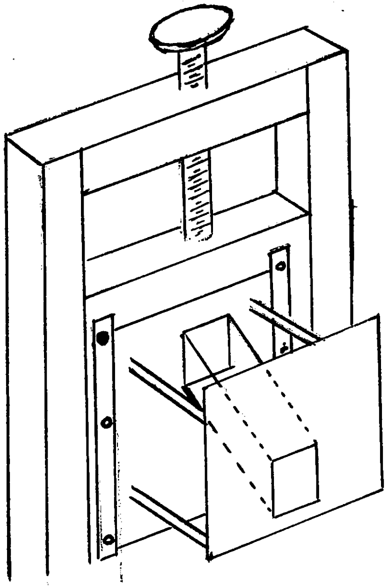
polarised light when the plane of the incident plane polarised ray made an angle of 45° with the plane of incidence. A ray plane polarised in the plane of incidence is transmitted unchanged and in any intermediate position, it is transmitted as an elliptically polarised ray. In the case of small angles, the ellipticity is again the tangent of the angle which the plane of the incident ray makes with the plane of reflection.

The ideal substance from which the rhomb should be made is, of course, fused silica, but it is only very recently that a sufficiently large piece could be obtained free from strain. Kuhn(33), to overcome this difficulty, used a hollow brass cell of the required shape, the light passing through quartz windows. We have been fortunate to obtain a rhomb of fused silica from The Thermal Syndicate, Ltd. This was tested visually, by means of a polarising microscope, and also photographically and found to be free from strain. The actual dimensions of the rhomb are 1.7 x 1.7 cm. aperture and an acute angle of 51° 47'. This angle was calculated from the equation given by Fresnel (Oeuvres, Completes, 1, 792.)

$$4n^2 \sin^4 i - (n^2+1)(\sqrt{2}+2)\sin^2 i + \sqrt{2}+2 = 0$$

The value of n used was n_{2743} = 1,4964

This rhomb is mounted immediately behind the polariser in a holder as illustrated in the diagram.



This enables the instrument to be used for the measurement of both dichroism and rotation, with no further alteration than the raising of the polariser by means of the screw shown. This is necessary because of the lowering of the incident ray by the internal reflection. Once the polariser and rhomb are in position, the procedure is similar to that for the measurement of rotation, except that in this case, the analyser is kept fixed and a series of positions of the polariser taken. The zero is obtained by setting the polariser and analyser so that the intensity of the light transmitted is a minimum, and then rotating the polariser through small angles, until both halves of the photograph are of the same intensity throughout their whole length.

While fused silica is the ideal substance to use for the rhomb from the point of view of transparency, it has the disadvantage of having a greater refractive dispersion than glass. Lowry (Optical Rotatory Power. p. 252-253) gives the experimental error for a uviol glass rhomb as 0.02° and for a fused silica rhomb, accurate at 2740, as 0.05°. For work in the near ultra violet therefore it would be more accurate to use such a glass rhomb.

The difference in molecular extinction coefficients for right and left circularly polarised light, may be obtained from the actual angle through which the polariser is rotated by means of the expression -

$$(\mathcal{E}_l \sim \mathcal{E}_r) = \frac{4\varphi}{c.l.} \log_{10} e$$

where φ is in radians
c is in gram. mols. per litre
l is length of solution in cms.

Application to the circular dichroism of camphor.

As in the case of rotation, it was necessary to test the instrument by measuring the dichroism of a substance in which this was known. For this purpose, camphor was again chosen. The results obtained with a 1% solution in hexane are given in Table 5 and illustrated in Graph I. The dichroism rises to a maximum of 1.42 at 2990 c.f. about 1.4 and 3000 given by Kuhn and Gore(22) who, unfortunately, give only a diagram and no numerical data. This displacement of the dichroism towards the red from the maximum of absorption, has been taken as a further proof of the composite nature of the carbonyl band.

TABLE 5

DICHROISM OF CAMPHOR IN HEXANE 1% SOLN.

Ellipticity in Degrees	Radians	$1/\lambda \times 10^{-1}$		$\varepsilon_r \sim \varepsilon_l$
0.5	.0087	39.84	31.60	.232
1.0	.0175	38.76	-	.467
1.5	.0262	37.95	31.80	.699
2.0	.0349	36.90	31.85	.932
2.5	.0436	36.25	32.05	1.167
2.8	.0489	35.34	32.68	1.308
2.9	.0506	35.21	32.89	1.353

[illegible]

[illegible] being defined as described in the [illegible] equation. This curve is shown in red in the graph and [illegible] noticed that the calculated values are too low on [illegible] wave side and too high on the short wave side. This [illegible] what would be the effect of the factor . This factor [illegible] an empirical nature in any case, and another curve [illegible]. The result of this is shown on the same graph [illegible]

From this agreement with published results, it was concluded that the instrument was correctly adjusted.

For the measurement of the dichroism of 2-2 dinitrocamphane, a solution of 0.156% in ethyl alcohol was used. This required exposure of 30 minutes. The maximum ellipticity recorded was -0.75°, giving a molecular ellipticity of -3.36. The results are given in Table 6 and Graph 6. In the graph the ellipticities have been plotted on a wave length basis and appear to be very symmetrical. From the wave length interval between the two points at which the dichroism is half the maximum, known as the half width, and the maximum value itself, a calculated curve was drawn from Lowry and Hudson's(25) modification of Kuhn's equation (Table 7)

$$(\varepsilon_l \sim \varepsilon_r) = (\varepsilon_l \sim \varepsilon_r)_{max}\, e^{-\left(\frac{\nu_0 - \nu}{\theta}\right)^2}$$ Kuhn & Szabo

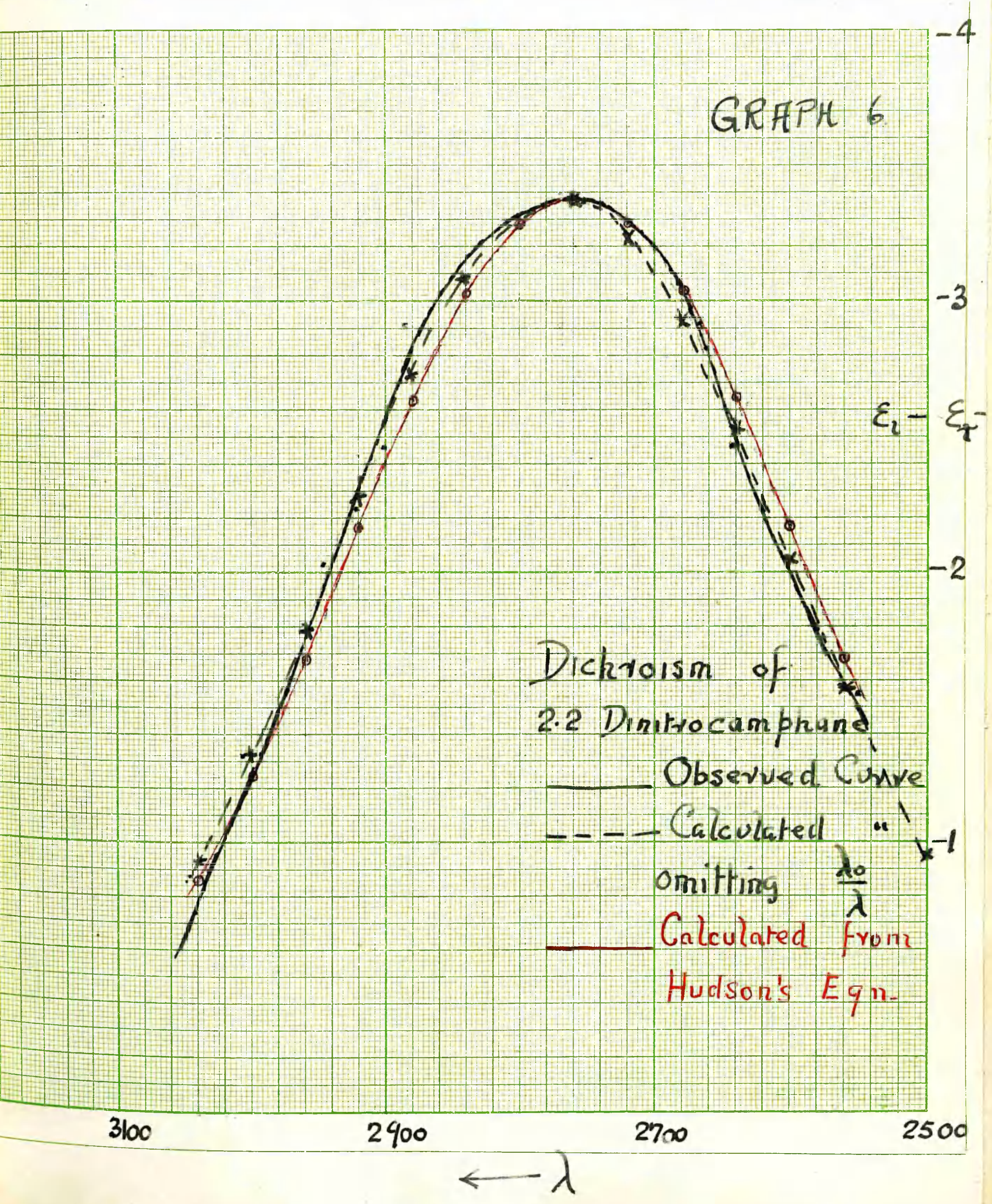
$$(\varepsilon_l \sim \varepsilon_r) = (\varepsilon_l \sim \varepsilon_r)_{max}\, \frac{\nu}{\nu_0}\, e^{-\left[\frac{\nu_0}{\nu} \cdot \frac{\nu_0 - \nu}{\theta}\right]^2}$$ Lowry & Hudson

The constants being defined as described in the rotation equation. This curve is shown in red in the graph and it will be noticed that the calculated values are too low on the long wave side and too high on the short wave side. This is just what would be the effect of the factor . This factor is of an empirical nature in any case, and another curve was drawn omitting it. The result of this is shown on the same graph and it will be seen that a much closer agreement is obtained with the experimental curve. In omitting this factor, we have the precedent of Kuhn and Szabo(34) with the exception that

TABLE 6

DICHROISM OF 2-2 DINITROCAMPHANE

λ	Ellipticity in Degrees	$\varepsilon_l - \varepsilon_r$ obs	$\varepsilon_l - \varepsilon_r$ calc $= (\varepsilon_l - \varepsilon_r)_{max} e^{-\left(\frac{\lambda - \lambda_0}{\theta}\right)^2}$
3031	-0.20	-.90	-1.036
3009	-0.30	-1.33	-1.252
2972	-0.35	-1.56	-1.66
2957	-0.40	-1.79	-1.84
2946	-0.45	-2.03	-1.97
2920	-0.50	-2.23	-2.28
2900	-0.55	-2.46	-2.51
2885	-0.65	-2.92	-2.68
2778	-0.75	-3.36	-3.36
2739	-0.75	-3.36	-3.31
2666	-0.65	-2.92	-2.79
2644	-0.55	-2.46	-2.56
2620	-0.50	-2.23	-2.28
2580	-0.40	-1.79	-1.80
2550	-0.35	-1.56	-1.45



GRAPH 6

-4
-3
-2
-1
$\varepsilon_l - \varepsilon_r$
3100
2900
2700
2500
← λ
Dichroism of
2.2 Dinitrocamphane
Observed Curve
Calculated "
omitting $\frac{\lambda_0}{\lambda}$
Calculated from
Hudson's Eqn.

TABLE 7

CALCULATION OF DICHROISM OF 2-2 DINITROCAMPHANE

λ	$\frac{\lambda-\lambda_0}{\theta}$	$\left(\frac{\lambda-\lambda_0}{\theta}\right)^2$	$e^{-\left(\frac{\lambda-\lambda_0}{\theta}\right)^2}$	$\frac{\lambda_0}{\lambda}$	$\varepsilon_l-\varepsilon_r$	omitting $\frac{\lambda_0}{\lambda}$
3040	1.124	1.263	.2828	.9111	.8682	.9528
3000	.9572	.9162	.4001	.9234	1.246	1.348
2960	7909	.6255	.5351	.9358	1.688	1.803
2920	.6243	.3898	.6770	.9486	2.164	2.281
2880	.4578	.2095	.8112	.9618	2.629	2.733
2840	.2914	.0849	.9186	.9754	3.019	3.095
2800	.1248	.0156	.9845	.9893	3.282	3.317
2760	.04162	.0017	.9983	1.003	3.376	3.363
2720	.2081	.0433	.9576	1.018	3.286	3.227
2680	.3745	.1403	.8691	1.034	3.028	2.929
2640	.5411	.2917	.7469	1.049	2.640	2.517
2600	.7074	.5004	.6062	1.065	2.176	2.043
2560	.8740	.7639	.4658	1.082	1.698	1.570
2500	1.124	1.263	.2828	-	-	.9528

$\lambda_0 = 2770$

$\theta = 240.3$

$\lambda' = 400.$

$(\varepsilon_l-\varepsilon_r)_{max} = -3.37$

they used frequencies throughout.

