THE PHOTOCHEMISTRY OF PARASANTONIDE

With an additional paper on

THE FLUORESCENCE SPECTRA OF SOME POLYCYCLIC AROMATIC HYDROCARBONS.

THESIS

for the degree of

Doctor of Philosophy

of the

University of Glasgow.

Submitted by

ERIC JAMES YOUNG SCOTT, B.Sc.

June, 1948.

The Photochemistry of Parasantonide.

CONTENTS.

Page

INTRODUCTION

RESULTS

INTRODUCTION.

Asymmetric Photochemical Action.

Since the pioneer work of Arago and Biot (1) in the field of Optical Activity, a large number of compounds have been discovered, which existed in two distinct forms, identical in chemical and physical properties but differing only in their behaviour to incident plane polarised light. These forms were called "enantiomorphs" and were designated "dextro-" or "laevo-" depending on whether the plane of polarisation of the light was "rotated" through a positive or a negative angle respectively. When attempts have been made to synthesise such compounds in the laboratory, equal quantities of each enantiomorph were produced simultaneously. Such a combination of two enantiomorphs would therefore be inactive and was termed a "racemic mixture".

In some cases, optically active compounds have been prepared artificially by the use of an intermediate reagent, which was itself optically active. This was the principle underlying the various methods of "resolution" of racemic mixtures into their corresponding enantiomorphs developed by Pasteur and others (2). It did not however seem likely, as Pasteur (3) himself pointed out, that an optically active compound could be prepared in the laboratory without the intervention of some asymmetric influence.

The fundamental problem was thus to discover what asymmetric physical force in nature was responsible for the production of optical activity. Of those forces capable of interacting with matter (i.e., the electric field, the magnetic field and electromagnetic radiation) the one which was most likely to yield results would be visible and ultra-violet radiation, since it was known to be capable of initiating chemical reaction and, at the same time, could occur in a form which embodied the necessary elements of symmetry (4). In order to conform to the latter restrictions, the physical agent should possess an axis of symmetry, but neither a centre nor a plane of symmetry.

Fresnel (5) in 1866 discovered that light could be circularly polarised, in which case the ether particles were regarded as moving with uniform velocity about a central point. He distinguished between right- and left-handed polarisation according to the direction of rotation of the particles. Thus a circularly polarised wave train would exhibit the symmetry properties of a right- or left-handed helix, i.e., it would have no centre nor plane of symmetry but the axis of propagation would be an axis of symmetry.

These symmetry conditions, it will be noticed, were similar to those which determined the occurrence of optical activity in chemical compounds, e.g., in tartaric acid (6). A further relation between circularly polarised light and optical activity was revealed by Fresnel (7). A circularly polarised wave could be shown to be formed by the addition of two plane polarised waves of equal amplitude and wave length but with displacements oriented mutually at right angles and differing in phase by a quarter of a wave length (8). In a similar manner, plane polarised light was considered as comprising two circular vibrations of opposite sense. Fresner made use of this idea to explain the rotation of the plane of polarisation by optically active compounds (9). Thus by considering a plane polarised wave as being split up into two circularly polarised waves, which traversed the medium with different velocities and recombined to give light polarised in a different plane from the original, he was able to express the rotation as a Circular Double Refraction:

$$\alpha = \frac{\pi c}{\lambda}\left(\frac{1}{v_l} \sim \frac{1}{v_r}\right) = \frac{\pi}{\lambda}\left(n_l \sim n_r\right)$$

where v_l, v_r were the velocities of the left and right handed light, n_l, n_r were the corresponding refractions, c, λ were the velocity and wave length of light in vacuo and α was the rotation per cm. thickness of the layer.

So far we have restricted the discussion to the consideration of the purely physical interaction of light with matter. It would, however, be expected that circularly polarised light would be most effective as an asymmetric force if it could bring about some change in the chemical structure of the compound concerned. It followed that photosensitive racemic mixtures would probably yield the most striking results. This was found to be the case and the process of partially resolving a racemic mixture in this way became known as Asymmetric Photochemical Action (or Asymmetric Photolysis).

Now, according to the Grotthus-Draper Law of Photochemistry (10), light could not initiate chemical reaction unless absorbed by the system. Thus it was of paramount importance to investigate the characteristic absorption of a compound before proceeding with any photochemical work.

The degree of absorption of a compound could be expressed by the well known Lambert-Beer formula, which defined the molecular extinction coefficient of a substance (ε) in terms of the reduction of intensity (from I_o to I) of a parallel beam of monochromatic radiation, the depth of solution (l cm.) and the concentration of the solution (c Moles/litre): $I = I_o . 10^{-\varepsilon c l}$ or $\varepsilon = \frac{\log_{10} I_o/I}{cl}$ (II). Absorption curves were usually constructed by plotting ε against wave length of light.

In general, absorption increased with decreasing wave length but, in many cases, maxima appeared in the curve ('bands'). This 'selective' absorption could be correlated with so-called "chromophoric" groups in the molecule. Thus a band with $\varepsilon_{max} = 40$ at $\lambda_{max} = 3000A$ was characteristic of carbonyl group absorption.

In the case of the absorption of a racemic mixture, if the molecular extinction coefficients of l- and d-enantiomorphs were $\varepsilon^-, \varepsilon^+$ and their concentrations c^-, c^+ respectively, then the fraction of light absorbed by the l-form would be $\frac{\varepsilon^- c^-}{\varepsilon^- c^- + \varepsilon^+ c^+}$. In the case of unpolarised light, both forms would absorb light to the same extent, i.e., $\varepsilon^- = \varepsilon^+$ and so if the compound was photosensitive, preferential decomposition would not occur. However, if it could be shown that, say, left handed circularly polarised light was absorbed to different extents by the enantiomorphs, i.e., $\varepsilon_l^- \neq \varepsilon_l^+$ then it was probable the racemic mixture might be partially resolved.

The first indication that d- and l-forms might absorb circularly polarised light to different extents in this way was the discovery of Circular Dichroism by Cotton in 1896.

Cotton (12) showed that when beams of right and left circularly polarised light passed through an absorption region of potassium chromium d-tartrate, then the former was absorbed more than the latter. This phenomenon he called "Circular Dichroism". If unpolarised or plane polarised light was used he found that the light became elliptically polarised. This could be shown to be a direct consequence of the circular dichroism and the ellipticity (ϕ in radians per cm.) was expressed by a formula analogous to that shown on page 3: $\phi = \frac{\pi}{\lambda}\left(K_l \sim K_r\right)$, K_l, K_r: absorption indices defined by $I = I_0 e^{-\frac{4\pi K l}{\lambda}}$ (II). For practical purposes this formula was usually written:

$\varepsilon_l - \varepsilon_r = \frac{4.\ 0.4343.\ \pi.\ \alpha}{c.\ l.\ 180}$, α: ellipticity (°), l : thickness of solution (cm.), c: concentration (Moles/litre), $\varepsilon_l, \varepsilon_r$: molecular extinction coefficients for left and right handed light, $\varepsilon_l - \varepsilon_r$: circular dichroism.

The curve drawn between circular dichroism (or ellipticity) and wave length had many features in common with the corresponding absorption curve, of which not the least important was that the maxima of both curves occurred at the same wave length. It will be seen later that the ratio of circular dichroism to absorption $\frac{\varepsilon_l - \varepsilon_r}{\varepsilon}$, which was defined by Kuhn (13) to be the "anisotropy factor" (g), was of great importance in connection with asymmetric photolysis.

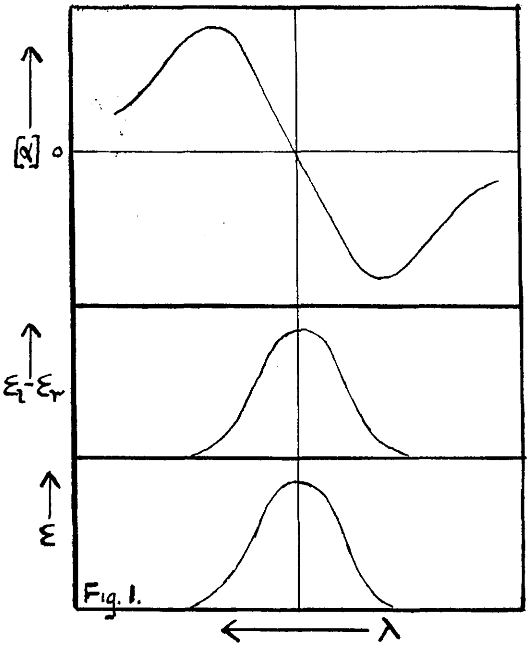


Fig. 1.

An even more striking discovery was the anomalous effect produced by circular dichroism in the rotatory dispersion curve, representing the variation of specific rotation* with wave length. Generally, in a region of transparency, the rotatory dispersion increased with decreasing wave length but the curve was found to pass through two maxima of opposite sense on either side of the dichroic absorption band, while at the absorption maximum, it crossed the axis of zero rotation. It has become customary to refer to the variation of rotations and circular dichroism within an absorption band of this type as the "Cotton Effect"(Fig.I).

It now became apparent that for asymmetric photochemical action to occur in a chemical system, it was necessary (but not sufficient) for one of the reactants of the system to exhibit circular dichroism in one of its absorption bands. One might have expected that this condition would have become "sufficient" if the qualifying restriction of "photosensitivity of the compound" had been appended to it. This would have been incorrect for two reasons. The radiation absorbed and causing photochemical reaction might not lie within a region of circular dichroism. Alternatively, subsidiary reactions might occur without the absorption

---

*Cotton, in his original work, used ordinary rotations and ellipticities instead of specific rotations and circular dichroism respectively, since the concentration of his solution was unknown.

of radiation (the so-called "dark reactions"), which would nullify the resolving effect of the light. Chain reactions (i.e., instantaneous dark reactions causing further decomposition of the starting material) would be the most effective in destroying any asymmetry developed. These reactions, however, could be detected by measuring the Quantum Efficiency of the reaction.

The concept of Quantum Efficiency was based on the Law of Photochemical Equivalence enunciated by Einstein (14) in 1912. This law stated that a photochemical reaction took place only when a molecule absorbed exactly a quantum of energy. The Quantum Efficiency (γ) of the reaction (i.e., the ratio of the number of molecules decomposed to the number of quanta absorbed in the same time) would thus be unity. Subsequent work by Warburg and others (15) showed that γ for many reactions deviated from unity; however, it became apparent that the law probably held for the primary reaction but that secondary reactions or deactivating processes might modify the value of γ. Chain reactions could thus be detected, since γ would be greater than unity.

The three necessary conditions for Asymmetric Photolysis could now be enunciated.

1) The optically active compound must exist in the racemic form.

2) The d- or l-form should exhibit a region of circular

dichroism.

3). The compound must be photosensitive to light within this circular dichroic region.

If the further restriction that γ was close to unity was added, then the four conditions taken conjointly became "sufficient". They did not, however, determine whether the asymmetry produced would be detectable by the instruments at one's disposal. To ensure the optimum results, the enantiomorph of the compound should exhibit the following desirable features (17):

1). High specific rotation.

2). High anisotropy factor (cf. p.6).

3). The destruction of optical activity when photolysed.

The first successful asymmetric photolysis was effected by Kuhn and Braun (16) in 1929 using ethyl α-bromopropionate. More convincing results were obtained by Kuhn and Knopf (17) in the following year. With r-α-azidopropionic dimethylamide, they obtained rotations of -1.04° and 0.78° per dm. for left- and right-handed light respectively. In 1930, also, Mitchell (18) measured the change in rotation throughout the photodecomposition of humulene nitrosite. Maxima of $\pm 0.21^{\circ}$ and $\pm 0.3^{\circ}$ were observed for mercury green and yellow light respectively. These latter experiments were extended to simpler compounds and in 1944, Mitchell and Dawson (19) obtained a rotation of about

$\pm 0.1^\circ$ with β-chloro-β-nitroso $\alpha\delta$-diphenylbutane.

Mention should also be made here of two asymmetric syntheses that have been reported. Karagunis and Drikos (20) successfully chlorinated a triarylmethyl radical in the presence of circularly polarised light to give a partially asymmetric product. Similarly, Davis and Ackermann (21) in 1945, reported a synthesis of ethyl d-tartrate from ethyl fumarate and anhydrous hydrogen peroxide. A rotation of 0.073° was observed in this case. A number of other asymmetric photochemical actions have been recorded by Davis and Heggie (22), Betti and Lucchi (23) and Ghosh (24) but none of these gave results as striking as those already mentioned.

It was thus shown, beyond any doubt, that circularly polarised light could effect asymmetric action. Since Byk (25) had shown that there was a predominance of one kind of polarised light at the surface of the earth, it might well be that such a physical force is the source of at least some of the asymmetry in nature (26).

There is still, however, much scope for new work in this field. The effects observed in all the cases described have never been more than 1.04°, which is subject to quite a high degree of error. Thus it is necessary (in order to obtain a more precise understanding of the subject) to attempt to find larger values, so that equations such as that derived by Kuhn (17) can be verified with some certainty.

It was with such ideas in mind that the present research (27) was embarked upon and, certainly, the remarkable optical properties of parasantonide, which will be described in the next section of the introduction, did suggest that fruitful results would be forthcoming.

The Suitability of Parasantonide for Asymmetric Photolysis.

In 1878, Canizzarro and his coworkers studied a number of compounds related to santonin, a naturally occurring substance extracted from the plant "Artemesia maritama" (28). Several of these substances had large specific rotations. In particular, santonide and parasantonide, both isomers of santonin, possessed values for $[\alpha]^{26}_{D}$ in chloroform of 744.61° and 897.25° respectively. Nasini (in 1883) examined their rotatory dispersions with visible light and observed that the specific rotations in each case increased rapidly with decreasing wave length (29).

It was not however till 1939 that further work was done on the optical rotatory power of these compounds. In that year, Mitchell and Schwarzwald (30) extended measurements into the ultra-violet and obtained some remarkable results. Both d-santonide and d-parasantonide exhibited two well defined maxima in their absorption curves at about 3000 A. and 2350 A., within the first of which, a Cotton Effect could be studied. In the case of santonide the specific rotations reached maxima of $[\alpha] = 25,000^\circ$ and $[\alpha] = -31,000^\circ$ on either side of the band, while for parasantonide the corresponding values were $[\alpha] = 32,000^\circ$ and $[\alpha] = -35,000^\circ$ respectively. These latter maxima represented the highest specific rotations hitherto recorded in homogeneous solution. Circular dichroism values were also high, e.g., $(\varepsilon_l - \varepsilon_r)_{max} = 36.8$ for parasantonide but the corresponding value for the anisotropy factor ($g = 0.037$) was not abnormally large. However, the value was still appreciable and, taken in conjunction with the high rotations, indicated that both compounds would be ideally suitable for asymmetric work. Since parasantonide gave the larger values, it was chosen for further work in this connection.

Carnellutti and Nasini (31) were the first workers to record that parasantonide in chloroform showed a change of rotation when exposed to sunlight. Mitchell and Schwarzwald (loc.cit.) confirmed this observation for alcoholic solutions exposed to radiation from an iron arc. However, it was not known with what specific absorption band (or bands) photochemical action was associated. Nor was it known to what extent optical activity was destroyed by irradiation.

At the time, further investigations were discontinued, since there seemed little likelihood of acquiring parasantonide in the racemic form. However, in 1943 a synthesis of santonin was reported (32), thus indicating that the racemic modification might be accessible.

Before embarking on synthetic work, further experiments were required to determine whether parasantonide satisfied the photochemical conditions for asymmetric photolysis (p.9).

An examination (33) was, first of all, made of the effect of irradiating alcoholic solutions of parasantonide with two different sets of wave-lengths: 1) the total radiation from a mercury vapour lamp, 2) radiation lying within the first absorption band ($\lambda_{max} = 3000$ A.). In the first case, after irradiating for 12 hours, the rotation of the solution fell from an initial value of 11.12° to a small negative value of -1.18°. When only wave-lengths within the absorption band exhibiting circular dichroism were used, the rotation fell from 10.7° to a constant positive value of 1.10°.

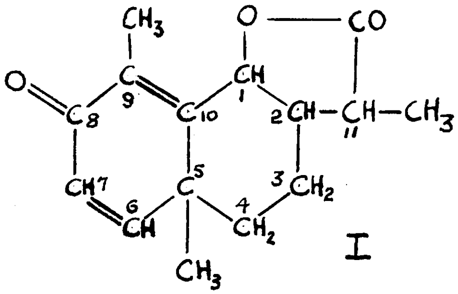
From what has been said, it will be realised that parasantonide in alcoholic solution seemed to be well suited for asymmetric photolysis. The dextro-modification exhibited normal anisotropy factors and exceptionally high specific rotations. Moreover, when photolysed within a region of circular dichroism, a large part of its rotatory power was destroyed.

It was still necessary, however, to establish that no chain or dark reactions occurred. In addition, further information was required on the influence of photolysis on the large Cotton Effect, which is present in parasantonide. Moreover, it was desirable that the photochemistry for both absorption bands should be investigated, since the course of the chemical reaction seemed to be dependent on the absorption band which enveloped the irradiating wave lengths.

These, in brief, were the problems which had to be solved before synthetic work could be commenced. The present work deals with their investigation. However, before giving an account of the results obtained, a general survey of the chemistry of parasantonide is given in the next section.

The Structure of Parasantonide.

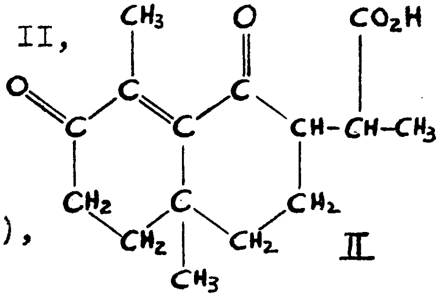
Although it is now over 70 years since parasantonide was first prepared, sufficient work has not yet been carried out to establish its structure. In fact, of those compounds closely related to it, only santonin can be represented by a formula which satisfactorily explains all its properties. The formula for santonin now generally accepted is the one proposed by Clemo, Haworth and Walton in 1929-30 (34) (structure I). Since then a synthesis confirming this structure has been reported (32), but other workers have not been able to reproduce it (p. 48).



I

Parasantonide is an isomer of santonin from which it may be prepared (essentially) in the following way. Santonin is converted into santonic acid by prolonged refluxing with alkali. This acid is then refluxed for 5-6 hours with acetic acid and distilled at 260-300° giving parasantonide. It therefore seems that before any attempt can be made to formulate a structure for parasantonide, the nature of santonic acid must be known.

However, even in this case, there is considerable doubt about the structure. The formula II, which was proposed by Abkin and Medvedev (35), is inconsistent with experimental facts reported by Wedekind and Engel (36), and Schwarzwald (37).


II

Wedekind and Engel showed that the reduction of santonic acid with hydrogen iodide gave a hydrocarbon with the formula $C_{15}H_{26}$. This would indicate that the acid consisted either of two rings with one double bond, or three rings. However, he was unable to detect an ethylenic double bond in santonic acid by catalytic hydrogenation. This suggested that the acid was a tricyclic compound.