From the fact that the maximum of ellipticity lies within 10 A.U. of the position of zero rotation, it may be deduced that in the case of the nitro group, the absorption band is "simple", i.e. consists of only one band, as compared with the composite band of camphor.

ABSORPTION.

Since the zero of rotation and the maximum of dichroism dhould occur at the maximum of absorption due to the active group or groups in the molecule, it was necessary to study the absorption of 2-2 dinitro camphane.

From a study of the literature, it appeared that the NO_2 absorption had been studied quantitatively only in the case of nitro-ethane vapour(35). In this it showed a shallow band between 2780 and 2500. The absorption has been studied qualitatively by several authors(36) and apart from the case just quoted, the only compound to show selective absorption was that of tetra nitro methane. In most cases an increase in the general absorption was noted and in some this was accompanied by a "step out".

The absorption of 2-2 dinitro camphane was first studied qualitatively by the Baly tube method and was found to have no selective absorption but a large step out about 2700 to 2800 A.U. Since a step out is due to a selective absorption band masked by general absorption, it would appear that on the long wave side at least, of the step out would represent the shape of the selective absorption due to the nitro group. To examine the form of this part of the curve accurately, the absorption was studied quantitatively by means of a Hilger Rotating Sector Photometer.

The optical arrangement of this is illustrated in the diagram below

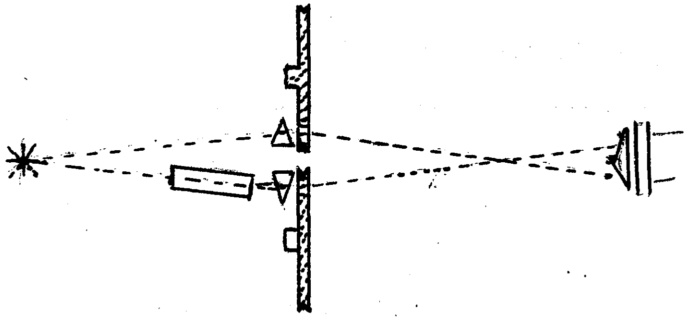


FIG. XII

Light from a Nickel spark passes through two wedge-shaped lenses, which render it convergent. The two rays then pass through two rotating discs. The lower of these has a fixed aperture, while the other has a variable aperture calibrated to read direct in log $\frac{I}{I}$. From this, the two rays fall on a biprism placed immediately in front of the spectrograph slit. This renders the rays parallel.

The resulting photographs consist of contiguous pairs of spectra. The liquid being examined is contained in a glass cylindrical cell with screw ends. These screw ends are to be preferred to ends stuck on by sealing wax or some other adhesive, since these are almost sure to leak. The cells are of different lengths, the one used in this case being 2 cms. long, that containing the solution being placed in front of the fixed sector, while a similar cell full of the solvent is placed in front of the variable sector, thus eliminating the effect of the solvent.

When the instrument is correctly adjusted the two spectra in each case match throughout their length as in the polarimeter. Since this adjustment may sometimes prove troublesome, a short description here may be of some help to subsequent workers in this field.

The first thing to attend to is the cleaning of the cells. These should be washed very thoroughly several times with soap and water and then with water. If, even after thorough cleaning, the spark fails to come through to at least 2200 A.U., the instrument must be tilted by raising the two screws on one side and lowering the single screw on the other or vice versa. In moving these screws, the single screw should be moved only by a half of the change in the others, since the sectors are not midway between the two sets of screws, but only about a third from the single screw. Whenever the instrument is tilted, the light source must always be moved to ensure that the image entirely covers the biprism.

If the resulting spectra do not match all the way along, but show a changeover, then the instrument is either too high or too low, and must be raised if the red end of the spectra is too light. The spectra may now match in the visible and in the ultra violet down to about 2500, but may differ beyond this. If the lower half is light beyond this, the double screws should be lowered, keeping the single screw fixed.

To find a suitable concentration of solution, the variable sector is set at 1.5 and photographs taken with various concentrations of a two cm. layer, until one is obtained in which the lower half of the spectrum is just darker than the upper, in the region of maximum absorption. Using this concentration, a series of photographs is taken for sector readings, from 0-1.5. The exposures may be calculated from the expression $A\frac{t'}{t}$ where A is a suitable exposure for the sector full open, and $\frac{t'}{t}$ the antilog of the sector reading.

In practice, it will be found that a slightly longer exposure than that given by this expression should be used for the smaller sector readings.

From the resulting photographs, the wave lengths at which the two spectra match are noted, and a curve drawn, plotting wave length against molecular extinction coefficient obtained from $\epsilon = \frac{\text{Sector reading}}{c.l}$ c being concentration in gm. mols. per litre; l the length in cms.

This instrument was tried out on camphor. For this a 2 cm. column of 0.0840 gms. in 25 c.c. hexane was used. The data is given in Table 8 and Graph I. The result for the maximum of absorption agrees with that taken from Kuhn and Gore's curve(22).

TABLE 8

ABSORPTION OF CAMPHOR IN HEXANE .084 gms./25c.c.

λ		ν		Sector	ε
2480	3330	40.32	30.03	.2	4.48
2520	3280	39.68	30.49	.3	6.72
2570	3230	38.91	30.96	.4	8.96
2600	3210	38.46	31.16	.5	11.20
2630	3160	38.02	31.63	.6	13.44
2700	3120	37.04	32.05	.7	15.68
2740	3070	36.50	32.58	.8	17.92
2820	3000	35.46	33.34	.9	20.16

Application to 2-2 dinitrocamphane.

For the absorption of 2-2- dinitrocamphane, a solution of 0.039 gms. in 100 c.c. alcohol was used in a 2 cm. column. The data for this is given in Table 9 and Graph 7, from which it will be seen that there is no selective absorption, but a very decided step out between 2800 and 2700, thus confirming the qualitative results.

Using Lowry and Hudson's modification of Kuhn's empirical equation for the course of an absorption band $\varepsilon = \varepsilon_{max} e^{-\left(\frac{\lambda - \lambda_0}{\theta}\right)^2}$. and substituting in this the values of λ_0 and θ as used in the dichroism and rotation curves, a calculated curve was drawn (Table 10). By dividing the maximum value of the ellipticity by the value of the anisotropy factor (this will be discussed later) at that wave length, a value of 280 was obtained for the maximum absorption and substituted in the above equation. From the close agreement between the two curves on the long wave side, we assume that this is the correct form of the band due to the nitro group. It will be seen that the maximum of absorption occurs at the same wave length as the maximum of dichroism and zero of rotation, thus confirming the unitary nature of the absorption band.

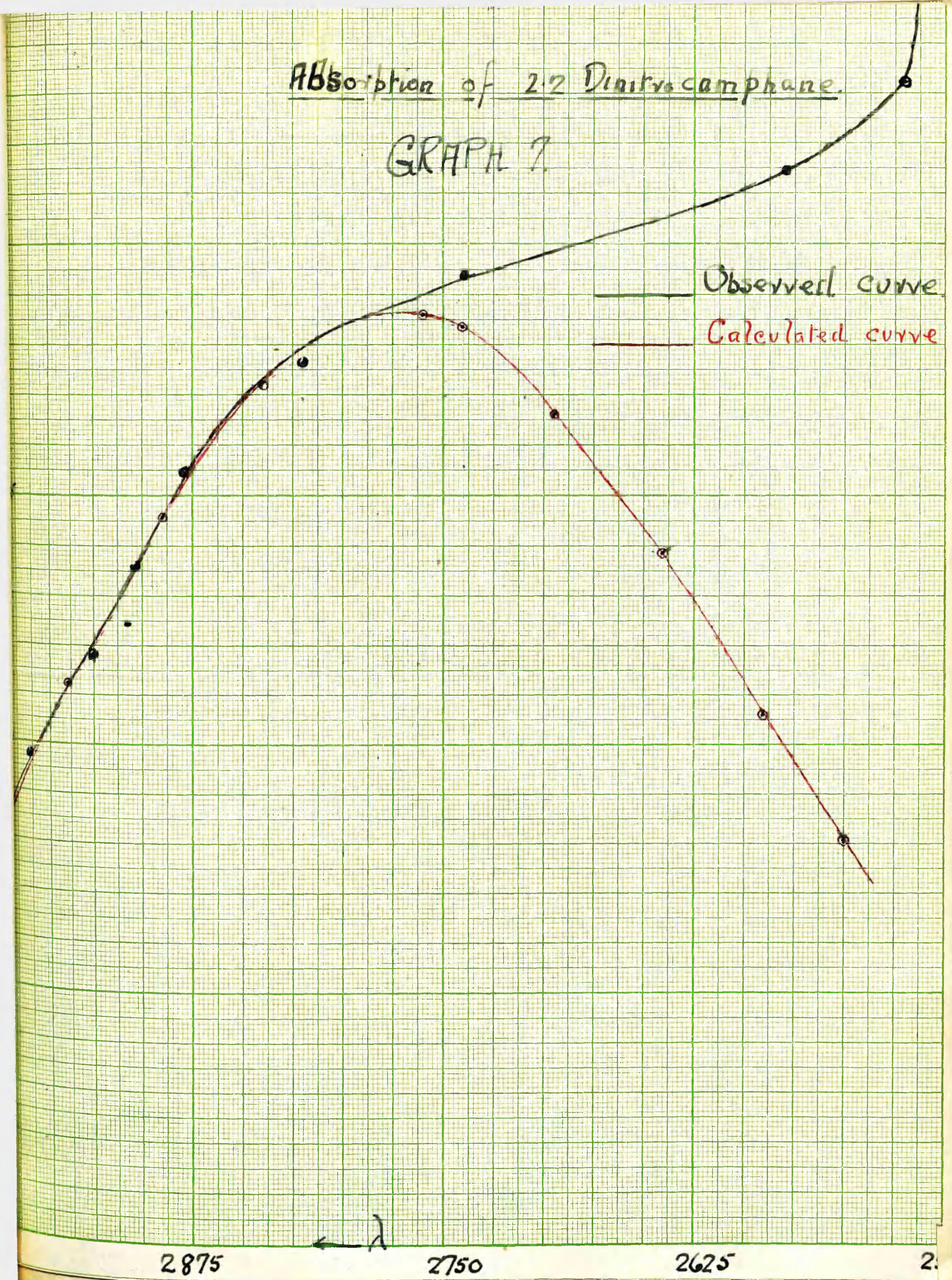
The anisotropy factor.

This term has been applied to the ratio of ellipticity to ordinary absorption $\frac{\varepsilon_l \sim \varepsilon_r}{\varepsilon}$. Some controversy(30) seems

TABLE 9

ABSORPTION OF 2-2 DINITROCAMPHANE

λ	Sector	ε
3570	0	0.00
3310	0.1	29.2
3165	0.2	58.4
3060	0.3	87.6
3000	0.4	116.8
2965	0.5	146.5
2925	0.6	175.5
2905	0.7	205.0
2880	0.8	233.
2820	0.9	264.
2740	1.0	292.
2580	1.1	322.
2520	1.2	351.
2515	1.3	380.5
2480	1.4	410.
2465	1.5	439.



Absorption of 2·2 Dinitrocamphane.

GRAPH 7.

TABLE 10

CALCULATION OF ABSORPTION OF 2-2 DINITROCAMPHANE

λ	$\frac{\lambda-\lambda_0}{\theta}$	$\left(\frac{\lambda-\lambda_0}{\theta}\right)^2$	$e^{-\left(\frac{\lambda-\lambda_0}{\theta}\right)^2}$	$\mathcal{E}$
3040	1.124	1.263	0.2828	79.18
2990	.9156	.8383	0.4325	121.2
2940	.7074	.5004	0.6062	169.7
2890	.4955	.2495	0.7792	218.2
2840	.2914	.0849	0.9186	257.2
2760	.0416	.0017	0.9983	279.6
2740	.1248	.0156	0.9845	275.7
2690	.3330	.1109	0.8949	250.5
2640	.5411	.2928	0.7461	208.9
2590	.7492	.5613	0.5704	159.7
2550	.9156	.8383	0.4325	121.2

to have arisen over this term which Lowry calls the "dissymmetry factor", holding that optical activity depends on the dissymmetry of the medium and not on its anisotropy. Kuhn, however, believes that while neither term is absolutely correct, yet the term "dissymmetry" has come to have a rather limited meaning, referring to the difference in the arrangement of the chemical substitutents as a whole according to Pasteur's Principle. The term "anisotropy factor" indicates in some measure the non-isotropic arrangement of the components of the total scattering moment. These, he holds, might be parallel, in which case, even if they were dissymmetrically arranged in the molecule, no optical activity would result. Kuhn, therefore, suggests that in future some such term as "activity-anisotropy" factor should be used, thus reverting to Drude's "activity coefficient".

A method perhaps of avoiding all controversy, would be to call the factor the ellipticity-absorption ratio.

The actual physical significance(37) of this factor is that it is the amount by which the contribution of an absorption band to the ordinary light refraction must be multiplied, in order to obtain the contribution of the band to the optical activity. It is also that quantity by which the ordinary refractive index within an absorption band, must be multiplied to obtain the circular dichroism for any wave length belonging to the band, and may be taken as a measure of the activity of a band towards optical activity.

When this is applied to the case of 2-2-dinitro camphane, it is found that g remains constant at 0.012 (Table 11) until beyond 2778 A.U. This is what would be expected in an absorption band containing one component and furnishes a further proof of this in connection with the nitro group. It is also a proof of the fact that the dichroism extends over the same range as the absorption due to the nitro group.

Note on size of d.

Kuhn, from his theory of coupled linear vibrators, has deduced an expression connecting the distance between the vibrators with the "anistropy factor". This expression is

$d = \frac{g_0 \lambda_0}{4\pi}$. Clearly, this should lead to a value of d which is less than molecular dimensions. This has been found to be fulfilled in some cases, but in others the size of 'd' is much greater than that of the molecule. Kuhn has attempted to explain this by modifying his original model, so that the vibrators are not mutually perpendicular. To bring 'd' within molecular dimensions, it is found that in some cases the vibrators would be removed from being parallel by an angle of only 2°. It is difficult to believe that such a small departure from a plane figure should give rise to large rotations.

When applied to the present case, the expression above gives a value of 2.866×10^{-8} cm. for d, which, it will be noted, is within molecular dimensions. It is difficult to say,

TABLE 11

THE ANISOTROPY FACTOR

λ	$\varepsilon_l - \varepsilon_r$	ε	g
3030	-.9	100.5	.009
3008	-1.32	112.5	.012
2972	-1.56	138.0	.011
2957	-1.79	152.0	.012
2946	-2.03	162.0	.012
2920	-2.23	189.0	.012
2900	-2.46	210.0	.012
2885	-2.92	227.0	.013
2778	- 3.36	283.0	.012
2740	-3.36	292.5	.011
2666	-2.92	307.5	.009
2644	-2.46	311.0	.008
2620	-2.22	315.0	.007
2580	-1.8	322.5	.006

however, how much faith can be placed in this as a true measure of the distance

From the following facts, it is proved that in the case of this compound, the nitro group is associated with a very marked example of the Cotton Effect.

(a) The rotation rises to a maximum, falls to zero and is thereafter positive.

(b) The nitro group is associated with an absorption band which, however, is masked by the general absorption so that it appears as a step out. The maximum of selective absorption occurs at zero of rotation.

(c) Circular dichroism extends over the same range as the absorption band and rises to a maximum at same wave length as maximum of selective absorption.

(d) The anistropy factor remains constant up to the maximum of the absorption band.

2-NITRO BUTANE.

Since it has been proved that the nitro group is associated with a Cotton Effect in 2-2 dinitro camphane, the same band should show a similar effect in other nitro compounds. For this purpose, it was decided to examine the simplest nitro compound which could be obtained in the optically active condition. This is 2-nitro butane.

Preparation.

The reaction used was the action of silver nitrite on secondary butyl iodide. The inactive form was first prepared by this method. The starting product was sec. butyl alcohol which should be freshly distilled immediately before use and that fraction boiling 99°-100° used.

The sec. butyl iodide was prepared according to the method given by Clarke(38) by the action of red phosphorus and iodine on the alcohol. In this, care should be taken that the phosphorus is absolutely dry and of a deep red colour. When distilling the iodide, it was found advisable to add a small quantity of mercury to the distilling flask. This prevents the last drops of iodide from being coloured by free iodine. Also if the iodide is to be kept for some time, a small piece of reduced copper should be added.

The iodide was then added alowly to a mixture of equal quantities of freshly ignited sand and silver nitrite.(39) The silver nitrite is prepared by adding a warm concentrated solurion of sodium nitrite (105 grms.) to a warm concentrated solution of silver nitrate (203 gms.). The precipitate is allowed to cool, filtered rapidly and washed with water, alcohol and finally ether.

The mixture of sand and nitrite should be kept at or below 0° during the addition of the iodide and, according to some authorities(40), the flask should not be shaken. When all the iodide was added, the flask was allowed to stand for some time (over-night) at 0° and then heated on a water bath for three hours. The mixture was then fractionated on an oil bath. A pale yellow liquid started to come over at 54°, the temperature thereafter rising steadily. The first fraction was collected up to 100° and the remainder of the liquid contents removed under reduced pressure. These were then fractionated under reduced pressure in a very small pear-shaped flask, with a condenser fitting over the side arm. In this way from 34 gms. of sec. butyl alcohol, 3.5 gms. of 2- nitro butane were obtained boiling at 55-56 / 47 mm.(31)

The only impurity which can arise in this preparation, is sec. butyl nitrite and before going on to the preparation of the active form, it was necessary to know how much of this was present in the 2- nitro butane of the 55-56 fraction. For this purpose, Lunge's(41) colorimetric method was used. This reagent consists of 0.1 gms. a-naphthylamine in 50 c.c. water + 10 c.c. aceticacid and 0.5 gms. sulphanilic acid in 50 c.c. water + 10 c.c. aceticacid. These solutions are mixed and made up to 300 c.c. with water. For purposes of comparison, that fraction boiling below 100° under ordinary pressure, may be taken as sec butyl nitrite.

The following results were obtained:

1 drop nitrite + 2 c.c. soln. + 2 c.c. KOH give a deep red colour.
1 drop fraction below 55/47 mm. + " " " yellow "
1 drop fraction above " + " " no colouration.

The fraction above 55/47 mm. was therefore taken as free from nitrite since this reagent is sensitive to 1 part nitrite in 50 of solution.

RESOLUTION OF SEC BUTYL ALCOHOL.

This was carried out according to the method of Pickard and Kenyon(42). Equal molecular proportions of phthalic anhydride and sec. butyl alcohol were heated on a water bath for ten hours. When cold, the contents of the flask were poured into a dilute solution of sodium carbonate and left for several hours. The solution was then extracted three times with ether to remove any unesterified alcohol and neutral phthalic esters which might be present. The acid ester was then precipitated by the addition of dilute HCl and the last traces of ether removed, by drawing air through for some time. By extracting three times with chloroform and then removal of the solvent, under reduced pressure, the phthalate was obtained as a thick syrup. This may crystallise on cooling, but if it does not, then the addition of a few drops of pet. ether (40-60) will have the desired effect. Then phthalate so obtained had a melting point of 57°-58°.

In the next part of the resolution, the combination with brucine, both the above authors and MacArthur(42) state that 322 gms. phthalate were dissolved in 1.5 litres acetone and 560 gms. brucine added. Whether it was due to a slight amount of water being present in the brucine supplied or not, this quantity of acetone was found quite insufficient to keep these quantities in solution. An excess of acetone was therefore used and, when all the brucine was added, the surplus acetone removed without any apparent ill effects on the resolution. The brucine complex was given three recrystallisations from acetone, large quantities being used. It was then recrystallised eight times from methyl alcohol, 360 c.c. being used each time. The rotation was found to be -6.0° in a 2 dm. tube, using mercury green light and a 2% alcohol solution. The melting point of the solid was 161°.

During this part of the resolution, the solutions were of a brownish tinge though, according to some authors (43), brucine, which gives a brown colour, is useless. In our case, this does not appear to have had much effect. It was also found that the solutions were not absolutely clear and had to be filtered, preferably during the acetone recrystallisation stage, since in the later stages, the solution was of a syrupy nature and almost impossible to filter.

Recovery of the brucine.

Since much larger quantities than those mentioned above are required and brucine is rather an expensive material, it was necessary that the same brucine should be used several times. The method first tried for its recovery, was to dissolve it in HCl (1:4) and precipitate with ammonia of the same concentration. The precipitate so obtained, however, was a sticky mass impossible to filter. It also contains four molecules of water of crystallisation and, on attempting to drive these off on the steam bath, the mass turned brown.

It was then dissolved in alcohol and boiled with animal charcoal. The filtrate was not colourless, nor could the brucine be induced to crystallise out.

The following method(44) was finally adopted and found to give satisfactory results. To the solution in HCl was added 20% of its volume of alcohol and the solution made alkaline with dilute ammonia. Complete precipitation is obtained after about three days. The product is definitely crystalline and can be filtered readily. Drying in the steam oven yields a pure white product melting at 171°. By this process one loses about 20% of the brucine each time.

Recovery of the active phthalate.

The active brucine salt obtained by the above process was dissolved in the minimum quantity of hot alcohol and poured into dilute HCl, thus being precipitated as an oil mass. This was extracted with ether, washed, dried and the ether removed in a vacuum. This left the phthalate as a white solid melting at 47° and with a rotation of $[\alpha]_{Hg} = 45.8^{\circ}$ in a 2 dm. tube and 5% solution in ethyl alcohol.

The active alcohol.

The active phthalate was dissolved in an excess of 25% NaOH warmed for a few minutes and the alcohol removed in a current of steam. Since it is impossible to free the alcohol from ether, it could not be extracted in the usual manner, but was "salted out" from the first fraction of the steam distillate, by means of K_2CO_3. It was then dried over successive lots of freshly ignited K_2CO_3 and finally for a week over barium oxide. The alcohol obtained boiled at 97°-98° and had a rotation of $[\alpha]_D = +10.9$ c.f. 11.07 for Pickard and Kenyon's best. The yield was 34 gms. from 137 gms. active phthalate.

The active iodide.

The alcohol was then saturated at 0° with dry hydrogen iodide obtained in the usual manner from iodine and red phosphorus, and dried by calcium iodide. A fairly large trap should be used during this part of the preparation. When saturated, the liquid was heated for 30 minutes in a sealed tube at 52°C (42). After washing with sodium sulphite (to prevent any risk of racemisation by NaOH from the hydrolysis of Na_2CO_3) and drying over sodium sulphate, the iodide distilled at 116-118 and had the rotation

Yield 40 gms.

Active 2- nitro butane.

40 gms. of the actice sec. butyl iodide were added over a period of four hours to a mixture of 50 gms. dried sand and 50 gms. silver nitrite dried over phosphorus pentoxide. After all the iodide had been added the mixture was allowed to stand overnight at 0° and was then heated for two hours on the water bath as before. Apart from the sec butyl nitrite boiling below 100° the liquid products amounted to 15 c.c. This was fractionated as above except that the fraction above 50/47 mm was fractionated twice. The final yield was 3.5 gms. of rotation $[\alpha]_D = +16.8^{\circ}$, for a 5.236% solution in ethyl alcohol in a 0.6 dm. tube (c.f. 17.6 by Kuhn and Albrecht for the pure liquid). It should be noted that these authors do not seem to observe the usual conventions with regard to a specific rotation but give figures, using a 0.5 dm. tube.

THE ROTATORY DISPERSION OF 2- NITRO BUTANE.

The rotatory dispersion of this compound is given in Table 12. It will be seen from this that the rotation rises slowly towards the ultra violet but that the actual magnitude is very small compared to that of 2-2 dinitrocamphane.

The rotatory dispersion in the ultra violet was studied using solutions varying from 5% to 0.163%, the date for this is given in Table 3 and Graph 8. From these it can be seen that, while it has been impossible to get to the

TABLE 12

ROTATION OF 2-NITROBUTANE IN THE VISIBLE

λ	α	$[\alpha]$
6500	.44	14.01
6000	.50	15.92
5896	.53	16.87
5500	.63	20.04
5400	.66	21.00
5300	.70	22.28
5200	.76	24.18
5100	.79	25.14
5000	.82	26,10