Schwarzwald examined the absorption spectrum of the acid in alcohol and has shown that it consists merely of a weak band ($\varepsilon_{max} = 42$) at 2920 A. This is inconsistent with the α-β -unsaturated ketonic system present in formula II. Many α/β -unsaturated ketones have been studied by Woodward (38) and in each case there is a second very intense band ($\varepsilon_{max} \doteq 10,000$) at about 2390 A. The spectrum observed by Schwarzwald is characteristic of an unconjugated ketone. It is reasonable to conclude that in santonic acid there occurs two isolated carbonyl groups in a tricyclic skeleton.

Parasantonide itself is a lactone, since warming with concentrated hydrochloric acid gives parasantonic acid $C_{15}H_{20}O_4$, from which parasantonide can be recovered by the action of acetic anhydride. However, there is no chemical evidence for either a carbonyl or hydroxyl group, which one would expect corresponding to the two carbonyl groups which are known to be present in santonic acid. No oxime can be formed, but treatment with hydroxylamine hydrochloride results in the addition of one molecule of NH_2OH.

The absorption spectrum of parasantonic acid (37) is similar to that of santonic acid, which confirms the presence of at least one carbonyl group. In the case of parasantonide, the band at about 3000 A. is intensified 20 times, and a new intense band appears (ε_{max} = 5000) at 2320 A. Comparison of these two spectra led Mitchell and Schwarzwald (30) to suggest the existence of an eight membered lactone ring in the molecule. The short wave band was assumed to be directly caused by the presence of this ring, while the position of the ring in close proximity to the carbonyl group was concomitant with the intensification of the band at 3000 A. A model has been constructed showing that such an octacyclic ring can be formed without any marked strain (33).

When the spectrum of parasantonide (a) is compared with that of santonin (b), it will be seen that the weak band in the latter has been increased in intensity, while the strong one has been decreased. In addition, both bands (in parasantonide) are shifted to shorter wave lengths. A similar observation has been made by Gillam and West (39). The curve of piperitone (a) is similar to that of santonin since they both contain an α,β-unsaturated carbonyl group. If the abnormalities in the absorption of umbellulone (c) are due to the additional effect of the cyclopropane ring (in "hyperconjugation and cross-conjugation"), then it seems likely that such a ring may also occur in parasantonide. In view of the suggestion already made that santonic acid involves a tricyclic system, it may well be that parasantonide is a tetracyclic compound.

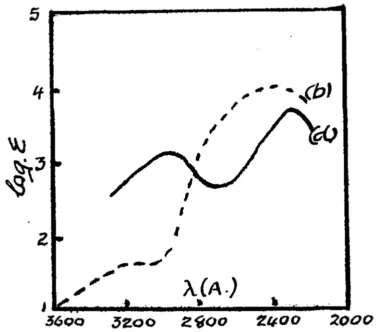


Fig. 2 Absorption Spectra of santonin (b) and parasantonide (d) in alcohol.

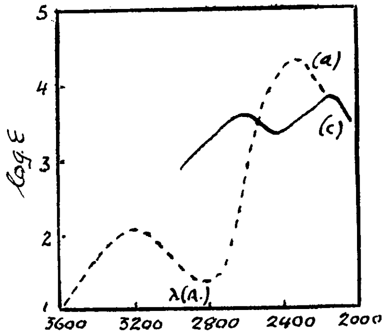
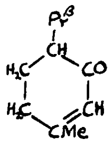
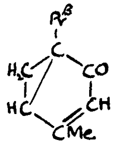


Fig. 3 Absorption Spectra of piperitone (a) and umbellulone (c) in alcohol.



(a)



(c)

The optical rotatory power of a compound may be influenced by many causes of a constitutional character such as conjugation, the presence of closed rings, the lactone ring, or the presence of a large number of asymmetric carbon atoms in the molecule (40). It is unfortunate that more work has not been done on the purely chemical aspects of parasantonide since it is theoretically of interest to know what structural factors are required to give rise to such a large Cotton Effect. The present thesis is submitted as a contribution on the physical side towards an understanding of this problem.

I. MEASUREMENT OF QUANTUM EFFICIENCIES.

Preliminary work had indicated that the irradiation of alcoholic solutions of parasantonide with light of wave lengths approximately equal to 3000 A. effected a photochemical change accompanied by a great reduction in its optical rotatory power. It was now necessary to show that no chain reactions occurred. This could best be done by measurement of the Quantum Efficiency of the reaction (see p.8).

In view of the fact that the nature of the photolyses seemed to be dependent on the band of parasantonide which absorbed the incident radiation (p.14), it was decided to measure the Quantum Efficiency for two different wave lengths corresponding to each of these bands.

A group of mercury lines was employed as the exciting radiation so that the reaction could be completed in a reasonable time. Thus, although the radiation was not strictly monochromatic, the error introduced by this approximation was not serious, since the optical centre could be determined well within the overall experimental error of 5%.

The measurement of the Quantum Efficiency of the reaction involved the estimation both of the amount of compound changed during photolysis (usually about 10% of the initial concentration) and of the energy absorbed during the change. It was found most convenient to measure the latter by irradiating with a source which gave a constant intensity and absorbing completely all the radiation incident on the solution. The amount of energy absorbed would then be the product of the intensity of the source and the period of irradiation.

In order to estimate the degree of decomposition various physical properties have been used in the past, e.g., conductivity, change in absorption of the solution, the volume of gas liberated during the reaction or the pressure developed during the reaction. Owing to the abnormally high optical rotatory power of parasantonide in alcoholic solutions and the marked fall in rotation of such solutions when photolysed with ultra-violet light, it was decided in the present case to use this property to estimate the change in concentration of parasantonide. This assumed, of course, that the specific rotation of alcoholic solutions of parasantonide did not change with concentration. Nasini (41) had already shown that for the range of concentration 1 gm./100 ml. to 5 gm./100 ml. the value of $[\alpha]_D^{20}$ changed by less than 0.5%. So that if an initial concentration of 2 to 3 gm./100 ml. is used, variation of $[\alpha]_D^{20}$ with concentration may be neglected.

Owing to the fact that prolonged exposure to ultraviolet radiation did not reduce the rotation to zero, a correction had to be introduced for the residual rotation. The following formula was developed for this purpose on the assumption that the rate at which the residual rotation was formed was equal to the rate of decomposition of parasantonide. Any deviation from this assumption would in any case be expected to lie well within the experimental error.

$$\alpha_p = \frac{\alpha(\alpha_n - \alpha_\infty)}{(\alpha - \alpha_\infty)}$$

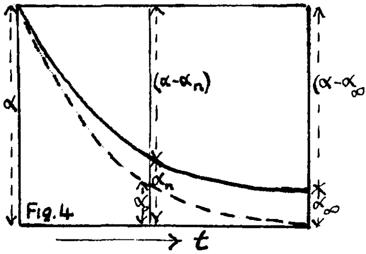


Fig.4

α is the initial rotation

α_n is the rotation after exposure for time t_n.

α_∞ is the final rotation after prolonged exposure.

α_p is the rotation due to parasantonide after time t_n.

Quantum Efficiency for the photochemical decomposition of parasantonide in alcoholic solution with the 3132-2895 A group of wave lengths.

Initial concentration: 3.040 gm./100 ml.

Initial rotation (α) + 18.79°

$$[\alpha]_D^{17} = \frac{18.79 \times 100}{0.75 \times 3.04} = 824^\circ$$

Rotation of solution after exposure for 11 hours: 17.08°

Rotation of solution after prolonged exposure : 1.28°

Corrected rotation $= \dfrac{18.79(17.08 - 1.28)}{(18.79 - 1.28)} = 16.96^\circ$

Final concentration $= \dfrac{16.96}{0.75 \times 824}$: 2.744 gm./100 ml.

Change in concentration : 0.296 gm./100 ml.

Volume of solution : 7.19 ml.

Molecular Weight of parasantonide : 246

Number of Moles decomposed : $\dfrac{0.296 \times 7.19}{246 \times 100}$

: 8.622×10^{-5}

Energy absorbed per sec. : 2.447×10^{-4} cals.

Time of exposure : 11 hours

Total energy absorbed : $2.447 \times 10^{-4} \times 660 \times 60$

: 9.69 cals.

Quantum Efficiency (γ) :

$$= \frac{\text{No. of gm.moles decomposed} \times 2.847 \times 10^8}{\text{Energy absorbed (cals)} \times \lambda\ (\text{A.})}$$

$$= \frac{8.622 \times 10^{-5} \times 2.847 \times 10^8}{9.69 \times 3000}$$

$$= \underline{0.85.}$$

Quantum Efficiency for the photochemical decomposition of parasantonide in alcoholic solution with the 2650-2537 A group of wave lengths.

Initial concentration : 1.740 gm./100 ml.

Initial rotation : 10.96°

$$[\alpha]_D^{17} = \frac{10.96 \times 100}{0.75 \times 1.74} : 840$$

Rotation after exposure for 18½ hours : 10.02°

Rotation after prolonged exposure : -3.18°

Corrected rotation : $\frac{10.96 \times (10.02 + 3.18)}{(10.96 + 3.18)}$: 10.23°

Final concentration : $\frac{10.23}{0.75 \times 840}$: 1.624 gm./100 ml.

Change in concentration : 0.116 gm./100 ml.

Volume of solution : 7.20 ml.

Molecular Weight of parasantonide : 246

Number of Moles decomposed : $\frac{0.116 \times 7.2}{246 \times 100}$

: 3.396×10^{-5}

Energy absorbed per sec. : 1.78×10^{-4} cals

Time of exposure : 18.5 hours

Total energy absorbed : $1.78 \times 10^{-4} \times 18.5 \times 3600$ cals

: 9.42 cals

Quantum Efficiency (γ):

$$: \frac{\text{No. of gm. moles decomposed} \times 2.847 \times 10^8}{\text{Energy absorbed (cals)} \times \lambda\ (\text{A.})}$$

$$: \frac{3.396 \times 10^{-5} \times 2.847 \times 10^8}{9.42 \times 2550}$$

: <u>0.40</u>

Discussion.

Preliminary experiments on the photolysis of para-santonide using different wave lengths had suggested that the course of the reaction depended on the wave lengths chosen. Thus wave lengths within the band (λ_{max} = 3000 A) gave rise to a positive residual rotation whereas the total radiation of the mercury lamp produced a negative rotation (cf. p.14).

The results of Quantum Efficiency measurements seemed to confirm this. Using the longer set of wave lengths a value of 0.85 was obtained. This value was twice as great as that found when shorter wave lengths were used (0.40). A further discussion of the difference in these values will be given in the next section which deals with the optical properties of the irradiated solutions.

However, at this stage it can be said that in the former case the Quantum Efficiency condition for Asymmetric Photolysis has been fulfilled (cf. p.8). The value of 0.85 is sufficiently close to unity to indicate the action involves one molecule per quantum absorbed but that owing to the collision of some excited molecules with other unreactive molecules, some of the energy is dissipated as translational energy. However, this deviation from a value of unity is not serious since γ was sufficiently large to ensure that the asymmetric photolysis experiment would be completed within a reasonable time.

It was possible during the measurement of these Quantum Efficiencies to check whether any appreciable dark reactions involving parasantonide occurred. No such reactions could be detected (p. 63).

In view of the anomalous results encountered, it was thought advisable to investigate the possibility of a photo-oxidation occurring. However, oxygen was shown to have no effect on the reaction (p. 64).

II. MEASUREMENT OF THE ABSORPTION, ROTATORY DISPERSION AND CIRCULAR DICHROISM OF THE IRRADIATED SOLUTIONS.

Various attempts were made at this stage to isolate crystalline products from the irradiated solutions. The resin formed (in both reactions) after evaporating off the alcohol was easily soluble in ether, alcohol and benzene, slightly soluble in petroleum ether but insoluble in water. It failed to crystallise directly from any of these solvents. Refluxing with animal charcoal and rigorous chromatographing using various solvents on an alumina column failed to yield crystals.

Important information could however be obtained about the decomposition products of the reaction by the examination of the absorption, rotatory dispersion and circular dichroism of the fully irradiated solutions.

It was hoped in this way to determine to what extent the Cotton Effect present in parasantonide had been destroyed. Moreover this new set of data was expected to indicate whether the two photochemical reactions, using different groups of wave lengths, gave similar or different products. In addition it was expected that some information might be gained concerning the nature of these products.

(a) Absorption Spectra

(i) Solution from the photolysis using 3132-2895 A.

The absorption of an alcoholic* solution containing 0.029 gm. parasantonide in 100 ml. was first of all measured. The results are shown in Table I and Fig.5. This solution was then irradiated with the 3132-2895 A. group until no further change in rotation could be detected. Absorption measurements were again taken, the results being shown in Table II and Fig.6.

The absorption data for parasantonide agreed well with those found by Schwarzwald (42), who recorded a band at 2980 A with density equal to 1.5 for a concentration of 0.03232 gm./100 ml. The second band, which Schwarzwald found at 2320 A, was not measured in this case, since it required a more dilute solution.

It will be seen that neither of these bands was completely destroyed by the irradiation, but that both still persisted to some extent. The first appeared at 3000 A, and the second at 2350 A. This seemed to suggest that a compound containing a similar chromophoric group to that in parasantonide was one of the decomposition products.

---

* The alcohol for these measurements was specially purified by the method described by Weigert (43).

Table I

Absorption Spectrum of Parasantonide in Alcohol

c : 0.029 gm./100 ml.

l : 1 cm.

Density (Log I_o/I)	λ (A.)		
2.0			2510
1.5			2525
1.3	2990		
1.2	3045	2945	2545
1.1	3080	2920	
1.0	3095	2900	2555
0.9	3110	2875	
0.8	3140	2845	2565
0.7	3155	2825	
0.6	3180	2810	
0.5	3200	2780	2580
0.4	3210	2760	2595
0.3	3215	2725	2635
0.2	3230	2680	
0.1	3250		

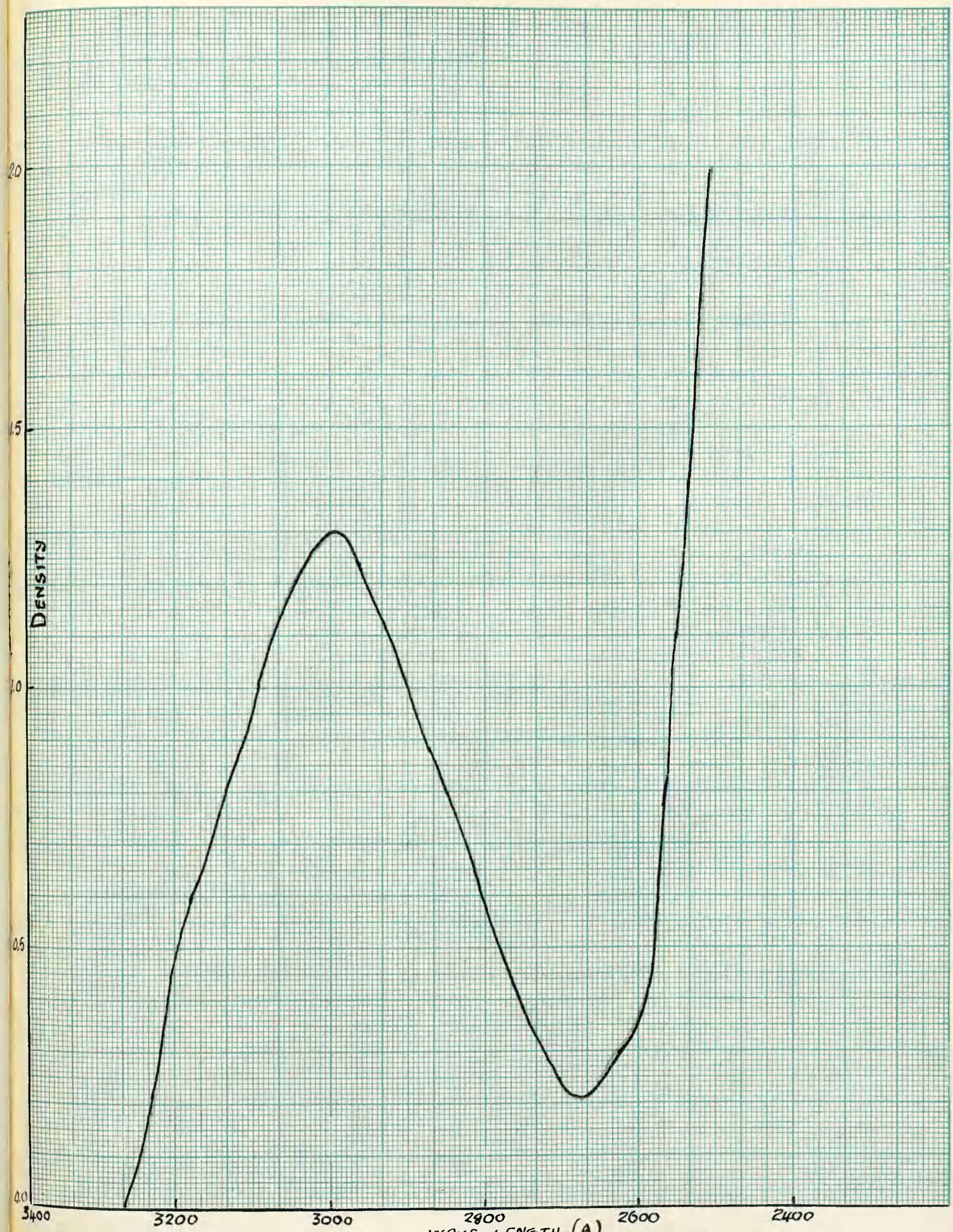


Fig. 5 The Absorption Spectrum of Parasantonide (alcohol)

Table II

Absorption Spectrum of Solution from photolysis using 3132-2895 A.

Concentration of parasantonide before
irradiation : 0.029 gm./100 ml.
l : 1 cm.