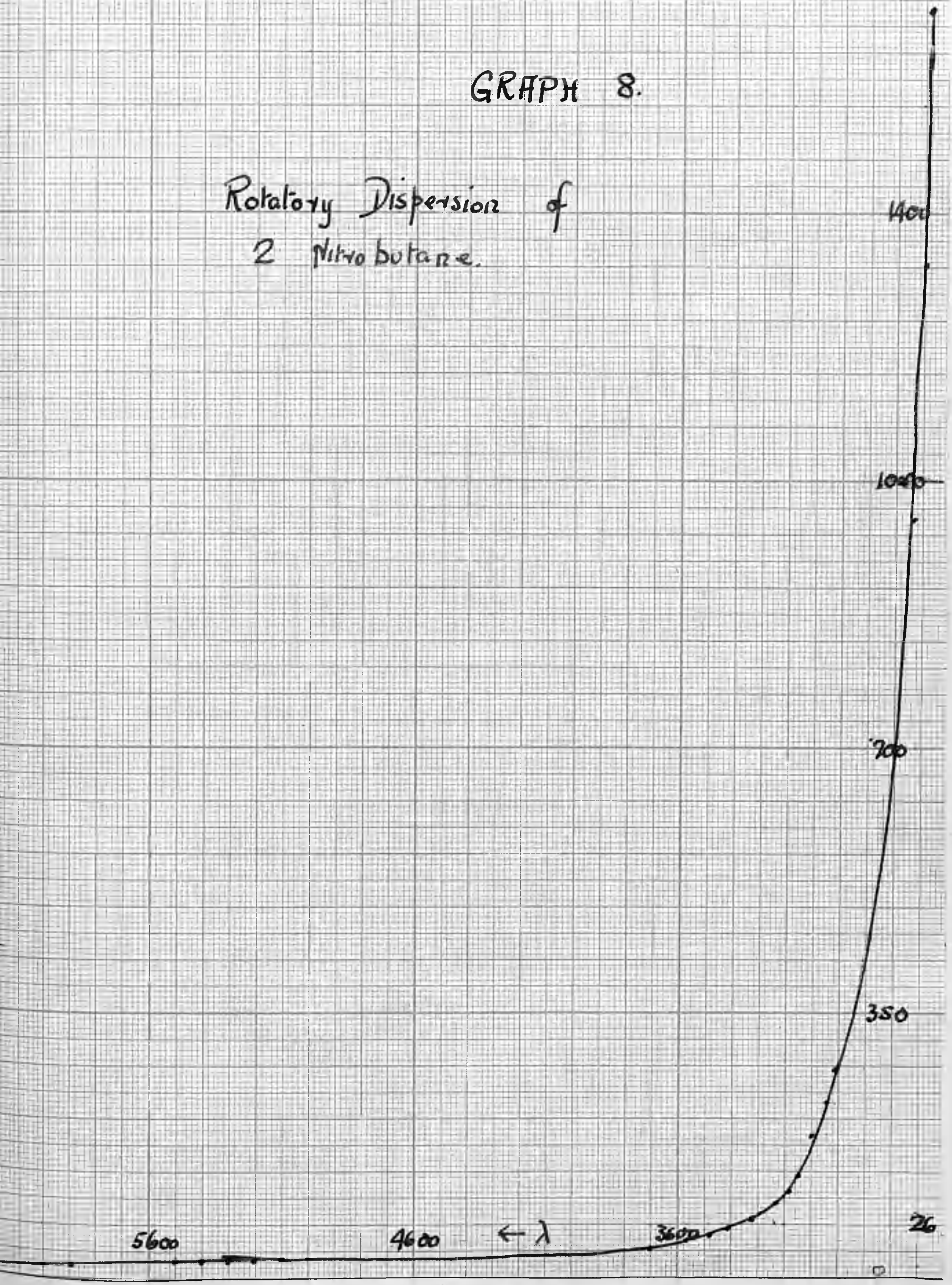
TABLE 13

ROTATION OF 2-NITROBUTANE IN ULTRA VIOLET

λ	α	$[\alpha]$	Conc.
3700	.20	38.4	5.236%
3570	.25	48.0	""
3480	.30	57.9	""
3415	.35	67.3	""
3325	.20	77.18	2.618%
3230	.25	96.48	""
3185	.30	115.8	""
3155	.35	135.1	""
3155	.20	154.3	1.309%
3100	.25	192.9	""
3045	.30	231.5	""
3015	.35	270.1	""
3095	.20	308.6	0.654%
3050	.25	385.8	""
2720	.15	1000.9	0.163%
2700	.20	1334.6	""
2680	.25	1668.2	""

GRAPH 8.

Rotatory Dispersion of
2 Nitrobutane.



maximum of the rotation from the form of the curve there can be little doubt that it exists in much the same position as in 2-2 dinitrocamphane or further into the ultra violet as might be expected from the molecule being slightly smaller. The fact that it has not proved possible to reach the actual Cotton Effect may be attributed partly to this reason and partly to the fact that the rotations are very much smaller.

Absorption of 2- nitro butane.

This was studied, using the same apparatus as before, the conc of the solution being 0.032%. The data is given in Table 14 and graph 9, from which it can be seen that here again there is no selective absorption, but a decided "step out" in the same region as for 2-2 dinitrocamphane.

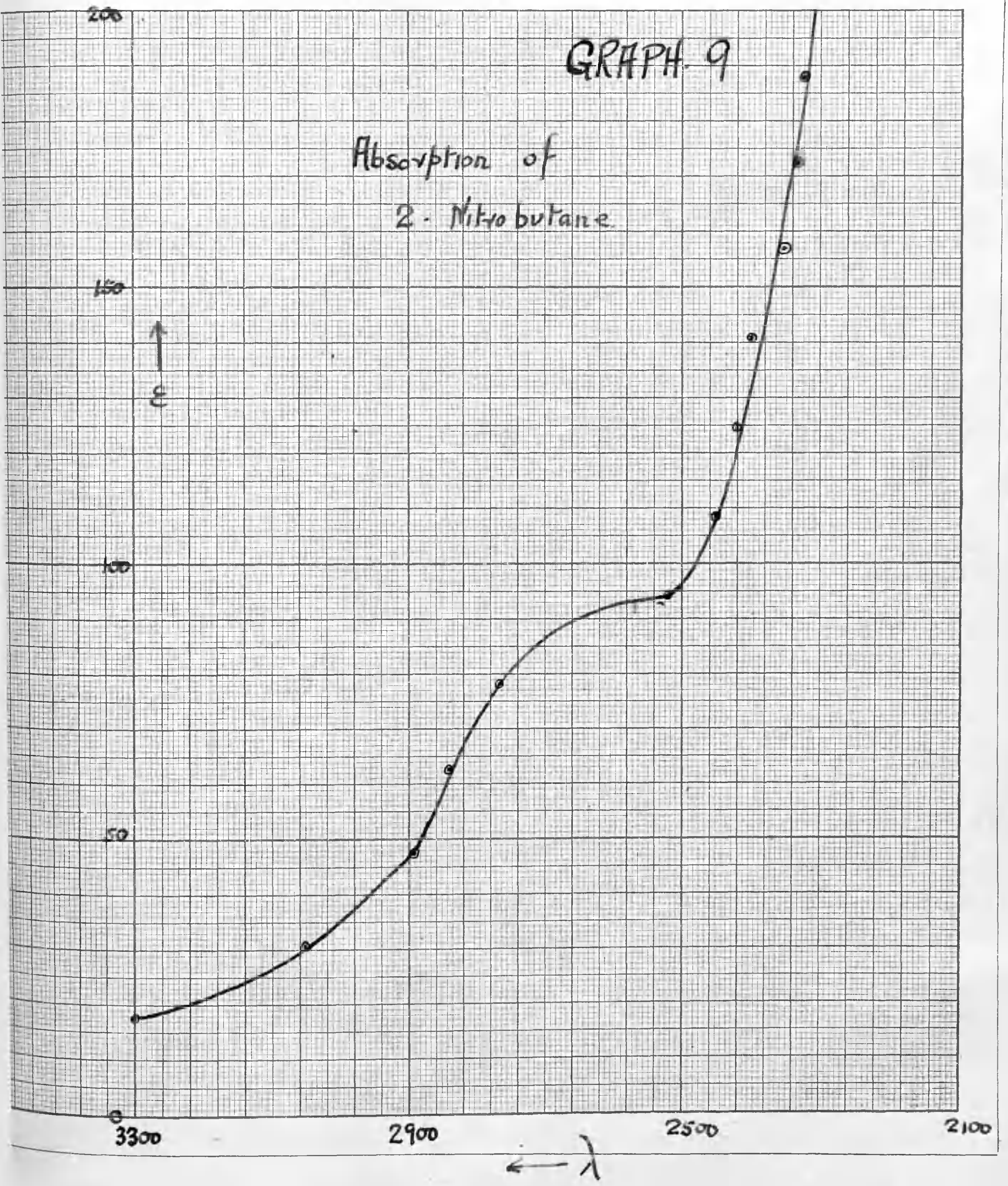
Some slight traces of dichroism were observed, but could not be followed owing to the reasons given.

From the form of the curve of rotatory dispersion, it is concluded that in 2- nitro butane the NO_2 group shows a Cotton Effect, which is situated further into the ultra violet than that described in the previous cases of 2-2 Dinitrocamphane.

TABLE 14

ABSORPTION OF 2-NITROBUTANE conc. .03277%

λ	sector	ε
3300	.1	15.71
3050	.2	31.42
2890	.3	47.13
2840	.4	62.84
2760	.5	78.55
2515	.6	94.26
2450	.7	110.
2420	.8	125.7
2400	.9	141.4
2370	1.0	157.1
2353	1.1	172.8
2350	1.2	188.5
2340	1.3	204.
2320	1.4	219.8
2310	1.5	235.5

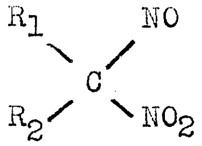


GRAPH 9

Absorption of
2-Nitrobutane

ADDITIONAL PAPER ON THE PHOTO-OXIDATION OF SOME PSUEDO NITROLS.

The psuedo nitrols have the general formula Several methods exist for the preparation of these compounds, two of these (A & B) being capable, theoretically at least, of yielding the nitrol in the optically active condition. The methods are briefly as follows:



A. By the action of nitrous acid on the secondary nitro paraffins.

B. By the action of sodium nitrate on the halogen acids (Meyer & Jacobsen, p. 411).

C. From liquid nitrogen tetroxide and the ketoximes.

D. From fuming nitric acid and the ketoximes.

Since the yields obtained by the first method are small and the method tedious, for preliminary work, the third method due to Kenner and Luciano was used.

Camphor psuedo nitrol.

This compound was prepared(45) by adding 0.65 c.c. of fuming nitric acid to a solution of 1 gm. camphoroxime in 15 c.c. glacial acetic acid. The mixture is allowed to stand for ten minutes in the dark and then 50 c.c. of water are added. The nitrol is then filtered through a sintered glass funnel, washed rapidly with water and dried on porous plate in a vacuum dessicator for two hours. The product so obtained varies in colour from a dark blue, rather sticky solid, to a pale blue, powdery solid. The best melting point obtained was 65 (c.f. 63 by Kenner and Luciano), by drying for 20 minutes to cut down oxidation to a minimum. In this method of preparation the yields are much better using small quantities (not more than 2 grams) and by adding the acid gradually. Cooling the solution during the reaction does not appear to make any difference to the yield. The substance so obtained is extremely soluble in organic solvents, giving solutions of a deep blue colour. Camphor pseudo nitrol is rather unstable even in the solid state, the melting point falling overnight to 52°, the colour changing through green to yellow. In solution the change takes place much more rapidly, being quickest in solvents containing hydroxyl groups. The reaction was also accelerated by the presence of light. To find out which wave length was effective in bringing this about, a number of small tubes containing a solution of the nitrol were exposed to the light from a carbon arc, the light being spread out into a spectrum by a large prism. By this means it was found that red light was most effective, a result which was to be expected from the blue colour of the solution.

ABSORPTION SPECTRA OF PSEUDO NITROLS.

The absorption spectra of the speudo nitrols were examined in order to find the position of the active band. For this purpose a spectrodensograph, lent by Dr. Weigert, was used.

This instrument can only be used for the visible region and depends for its action on the reduction of the intensity of a beam of light by means of a neutral grey wedge which has been calibrated to give known intensities; the optical arrangement is illustrated in the sketch below.

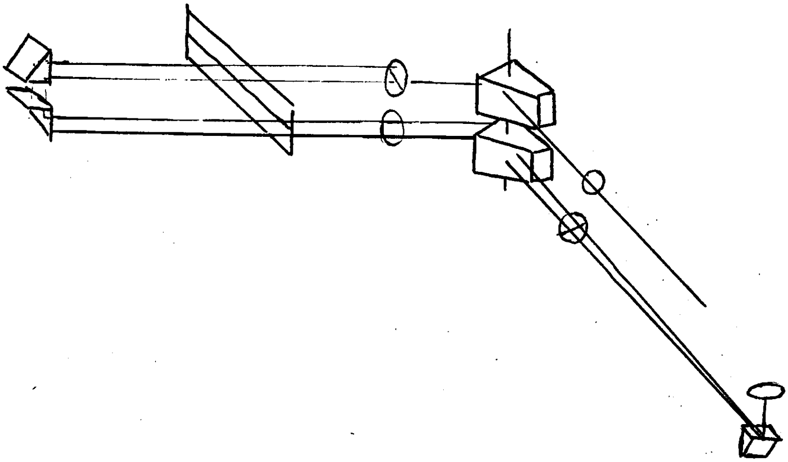


FIG. XIV.

Light is supplied by a 100 watt Osram Projection Lamp, and, after passing through the top prism of the constant deviation spectroscope, is split up into two rays by a biprism. For the sake of compactness and increased dispersion the rays are returned along a parallel path through the second constant deviation prism, through a converging biprism and by reflection are focussed on a pinhole.

The solution is contained in a cylindrical glass cell. Half of this is filled by a half cylinder of optical glass exactly 2 cm. in depth. To fill the cell this glass is removed, a little liquid run in and the glass dropped in, so that a thin film of solution is between the face of the cell and the glass. The rest of the cell is now filled and the end slid on. This gives a difference in the thickness of solution traversed by the light of 2 cm. The cell is placed after the wedge and in front of the spectroscope.

On looking through the pinhole two fields are seen which can be made to match by pulling in a sufficient thickness of wedge. The instrument is so constructed that the wave length and wedge may be adjusted simultaneously and the position of matching recorded on a sheet of graph paper by puncturing a hole.

Some of these graphs are shown below and the corresponding graphs for molecular extinction are shown in graphs 10 and 11.

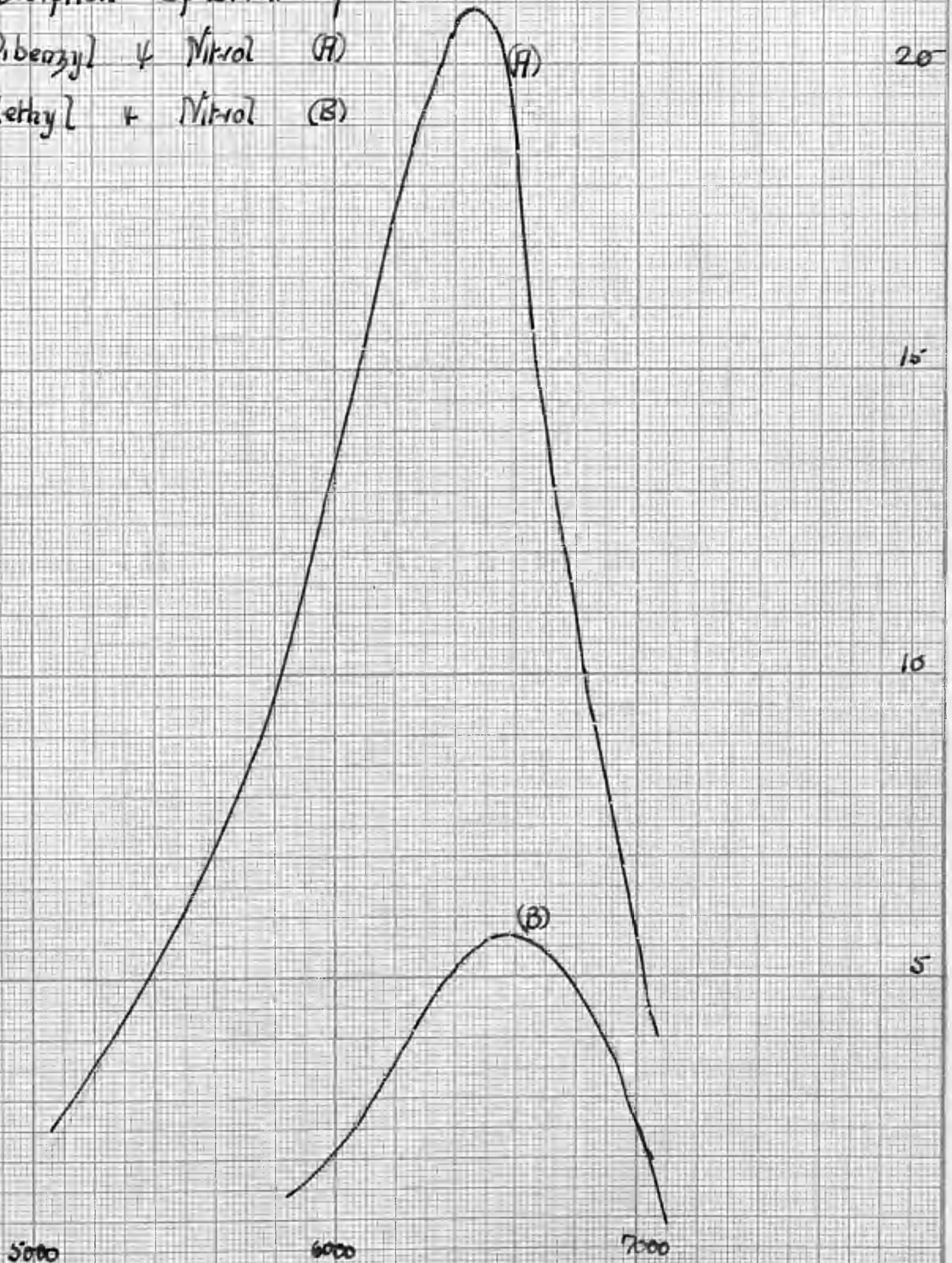
Care should be taken in choosing the concentration of solution so that a true match is obtained even in the region of maximum absorption. If the solution is too concentrated the two fields will be found to be of different colours at that point.

From an examination of the graphs it will be seen the pseudo nitrols have an absorption band situated at 6450 to 6550. This is the only band in the visible and is the region of photochemical activity.

The most likely reaction to take place was the oxidation of the NO to NO_2. This was found to be the case using the apparatus illustrated in the sketch.

GRAPH. 10.

Absorption Spectra of
Dibenzyl ψ Nitrol (A)
Benzyl Methyl ψ Nitrol (B)

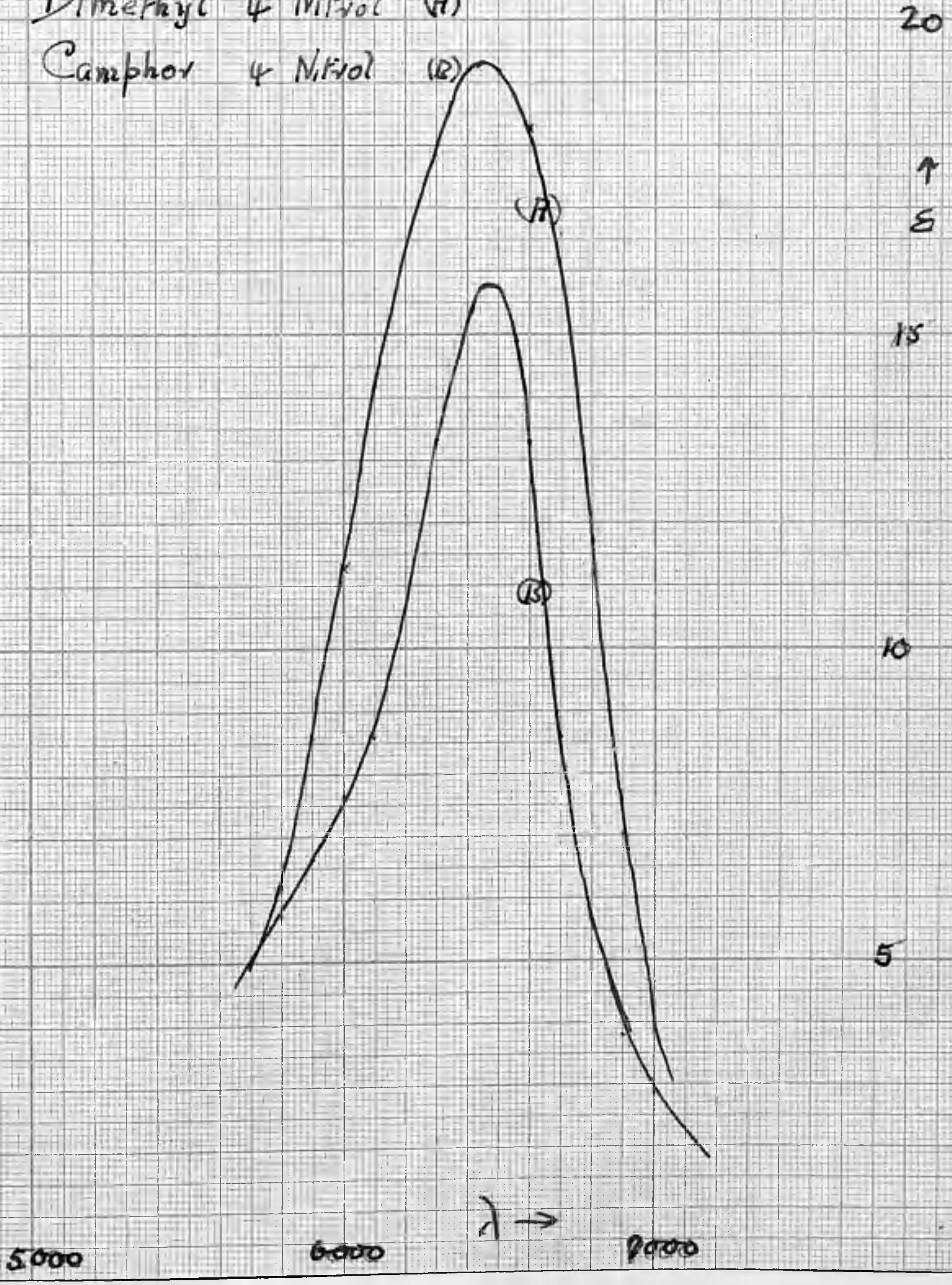


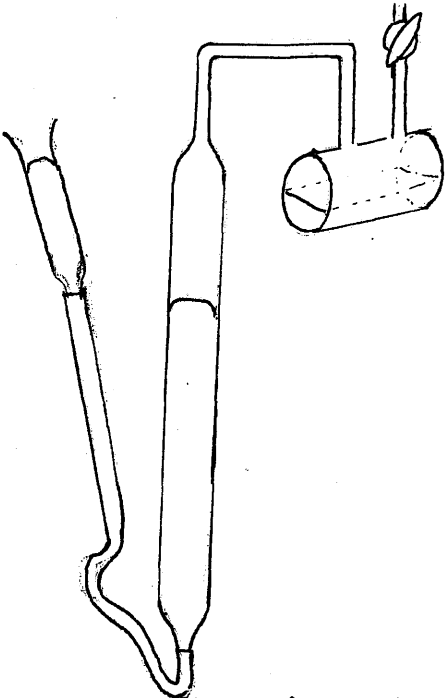
GRAPH II

Absorption Spectra of.

Dimethyl 4 Nitrol (A)

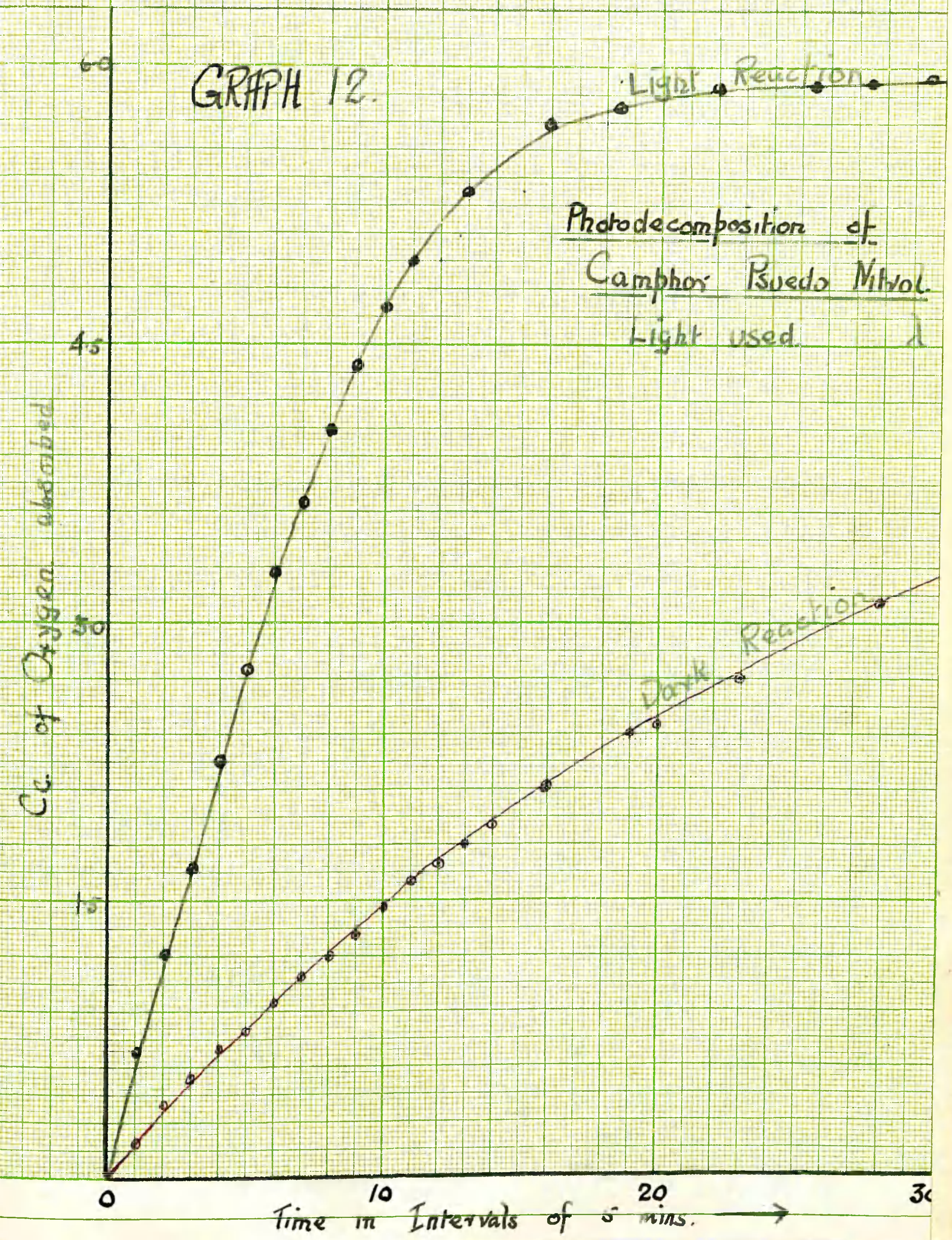
Camphor 4 Nitrol (B)





The light source was an automatic carbon arc, the heat rays being removed by a water filter and the red portion of the spectrum isolated by a red gelatine filter. All the air was swept out of the apparatus by a current of oxygen and the solution run in by the side tube. Mercury or water was then run in until the whole of the burette was filled and then oxygen blown in until the burette was filled with oxygen. Readings of the volume of oxygen were taken every five minutes. The results are shown in graph 12 along with a similar reaction from which light had been excluded. It will be seen from this that there is a considerable dark reaction and also that the volume of oxygen absorbed is slightly in excess of the amount required for a plain oxidation to the dinitro compound which would have been 5 c.c. This excess absorption will be referred to later in connection with other nitrols.