Density (Log I_o/I)	λ (A.)		
1.9		2350	
1.8		2375	2325
1.7		2400	2310
1.6		2410	2290
1.5		2420	2265
1.4		2430	2240
1.3		2435	
1.1		2455	
0.9		2480	
0.7		2495	
0.5		2520	
0.4		2550	
0.3	3020	2560	
0.2	3165	2885	
0.1	3250		

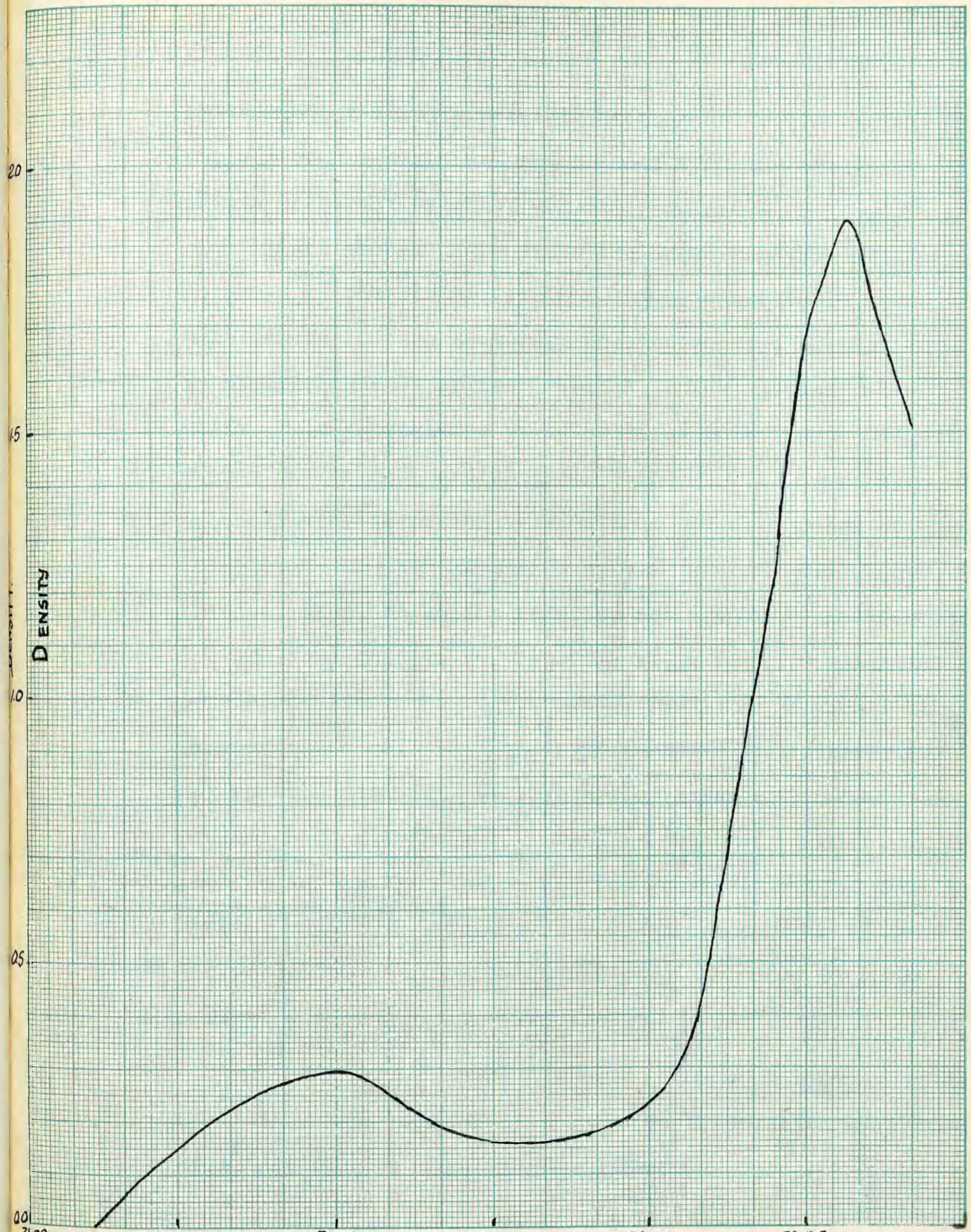


Fig.6 The Absorption Spectrum of Solution from photolysis using 3132-2895 A.

However, it was quite possible, though not probable, that the absorption curve was concomitant with the existence of two different types of absorbing molecule.

Since the solution after prolonged exposure still absorbed in the 3000 A. region, it was conceivable that this was one of the factors producing a value of the Quantum Efficiency of the reaction, which was less than unity. An approximate calculation of this "inner filter" effect can be made and is given below.

If the assumption is made that the absorption of the irradiated solution is caused by one type of molecular species, then, since the relative absorption of parasantonide and product will be proportional to their respective Densities, i.e., the proportion of radiation absorbed by parasantonide will be $\frac{\varepsilon_1 c_1}{\varepsilon_1 c_1 + \varepsilon_2 c_2}$ where $\varepsilon_1, \varepsilon_2$ are the molecular extinction coefficients of parasantonide and product respectively and c_1, c_2 are their concentrations (mol/l) (cf. p.5). Now from the above absorption measurements, $\frac{\varepsilon_1}{\varepsilon_2} = \frac{1.3}{0.3}$ so that for 10% decomposition of parasantonide, the proportion of radiation absorbed by parasantonide will be

$$\frac{1.3 \times 0.9}{1.3 \times 0.9 + 0.3 \times 0.1} = \frac{1.17}{1.20}$$

$$= \underline{0.975}.$$

Thus less than 3% of the incident radiation must have been lost by this inner filter effect.

Complete destruction of the band at λ_{max} = 3000Å in parasantonide would have indicated the annihilation of the Cotton Effect associated with it. The fact that some residual absorption was still present suggested that the Cotton Effect might still be present. Measurements on rotatory dispersion and circular dichroism were thus necessary to confirm this point.

(ii) <u>Solution from the photolysis using 2650-2537 A.</u>

The data recorded in Table III and Fig.7 were obtained from a solution containing 0.0252 gm. parasantonide/100 ml., which was irradiated with the 2650-2537 A group.

It will be seen that the position and intensity of each of the bands were similar to those recorded in the case of longer wave irradiation (see p.29). They now appear at 3020 A and 2310 A respectively. This was the first indication that there was any correspondence between the two photoreactions.

In the case of short wave irradiation, a Quantum Efficiency of 0.40 was found which was only half the value observed for the other photolysis (see p.26). This difference could not be explained by an "inner filter" effect, since it would be necessary, if this were the case, for the intensity of absorption of the products to be about

Table III

Absorption Spectrum of Solution from photolysis using 2650-2537 A.

Concentration of parasantonide before irradiation : 0.0252 gm./100 ml.

l : 1 cm.

Density (Log I_o/I)	λ (A.)			
2.0			2310	
1.9			2340	2270
1.8			2350	2250
1.7			2370	2240
1.6			2380	2220
1.4			2410	
1.2			2430	
1.0			2460	
0.9			2480	
0.8			2490	
0.7			2500	
0.6			2510	
0.5			2520	
0.4	3150	2960	2540	
0.3	3220	2860	2550	
0.2	3280	2700		

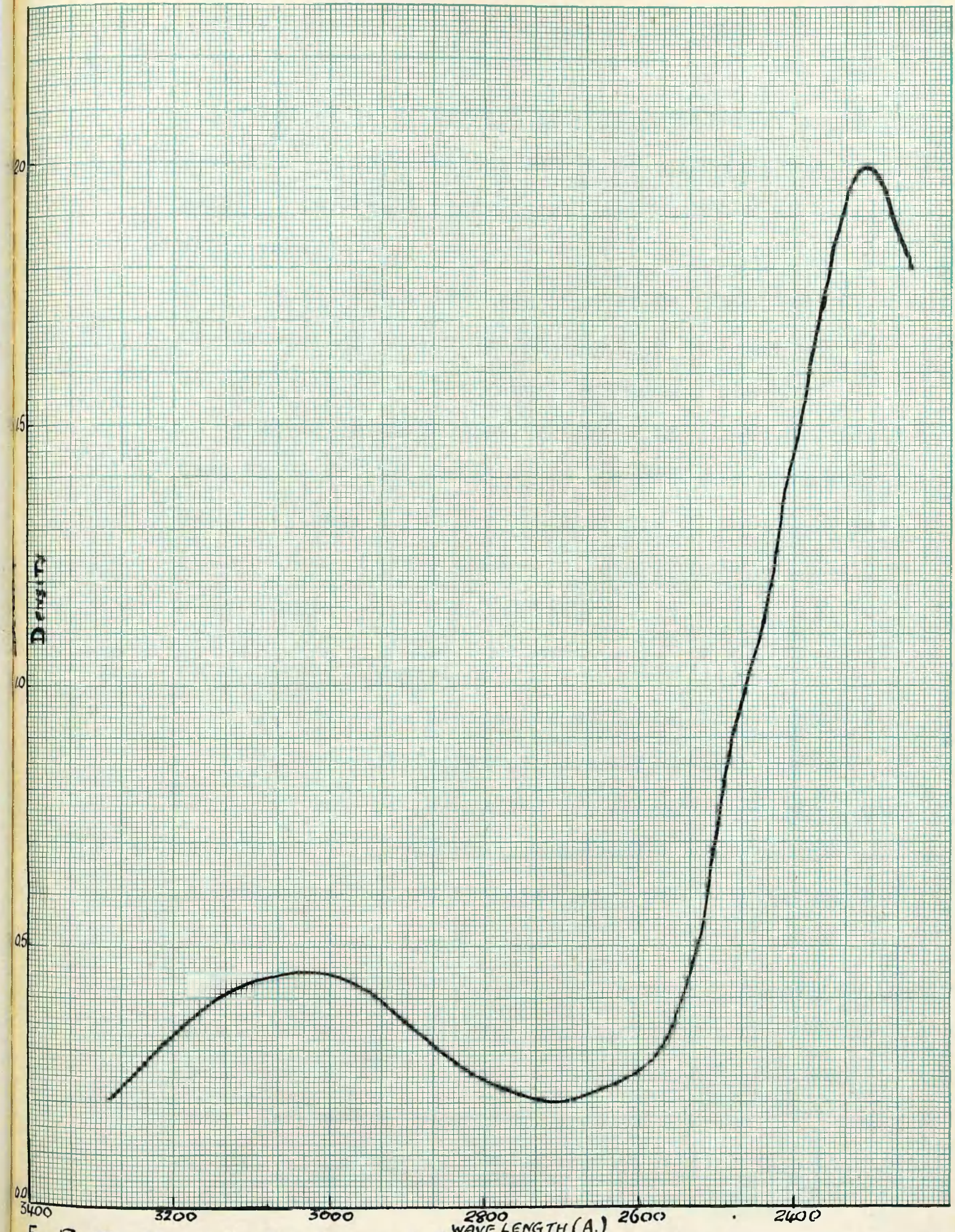


Fig. 7 The Absorption Spectrum of Solution from photolysis using 2650 - 2537 A.

ten times as great as that of parasantonide at about 2550 A., in order to diminish γ to 0.50 (cf. calculation p.32). In actual fact it was less than 30% as intense as in parasantonide.

It therefore remained to attribute the low value of γ to dissipation of the energy in about half the excited molecules by collision with solvent molecules.

These absorption measurements did, however, indicate that there was a similarity in the products obtained in the two reactions. Further confirmation of this fact was gained from rotatory dispersion and circular dichroism measurements.

(b) Rotatory Dispersions.

(i) Solution from the photolysis using 3132-2895 A.

In order to facilitate comparison with the optical rotatory power of parasantonide, specific rotations were calculated, assuming the concentration c to be that of the parasantonide before irradiation. The results are shown in Table IV and Fig. 8.

In the visible, rotations increase with decreasing wave lengths. A positive maximum is reached, however, at about 4200 A, and the zero axis is crossed at 3660 A. The curve then passes through a negative maximum $[\alpha]^{17} = -3400^{\circ}$ at 3280 A, and the axis is again crossed at 3245 A. The rotation increases to another positive maximum $[\alpha]^{17} = 7600^{\circ}$ at 3065 A.

Table IV.

Rotatory Dispersion of Solution from photolysis using 3132-2895 A.

Visual readings c : 1.65 gm./100 ml.
1 : 0.75 dm.

λ(A.)	α	$[\alpha]^{17}$	λ(A.)	α	$[\alpha]^{17}$
7000	0.41°	33.1°	5500	0.77°	62.2°
6500	0.52	42.0	5000	0.94	76.0
5900	0.64	51.7	4750	1.10	88.9

Photographic readings c : 1.65 gm./100 ml.
1 : 0.75 dm.

λ(A.)	α	$[\alpha]^{17}$	λ(A.)	α	$[\alpha]^{17}$
3870	0.80°	64.6°	3620	-1.00°	-80.8°
3685	0.40	32.3	3585	-2.00	-161.6
3660	0.00	0.0	3530	-4.00	-323.2

6 : 1.65 gm./100 ml.
1 : 0.1 dm.

λ(A.)	α	$[\alpha]^{17}$	λ(A.)	α	$[\alpha]^{17}$
3490	-1.00°	-606.0°	3410	-2.20°	-1333°
3460	-1.40	-848.3	3390	-2.60	-1576
3435	-1.80	-1091	3360	-3.40	-2061

Table IV (Continued)

c : 0.165 gm./100 ml.

l :0.1 dm.

λ(A.)	α	$[\alpha]^{17}$	λ(A.)	α	$[\alpha]^{17}$
3320	-0.40°	-2425°	3250	-0.10°	-606.0°
3295	-0.50	-3031	3240	0.10	606.0
3265	-0.50	-3031	3235	0.30	1819
3260	-0.40	-2425	3230	0.50	3031

c : 0.0825 gm./100 ml.

l :0.1 dm.

λ(A.)	α	$[\alpha]^{17}$	λ(A.)	α	$[\alpha]^{17}$
3195	0.40°	4849°	2965	0.50°	6060°
3170	0.50	6060	2945	0.40	4849
3110	0.60	7273	2925	0.30	3637
3010	0.60	7273	2900	0.20	2425

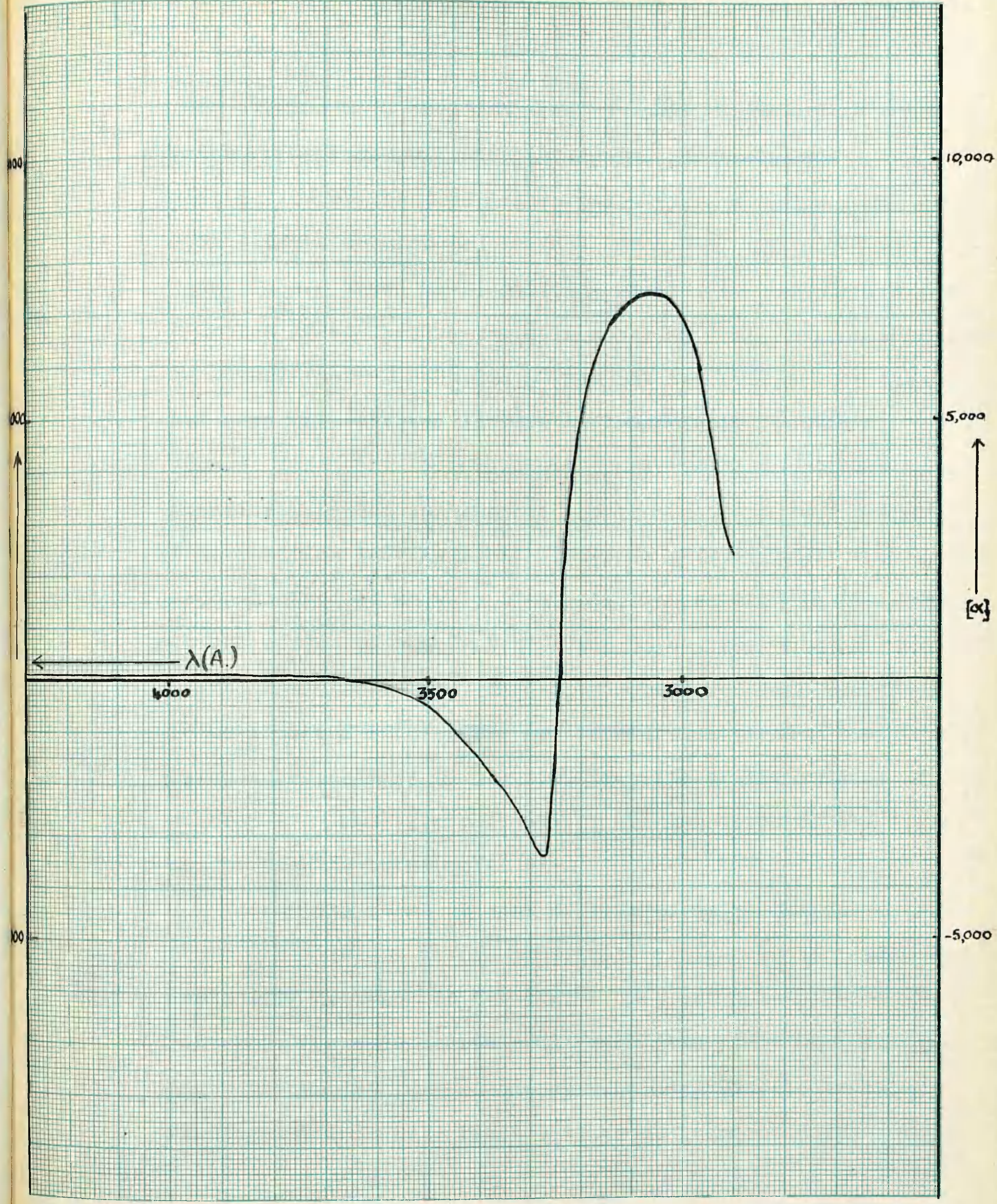


Fig. 8 The Rotatory Dispersion of Solution from photolysis using 3132 - 2895 A.

The results obtained were, in part, unexpected. As has already been indicated, owing to the incomplete destruction of the 3000 A absorption band, a reduced Cotton Effect might be expected (p.33). However, the residual rotation was known to be positive (p.14), so one might expect a Cotton Effect having the same sense as that in parasantonide. In actual fact, the Cotton Effect has not only been reduced, but also inverted and shifted to longer wave lengths. Another important feature about the curve is that there is a positive rotation superimposed on the Cotton Effect proper. This rotation increases with decreasing wave length and accounts for the anomaly of a positive rotation in the visible. At the centre of the Cotton Effect (i.e., the point of inflection on the curve), the superimposed rotation reaches a value of about 2000°, thus the rotatory dispersion curve is moved substantially to the positive side of the axis. If allowance is made for this shift, the magnitude of the Effect can be seen to be ±5500°.

From the point of view of asymmetric photolysis experiments, this result is not important, since rotation measurements will be taken in the visible region. In view of the fact that the curve crosses the zero axis at 3660 A, it might be considered feasible in these experiments to take readings at this wave length, since the corresponding specific rotation of parasantonide is 7200°, while that of the products will be virtually zero.

(ii) Solution from the photolysis using 2650-2537 A.

It will be seen from the results shown in Table V and Fig.9 that the "specific rotations" increase towards the ultra-violet and reach a negative maximum $[\alpha]^{17} = -9270^{\circ}$ at 3295 A. The curve then crosses the axis at 3175 A, and passes through a positive maximum $[\alpha]^{17} = 7500^{\circ}$ at 2800 A.

The similarity between this curve and that in Fig.8 is striking. This time, however, a Cotton Effect having the opposite sense to that of parasantonide was not unexpected, since the residual rotation in the visible was negative (p.14). The curve is again shifted to longer wave lengths (to 3200 A) and is reduced compared with that of parasantonide (cf. p.35).

There are, however, a number of differences which should be noted. Firstly, the magnitude of the Effect is larger in this case (about 8500° compared with 5500°). Moreover the curve is shifted to the negative side of the axis. This indicates the superimposition of a negative rotation, which increases with decreasing wave length. In Fig.8 there is a positive rotation superimposed.

Table V

Rotatory Dispersion of Solution from photolysis using 2650-2537 A.

Visual readings
c : 1.51 gm./100 ml.
l : 0.25 dm.