When a solution of camphor pseudonitrol is allowed to decompose and the solvent removed, a sticky, yellowish mass is left. By allowing the reaction to take place on a porous plate, how-


GRAPH 12.
Photodecomposition of
Camphor Psuedo Nitrol.
Light used λ
Light Reaction
Dark Reaction
Cc. of Oxygen absorbed
60
45
30
15
0
10
20
3
Time in Intervals of 5 mins. →

ever, the decomposition product may be obtained as a yellow, fairly dry solid. This was found to be exceedingly soluble in all organic solvents and all attempts to recrystallise it from these were unsuccessful. It was found, however, that it could be recrystallised from a mixture of alcohol and water in the proportions of one of water to two of alcohol. If more water than this was used the product was sticky. After five such recrystallisations a pure white solid was obtained, smelling strongly of camphor. Difficulty was met with in securing a sharp melting point, but by using rather a wide tube and packing the material in with a needle, the substance melted between 107.5° and 108.5°. After three recrystallisations the rotatory power remained constant.

An analysis of this compound gave the following results.

	Calc. for $C_{10}H_{16}N_2O_4$	Obs.
Carbon:	52.6%	53.0%
Hydrogen:	7.0%	7.0%
Nitrogen:	12.3%	12.5%

These results taken in conjunction with the oxygen absorption show that the oxidation product is 2-2 dinitrocamphane. This is a new nitro derivative of camphor to which reference was made in Section I.

Dimethyl pseudo nitrol.

This compound was prepared by the action of liquid nitrogen tetroxide on the ketoxime.(46) 1.2 c.c. (or 1.8 gms.)

of liquid N_2O_4 were added to 2 gms. oxime dissolved in 40 gms. ether. The mixture was allowed to stand in ice for three hours in the dark. The ether was then removed in a vacuum, keeping the temperature as low as possible since the pseudo nitrols are volatile in ether vapour. The product so obtained was a pure white solid, melting at 76° to a blue liquid. It yields blue solutions in organic media, this being due to the dissociation into single molecules in solution. A quantitative examination of the oxygen absorption showed that 0.0316 gm. in 5 c.c. chloroform absorbed 8 c.c. oxygen when exposed to red light, while a similar solution kept in the dark absorbed 2.2 c.c. The reaction here is much slower than in the case of camphor pseudo nitrol. Moreover the dark reaction is practically negligible, the volume of 2.2 c.c. being absorbed over a period of 24 hours. The theoretical volume for oxidation to the dinitro compound here was 3 c.c., so that the volume actually absorbed was almost three times the theoretical. When extracted with water the extract was found to have an acid reaction, although the original solution was neutral. This effect was obtained no matter what solvent was used, so that the possibility of its being due to an oxidation of the solvent was eliminated. On testing qualitatively the acid was found to be nitric acid. This indicated the possibility that the remainder of the nitrol, having lost its nitrogen as nitric acid, might be present as ketone according to the equation, —

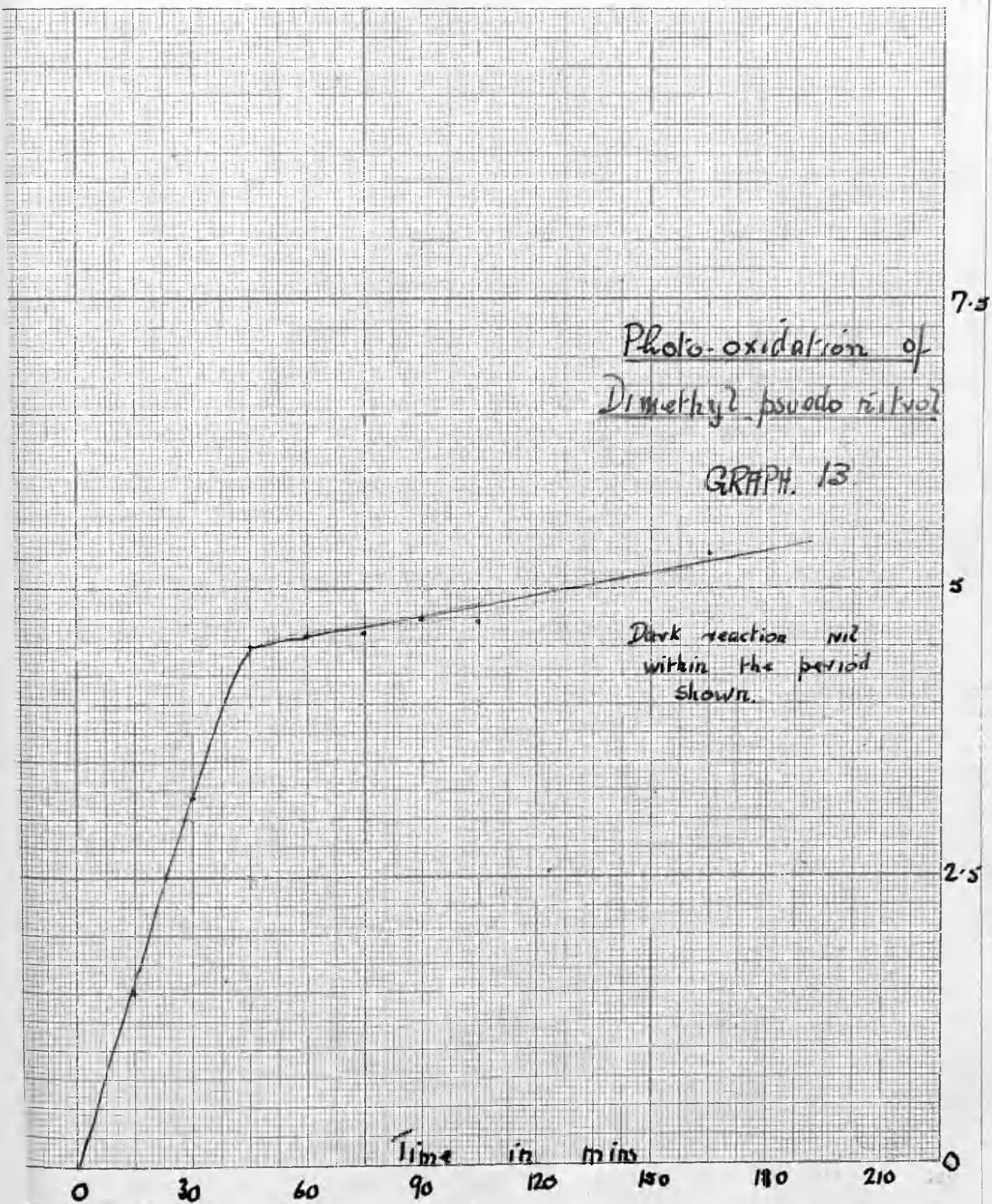


Photo-oxidation of Dimethyl psuedo nitrol

GRAPH. 13

Dark reaction nil within the period shown.

The presence of this was shown by obtaining the derivative of 2-4 dinitrophenylhydrazine. This was obtained as an orange coloured, crystalline solid, melting at 118°, c.f. 128° for the derivative from pure acetone. The above equation may, therefore, be taken as representing the chief reaction taking place. From a consideration of the course of the reaction as shown by graph 13 it would appear that the reaction actually takes place in two stages; first, the oxidation to the dinitro compound corresponding to the rapid absorption of oxygen, and second, the slow oxidation of this to the ketone and nitric acid. This second reaction is a dark reaction since, if the light be shut off when the oxygen absorption is about 5 c.c., the solution will still go on absorbing.

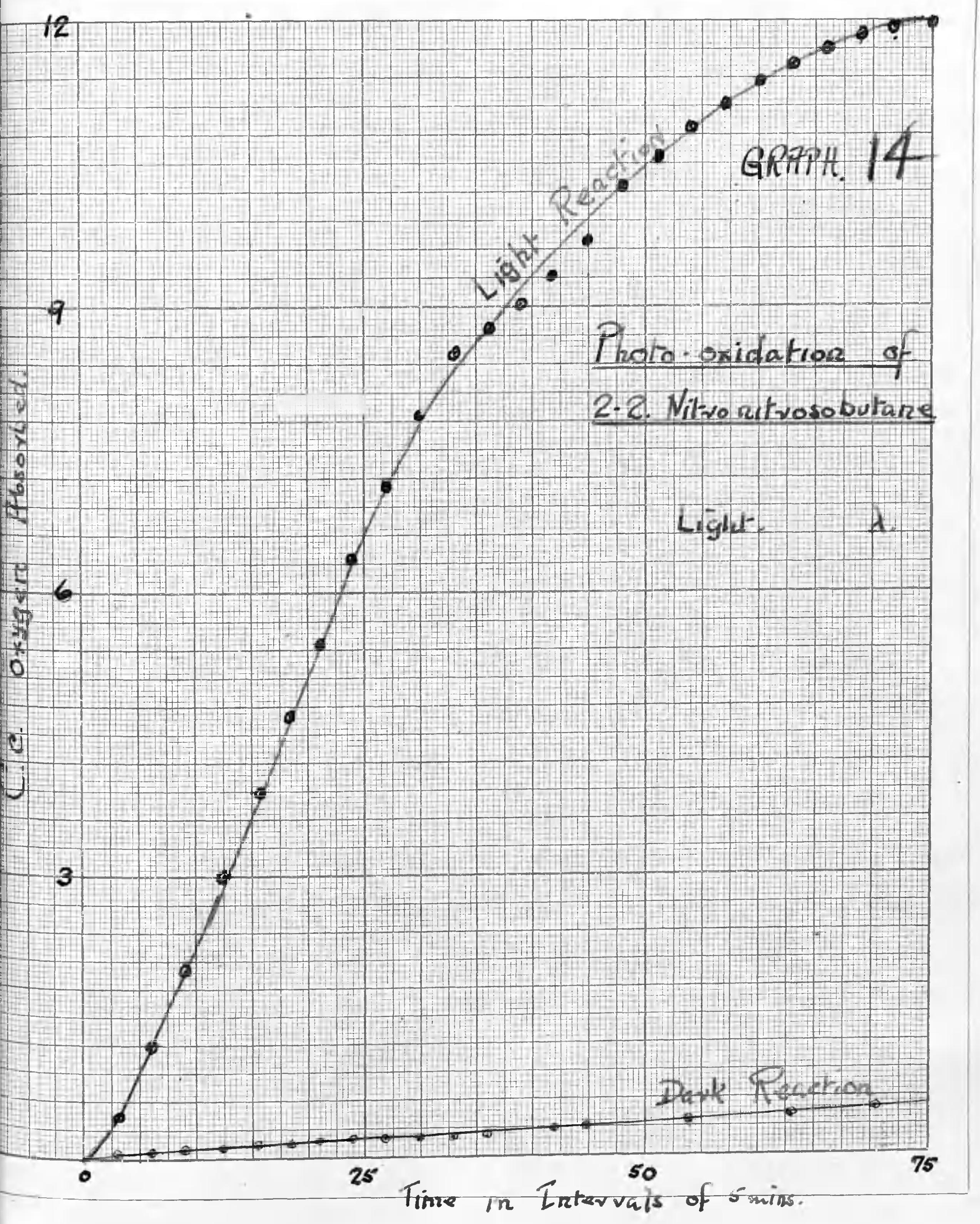
2-2 Nitronitroso butane.

This pseudo nitrol was prepared in a similar manner to the dimethyl compound. 1.6 gms. liquid nitrogen tetroxide were added to 2 gms. methyl ethyl ketoxime (b.pt. 148 to 151), dissolved in 40 gms. ether. The mixture was allowed to stand for three hours and the ether removed as before. According to Scholl this should have given a yield of 1 gm. nitrol, but in no case was this found to be obtained. The usual yield was about 9% as compared with Scholl's 33%. The solid deposited must be pressed on porous plate to free it from oily by-products. Since it is not very soluble in ether this may be used to remove the last traces of blue from the nitrol, leaving a white solid melting at 58°. It is very soluble in chloroform, giving a deep blue solution.

When exposed to red light, this pseudo nitrol behaves in a similar manner to the dimethyl compound. The results of the photo-oxidation are shown in graph 14. From this it will be seen that here we have a slight dark reaction and also that the oxygen absorption is a little less than in the previous example (12.8 c.c. in place of a theoretical 5 c.c.). When allowed to stand for 14 days the oxygen absorption rose to 14.8, showing that the maximum is the 15 c.c. required for oxidation to the ketone and nitric acid. The presence of these two substances was proved as before by 2-4 dinitro phenyl hydrazine, the product being compared with a sample obtained from methyl ethyl ketone. The reaction here also may be represented by the same equation as before,

METHYL BENZYL PSEUDO NITROL.

This compound may be prepared either by the action of fuming nitric acid on the ketoxime or by the action of liquid nitrogen tetroxide. The starting product was methyl benzyl ketone, b.pt. 216-220°. The oxime was prepared from this in just the same way as for acetoxime. The oxime is a yellowish-brown oil, distilling at 132-137°/13 m.m. Some decomposition


GRAPH 14
Photo-oxidation of 2-2. Nitro nitrosobutane
Light λ.
Light Reaction
Dark Reaction
C. C. Oxygen Absorbed.
Time in Intervals of 5 mins.
12
9
6
3
0
25
50
75

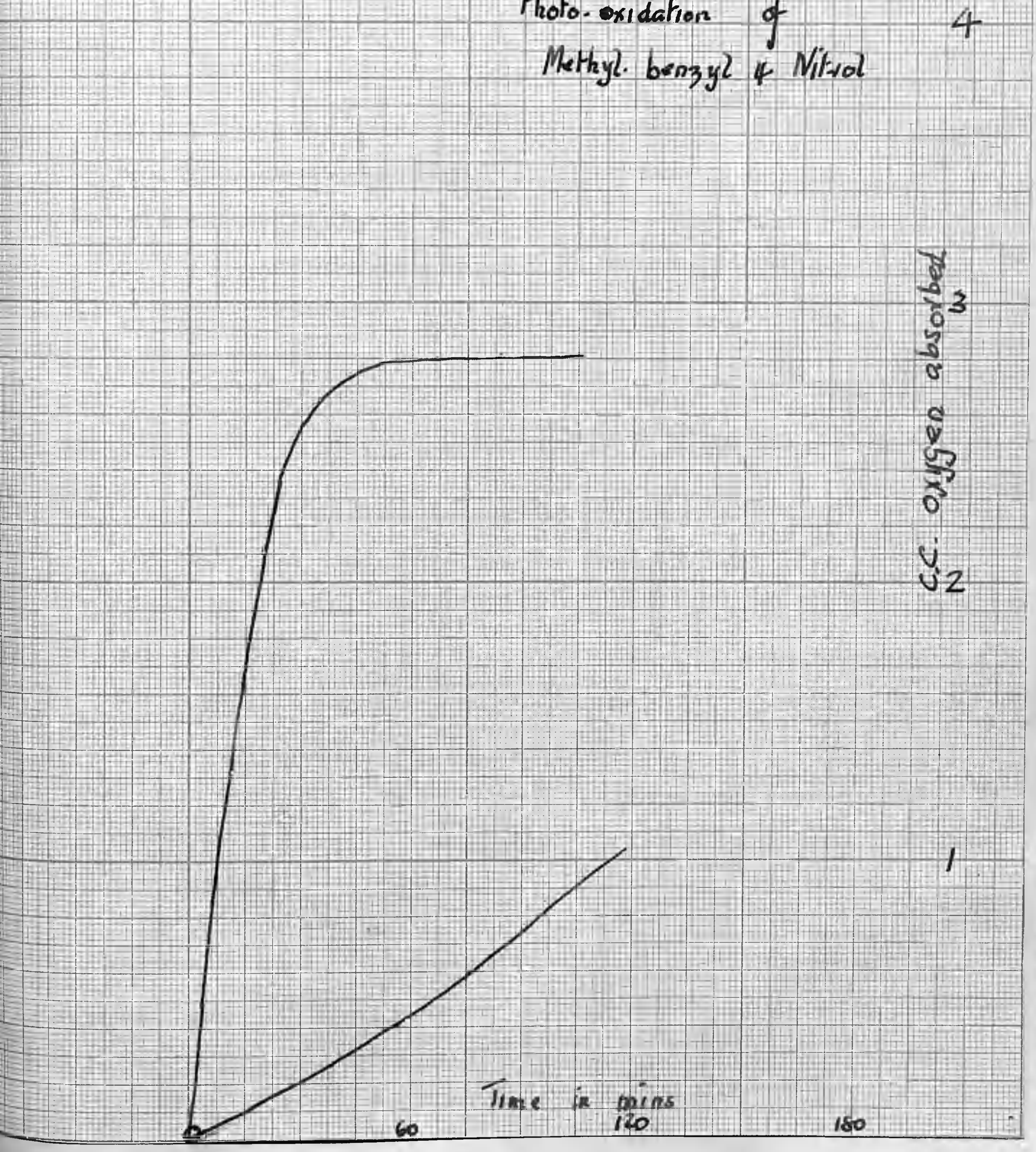
occurs on re-distilling, while there is no apparent difference in the nitrol obtained from this than from the original oil. The nitrol is prepared by adding 0.69 c.c. fuming nitric acid to o gm. oxime in 15% glacial acetic acid and leaving for 10 to 15 minutes in the dark. 50 c.c. of ice-cold water are then added, the flask well shaken and left to stand in ice for some time. By this means the nitrol, which first appears as a green oil, is obtained as a green solid. This is filtered and washed with water and ethyl alcohol in which it is soluble only to a very slight extent. The nitrol left is almost a pure white solid, melting at 87° to a blue liquid. This pseudo nitrol is not mentioned in the literature.

By the action of liquid nitrogen tetroxide on the ketoxime, a good yield of nitrol is obtained, but the method is not so satisfactory as that described above.

For the photo-oxidation 0.0519 gms. were dissolved in 5 c.c. chloroform. The oxidation was complete in an hour when irradiated with red light. The volume absorbed was 2.8 c.c., compared with a theoretical of 3 c.c. for oxidation to the dinitro compound. A similar solution kept in the dark absorbed 1.0 c.c. in the same time. These results are illustrated in graph 15.

GRAPH 15

Photo-oxidation of Methyl. benzyl & Nitrol



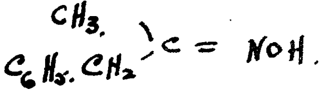
DIBENZYL PSEUDO NITROL.

This was prepared by the action of fuming nitric acid(45) on dibenzyl ketoxime, and is a dark blue solid melting at 69° (c.f. 72° for a recrystallised sample by Kenner and Luciano). It was found that this substance in chloroform solution under the influence of red light, absorbed the theoretical amount of oxygen (5 c.c.) to give the dinitro di-dibenzyl methane. No difference in velocity could be observed between the light and dark reactions. The results are given in graph 16.

Attempts to prepare the pseudo nitrols of FENCHONE, BENZYL ACETONE AND CEDROME OXIME.

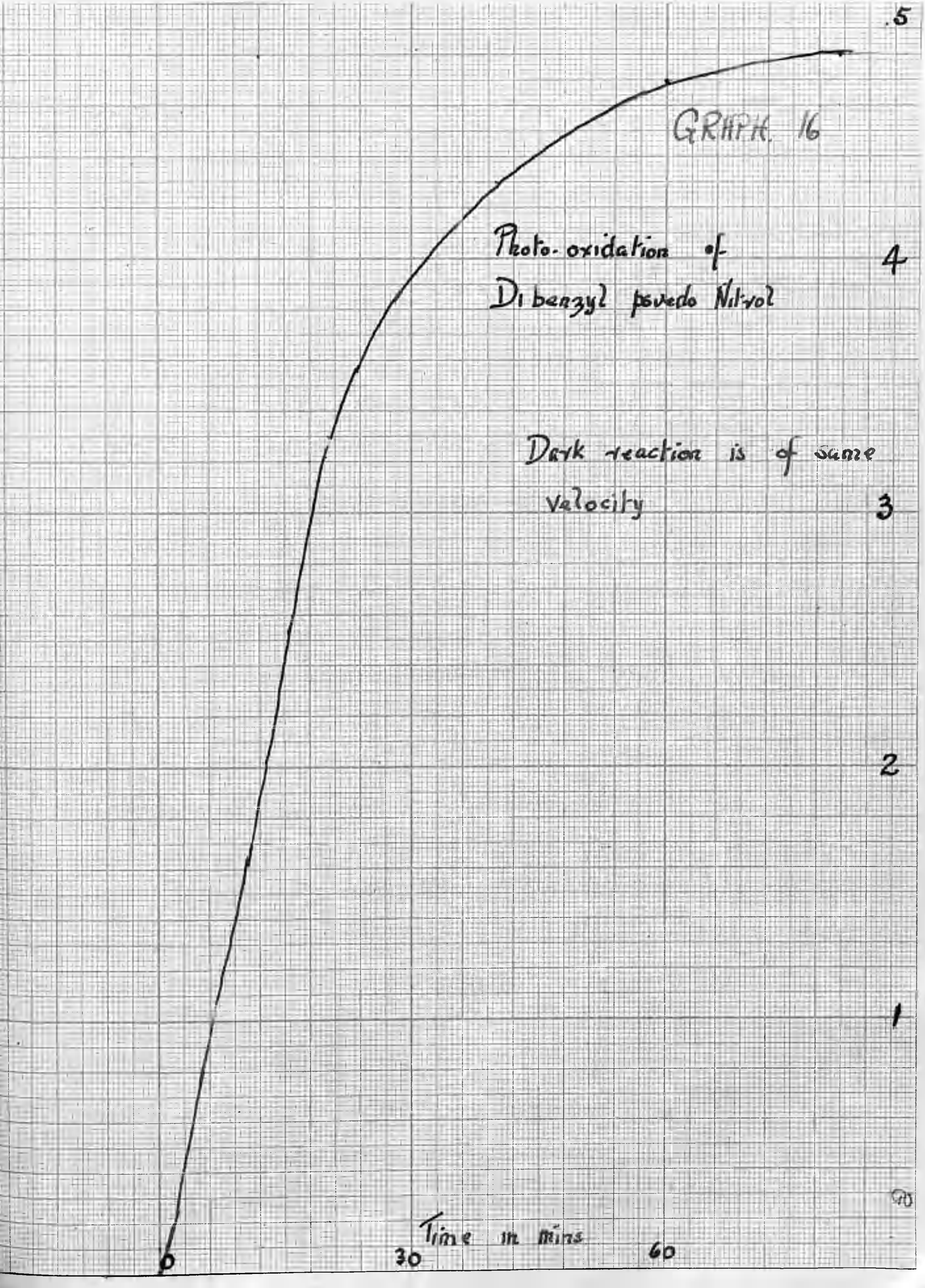
Fenchone yields an oxime melting at 152°. Liquid N_2O_4 has no action upon this. By addition of 0.65 c.c. fuming nitric to 1 gm. oxime in 15 c.c. acetic acid, a heavy blue oil was obtained. This was extracted with ether and the ether removed in a vacuum. The residue was a heavy blue oil which could not be solidified by freezing.

By the action of liquid N_2O_4 on benzyl acetone oxime



$\begin{matrix}CH_3\\ C_6H_5.CH_2\end{matrix}\!\!>C = NOH$

, in ether solution a heavy blue oil was obtained on removal of the ether. This could not be solidified. By the action of fuming nitric acid on the oxime, a heavy oil separates which appeared to solidify on freezing. The yield was very small, however, and the preparation of the ketonic starting product is difficult, so that this attempt was not



GRAPH 16

Photo-oxidation of Dibenzyl pseudo Nitrol

Dark reaction is of same velocity

continued.

Cedrone may be obtained from cedrene by oxidation with chromic acid.(47) The oxime of this ketone did not yield a pseudo nitrol with either fuming nitric acid or liquid N_2O_4.

A useful summary of pseudo nitrols is to be found in Ber. 29, 94 et seq. Many of these, however, are either liquids or are very unstable.

Summary of the photo-oxidation of pseudo nitrols.

These compounds are all oxidised in an atmosphere of oxygen under the influence of red light. It is very probable that the first reaction in every case is the oxidation to the di-nitro compound. This reaction, however, is often followed by a second reaction, the oxidation to Ketone and ~~Nitrol~~ Nitric acid., which occurs in the dark. With regard to this reaction, it appears from the examples studied that it decreases with increasing complexity of the nitrol, or rather of the dinitro compound. This may be due to steric hindrance. It should be noted in this connection that those nitrols which are oxidised to the dinitro compound only, either consist entirely of single molecules in the solid state or may be practically so in the case of methyl benzyl pseudo nitrol which is never obtained in a pure white condition, indicating that it may consist partly of double and partly of single molecules. This parellelism between the state of association in the solid state and the oxidation products would appear to be explained by the above suggestion of steric hindrance.