λ(A.)	α	$[\alpha]^{17}$	λ	α	$[\alpha]^{17}$
7000	-0.42°	-111.3°	5500	-0.84°	-222.5°
6500	-0.48	-127.2	5000	-1.16	-307.3
6000	-0.64	-169.5	4750	-1.47	-389.4

Photographic readings
c : 0.151 gm./100 ml.
l : 0.1 dm.

λ(A.)	α	$[\alpha]^{17}$	λ	α	$[\alpha]^{17}$
3425	-0.60°	-3973°	3345	-1.2°	-7946°
3405	-0.80	-5297	3295	-1.4	-9270
3370	-1.00	-6622			

c : 0.0454 gm./100 ml.
l : 0.1 dm.

λ(A.)	α	$[\alpha]^{17}$	λ	α	$[\alpha]^{17}$
3265	-0.40°	-8810°	3130	0.10°	2202°
3240	-0.30	-6608	3080	0.20	4404
3220	-0.20	-4404	2965	0.30	6608
3195	-0.10	-2202	2625	0.30	6608
3175	0.00	0000	2530	0.20	4404

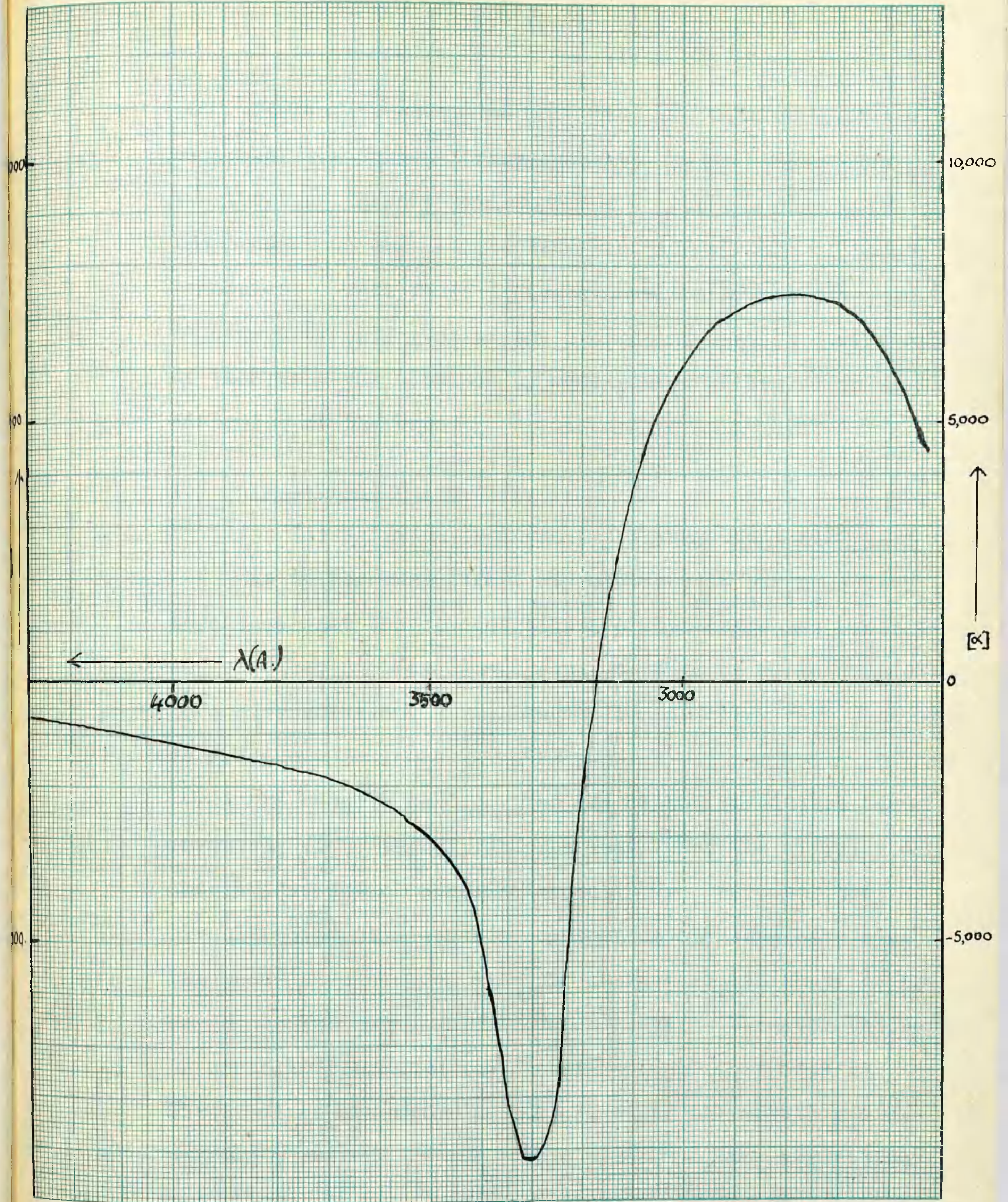


Fig. 9 The Rotatory Dispersion of Solution from photolysis using 2650-2537A.

It is interesting to note that (in both curves) the centre of the Cotton Effect seems to lie at longer wave lengths than that in parasantonide. But the absorption of the products occurs at the same position as that of parasantonide. This would indicate that the Effect observed is caused by only part of the absorption band. Confirmation of this fact was obtained by measurement of the circular dichroism of the band.

(c) Circular Dichroism.

(i) Solution from the photolysis using 3132-2895 A.

As in the measurement of rotations it was necessary to assume that the concentrations of the compounds exhibiting circular dichroism were equal to that of parasantonide before irradiation. The results for the long wave photolysis are shown in Table VI and Fig.10.

The results confirm that the Cotton Effect has been inverted, since the ellipticity (and hence the circular dichroism) is now of opposite sense. The fact that the circular dichroism curve is steeper on the long wave side of the band is consistent with the characteristic shape of the corresponding rotatory dispersion curve. Moreover the head of circular dichroism now appears at 3210 A. This is identical to the point of inflection of the rotatory dispersion curve but is not at the maximum of the absorption band (3000 A). This suggests that at least two substances

Table VI.

Circular Dichroism of Solution from photolysis using 3132 - 2895 A.

c : 0.825 gm./litre; M : 246; l : 1 cm.

λ (A.)	α	$\varepsilon_r - \varepsilon_l$	ε	$g = \frac{\varepsilon_r - \varepsilon_l}{\varepsilon}$
3320	-0.2°	1.81		
3295	-0.3	2.71	32.8	0.083
3275	-0.4	3.62	65.6	0.055
3260	-0.5	4.52	82.0	0.055
3160	-0.5	4.52	164.0	0.028
3080	-0.4	3.62	230.6	0.016
2950	-0.3	2.71	213.2	0.013
2740	-0.2	1.81	196.8	0.009

Table VII.

Circular Dichroism of Solution from photolysis using 2650 - 2537 A.

c : 0.660 gm./litre; M : 246; l : 1 cm.

λ (A.)	α	$\varepsilon_r - \varepsilon_l$	ε	$g = \frac{\varepsilon_r - \varepsilon_l}{\varepsilon}$
3360	-0.1°	1.13		
3310	-0.2	2.26		
3305	-0.3	3.39		
3295	-0.4	4.52		
3285	-0.5	5.65	195	0.029
3270	-0.6	6.78	225	0.030
3220	-0.6	6.78	292	0.023
3210	-0.5	5.65	302	0.019
3180	-0.4	4.52	341	0.013
3130	-0.3	3.39	410	0.008
3050	-0.2	2.26	438	0.005

Fig. 10.