There is also an increase in the velocity of the dark reaction with an increase in the molecular weight of the nitrol. Thus for dimethyl pseudo nitrol it is zero; for camphor pseudo it is about half, while for the dibenzyl compound it equals the light reaction. A possible explanation of the increasing velocity of reaction with increasing complexity would be that an equilibrium exists between the double and single molecules in solution, and that this is disturbed by the oxidation of some of the single molecules. In the case of the simpler molecules which are not so completely dissociated, this will take time, thus giving a slower light reaction.

ATTEMPTED ASYMMETRIC DECOMPOSITION OF 2-2 NITRONITROSO BUTANE.

From what has been said on the photo-oxidation of the pseudo nitrols they would appear to be suitable so far as physical properties are concerned for asymmetric decomposition. Such a decomposition was attempted in the case of 2-2 nitronitroso butane.

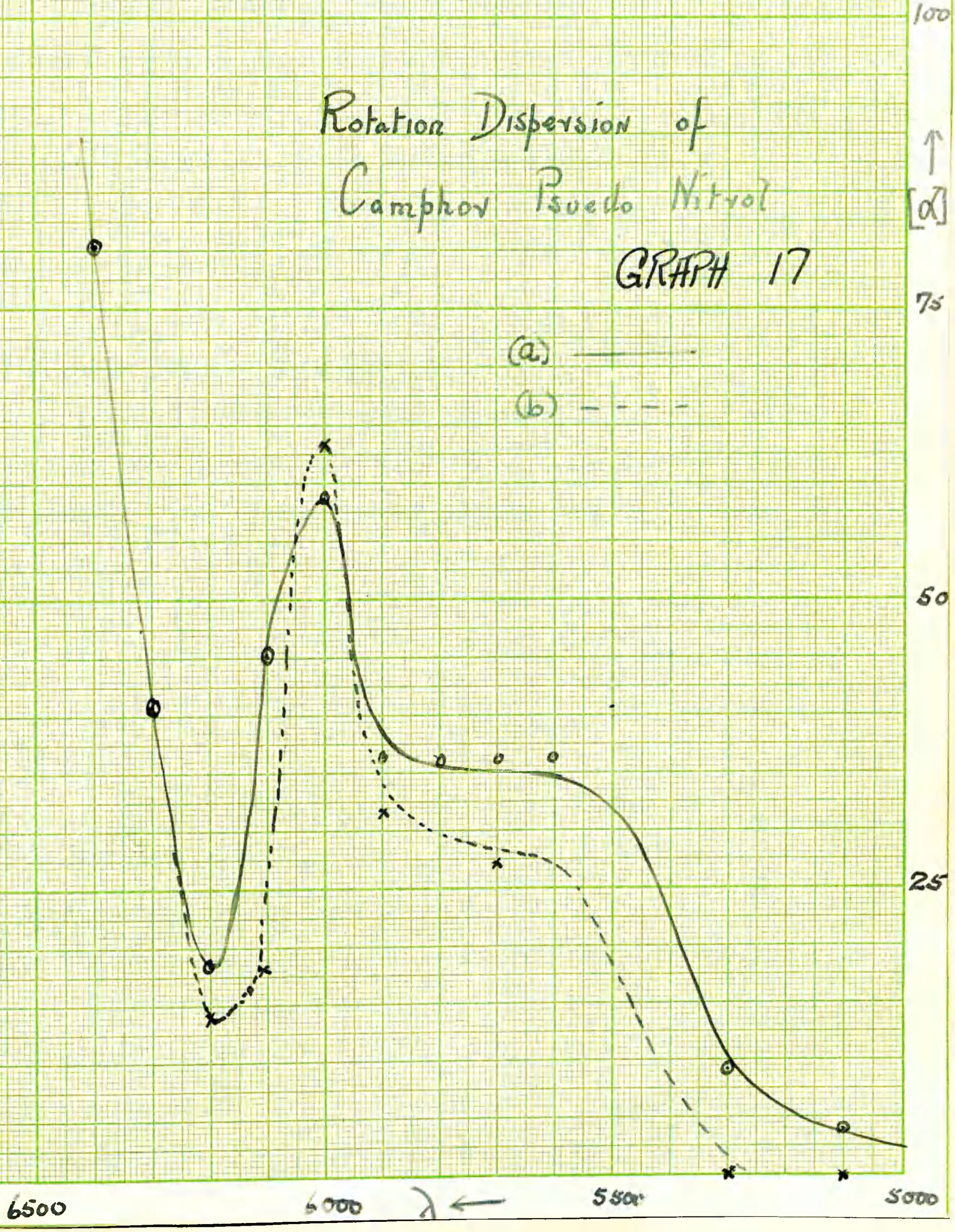
The apparatus used for this was the same as that used for the ordinary oxidation, with the addition of a quarter wave plate, or rather two quarter wave plates, placed so that they gave the two forms of circular light. Two exactly similar solutions were exposed for equal periods, one to right and the other to left, circularly polarised light, for equal periods. At the end of two, three and five hours the solutions were transferred to polarimeter tubes, but no rotation could be observed.

This failure to observe a rotation might be due to the form of the dispersion curve in the visible on the short wave side of the absorption band, and the rotation dispersion curve of camphor pseudo nitrol was examined to obtain some information on this point. This substance, although its oxidation product has a fairly large rotation, has itself a very small rotation, as is shown in Graph 17 and Table 15. Since the oxidation product has a larger rotation than the nitrol itself, racemisation may be ruled out as the cause of this small rotation. The other possibility is that a new asymmetric carbon atom has been formed and that this has some effect on the other two already present. Since the effect is smaller than if both groups attached to this carbon atom were nitro groups, it suggests that the two groups in some way neutralise one another. This point of view is supported from the form of the dispersion curve of the pseudo nitrol in which the nitroso group has a small Cotton Effect in the red, but the rotation falls towards the ultra violet contrary to the usual behavious of such curves, thus suggesting that the nitro has a large Cotton Effect in that region of the same sign as in the oxidation product. This effect has been overcome by the nitroso group effect just sufficiently to cause the rotation in the

TABLE 15

ROTATION OF CAMPHOR PSUEDO NITROL .368 gms/100 c.c. CCl

α		$[\alpha]$		λ
a	b	a	b	
.18	-	81.53	-	6400
.09	.09	40.76	40.76	6300
.04	.03	18.11	13.58	6200
.10	.04	45.29	18.11	6100
.13	.14	58.87	63.40	6000
.08	.07	36.23	31.71	5900
.08	.08	36.23	36.23	5800
.08	.06	36.23	27.24	5700
.08	.07	36.28	31.71	5600
.09	-	40.76	-	5500
.00	-	0.00	-	5400
.02	0.00	9.06	0.00	5300
-	0.00	-	0.00	5200
-.01	0.00	-4.53	0.00	5100
0.00	-	0.00	-	5000
-.01	.03	-4.53	13.28	4900



Rotation Dispersion of Camphor Psuedo Nitrol

GRAPH 17

red to be slightly positive, while the rotation nearer the blue is practically zero.

As a further verification of this point the preparation of the active form of the pseudo nitrol of active 2- nitro butane was attempted. The sodium salt of this has already been obtained in the optically active condition.(31)

The method of Schreiner and Young for the preparation of the sodium salt was followed. .24 c.c. of 0.416 N NaOEt were added to 1 gm. active nitro butane, both being at a temperature of -12°C. This was left to stand for 30 minutes, 0.67 gm. sodium nitrite added, with a small amount of water and then an excess of dilute sulphuric acid added slowly. The flask was then shaken briskly and the nitrol filtered off. It showed no rotation in toluene solution.

Schreiner and Young found that the nitro octane recovered from the sodium at -18° had only 24% of the activity of the original compound, while recovered at -70° it retained 71%.

Another attempt was made, therefore, using the same quantities as above at the temperature of a mixture of solid CO_2 and ether. No rotation was observed. A similar result was obtained using 0.6 N alcoholic HCl in place of the sulphuric acid. Still another attempt was made using amyl nitrite and alcoholic HCl, but the nitrol formed dissolved in the amyl nitrite layer on the addition of water. The difficulty in using such low temperatures is the tendency of the sodium nitrite to freeze out. A negative result was also obtained using Kuhn and Albrecht's method for the preparation of the sodium salt, i.e., 1 gm. nitro butane, 10 c.c. 1N sodium methylate made up to 14 c.c. at -18°. The sodium nitrite was added to this and then the dilute sulphuric acid. The yield in this case was 0.0618 gm.

From the fact that the sodium salt can be obtained in the optically active condition and the nitro compound can be recovered from this using sulphuric, it would appear that the absence of rotation in the nitrol is due to the form of the dispersion curve in the visible causing the rotations to be too small to be measured rather than to racemisation.

The pseudo nitrols then, while suitable in photochemical behaviour and in most physical properties but that of optical activity, would not appear to be suitable for asymmetric decomposition by reason of the peculiar form of the dispersion curve in the visible. This is due to the presence in the molecule of two absorption bands which are not removed from one another by a sufficiently large range of wave lengths to prevent their contributions, which are opposite in sign, from overlapping.

Another fact which causes them to be unsuitable for asymmetric decomposition is that, with increasing molecular weight, which would cause us to expect larger rotations, there is an increase in the velocity of the dark reaction. This reaction, of course, acts equally on both active forms, and by the time we reach the dibenzyl compound, equals the light reaction, thus preventing the formation of any rotation.

[illegible]

To [illegible]

[illegible]

[illegible] during the course of the work just brought

To the Trustees of the Carnegie Trust for Universities of Scotland for a Scholarship.

To Mr. Robert McCulloch, mechanic to the [illegible] his help in the adjustment of the ultra violet [illegible]

To Dr. Fritz Weigert for the loan of a spec [illegible]

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APPENDIX.

Examples of the Cotton Effect arranged according to the active group.

The carbonyl group.

Camphor.

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Kuhn and Gore. Z.Phys. Chem. (1931) B 12, 389-397.
Kuhn and Lehmann. Z. Electrochem. (1931) 37, 549.
Z. Phys. Chem. (1932) B 18, 32-48.

Camphor Sulphonic acid.

Lowry and French. J.C.S. (1932) 2657.

Camphor Quinone.

Complexes. Mathieu. C.R. (1932) 194, 268, 367.
Lifschitz Z. Phys. Chem. (1923) 105, 27-55.
Weedeneewa. Ann. Physik. (1923) 72, 122.

Aldehydic Sugars.

Tetra acetyl arabinose. Lowry, J.C.S. (1933) 1179.

Pentyl acetyl fructose.

Carvo menthone

Lowry & Lishmund, J.C.S. (1935), 709.

Menthone

Acetoin. Lowry & Baldwin, J.C.S. (1935), 704.

Xanthates.

Tschugaeff. Ber. (1909) 42, 2244.

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" " Z. Phys. Chem. (1910) 74, 503-512

" " " " " (1912) 79, 471-480

" " " " " (1913) 85, 481-511

Lowry and Hudson. Phil. Tran. (1933) A 232, 117-154.

NITRITE.

Octyl, Kuhn & Lehmann (see ref. above)

Methyl phenyl carbinol

" cyclohexyl carbinol. Kuhn & Biller. Z. Phys. Chem.

" n-hexyl " (1935) 29, 1-41.

CO-ORDINATION COMPOUNDS.

Jaeger. Z. Anorg. Chem. (1928) 175, 161-230.

Lifschitz. Z. Phys. Chem. (1923) 105, 27-54.

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Kuhn & Szabo. Z. Phys. Chem. (1931) B 15, 59-73.

IODO COMPOUNDS.

Kuhn & Biller. Z. Phys. Chem. B29 (1935), 256.

Levene & Rothen. J. Biol. Chem. (1934) 107, 555.
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J.A.C.S. 55, 429 (1929)
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AZIDO COMPOUNDS.

Dimethylamide of α azido propionic acid. T.F.S. (1930) 26, 293-308.
Methyl α azidopropionate T.F.S. " "
Kuhn & Braun. Z. Phys. Chem.(1930),B8, 281.

CHLORO AND BROMO COMPOUNDS.

Ethyl α bromopropionate " " " " "
Methyl α Chloropropionate. Kuhn, Freudenberg & Wolf. Ber. (1930), 63, 2367-2379.
Chloropropionic dimethylamide " " " "

PHENYL COMPOUNDS.

Methyl phenyl carbinol. Kuhn & Biller. Z. Phys. Chem.
" " " acetate. (1935) 29, 1-41.
Carbomethoxymethyl phenyl carbinol " " "
Phenylmethoxyacetic acid methyl ester " " "
" " " " dimethylamide " " "
" " propionic acid methyl ester " "
" " " " dimethylamide " "

MISCELLANEOUS.

Mandelic acid ethyl ester. Kuhn & Biller. Z. Phys. Chem. (1935), 29, 1-41.

" " nitrile

Carbethoxy l lactic acid ethyl ester. " " ""

" " " dimethylamide " " ""

" l alanine ethyl ester " " ""

" " " dimethyl amide " " ""

Pinene Servant Compt. Rend. (1932) 194, 368.

Ethane sulphonyl l lactic acid ethyl ester. Kuhn & Biller,

dimethylamide (see above)

l alanine ethyl ester

dimethylamide