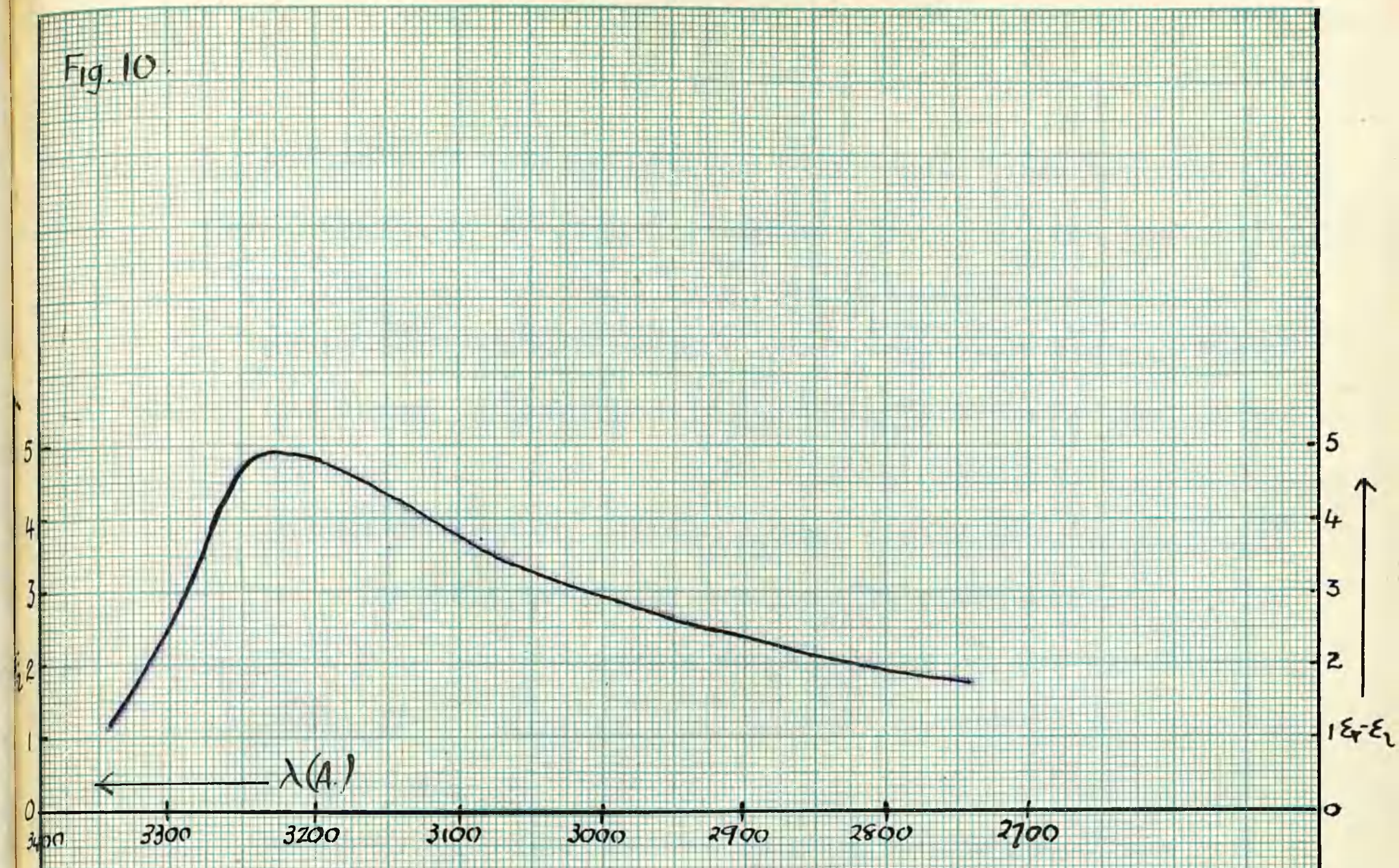


Fig. 11

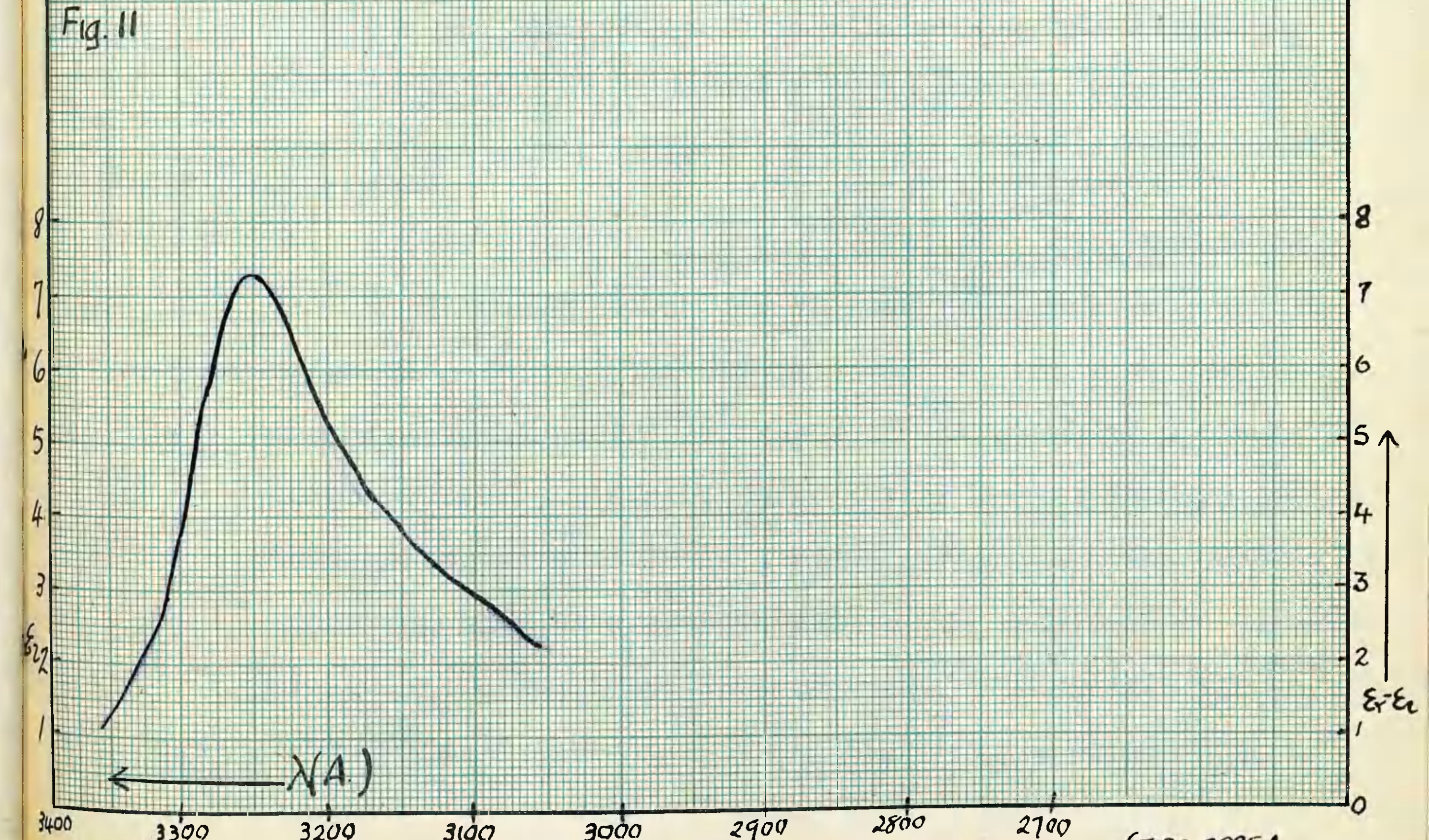


Fig 10 }
Fig 11 } THE CIRCULAR DICHROISM of SOLUTION from photolysis using { 3132-2895A.
{ 2650-2537A.

absorb independently in the same region 2800-3400 A., one of which has a head of circular dichroism (and absorption) at 3210 A. Alternatively, the selective absorption may be entirely due to one substance, the band comprising two components, of which only the long wave component exhibits circular dichroism. This phenomenon appears in the Cotton Effect of a number of compounds, including camphor (44).

The dissymmetry of the band is also manifest in the values of the anisotropy factor g, which are appended to Table VI. They are not constant throughout the band but have a value of 0.055 at 3260 A. This is interesting because, although the values of circular dichroism are much smaller than those of parasantonide, the anisotropy factors are of the same order of magnitude, especially at the maximum of circular dichroism.

(ii) <u>Solution from the photolysis using 2650-2537 A.</u>

The circular dichroism in this case reaches a maximum value of ($\varepsilon_r - \varepsilon_l$) = 7.30 at 3245 A. (see Table VII, Fig.11). This value is closer to the point of inflection on the rotatory dispersion curve than to the maximum of the absorption curve (3000 A). This agrees with the observations for long wave irradiation. The magnitude of circular dichroism in this case is larger and so parallels the larger effect noticed in the rotatory dispersion curve (p.39).

The anisotropy values are again comparable with those of parasantonide.

The General Significance of the Measurements on the Cotton Effect.

It can now be said that the large Cotton Effect of parasantonide is almost destroyed by irradiation. This indicates that the main centre of optical activity in that compound is no longer present. From the point of view of asymmetric photolysis experiments, any optical activity remaining may be considered negligible (p.38).

A point of considerable importance in connection with these asymmetric experiments is that the decomposition products are entirely resinous, so that parasantonide may be easily separated from any contaminating products by crystallisation. This fact was noted by Carnellutti and Nasini (31) in their original studies.

Owing to the insufficient knowledge about the structure and chemistry of parasantonide, little can be said about the types of chemical reactions involved. What one can deduce from these investigations is whether the reactions with different wave lengths produce characteristic variations in the products obtained. Preliminary experiments indicated that, in fact, two different sets of products were formed in each case, since a positive residual rotation was observed when long waves were used, while with shorter wave lengths a negative rotation was obtained (see p.14). The investigation of the respective Cotton Effects has shown that such observations were fortuitous and that the curves obtained in each case differ, not in type, but only in degree. The difference in the two Effects may be attributed to the different amounts of products formed.

It is pertinent to enquire, at this stage, whether these results give any indication of the type of reaction product to expect. The absorption spectra suggest that some compound is present, which contains a similar chromophore to that in parasantonide. However, the Cotton Effect was centred at about 3200 A., which indicated the presence of a weak band at that wave length. Such a band, in conjunction with the intense band at 2300 A., is characteristic of an $\alpha\beta$ -unsaturated carbonyl group (cf. p. 5I).

III. SOME ATTEMPTS TO PREPARE RACEMIC PARASANTONIDE.

For asymmetric photochemical experiments with parasantonide, the racemic form is required. Up till this stage, all the work had been carried out with the dextro-form, but it was now necessary to consider the various methods which might yield parasantonide in the racemic form.

There were three possible ways of approach.

(1) Racemisation of the dextro-form.

(2) Preparation from the racemic form of a closely related compound.

(3) Synthesis.

Each of these alternatives was considered in turn.

(1) The structure of parasantonide is not yet known but probably involves about three asymmetric carbon atoms embedded in a three or four ring system. It did not seem likely that ordinary racemising methods would be applicable in this case.

(2) Parasantonide is prepared from santonin by the method indicated on page 16. It will be seen that in order to obtain the racemic form, it is necessary to prepare inactive santonin or santonic acid. No methods are known for producing either of these compounds in the racemic form from related substances but there did appear to be one possible way in which r-santonic acid might be prepared.

Santonic acid is known to be a diketo acid. If it is assumed that the new $>C = 0$ group is created from the I-hydroxyl group which exists in santoninic acid (corresponding to the lactone santonin), then it seemed likely that by the prolonged action of alkali, the hydrogen atoms on carbon atoms 2 and II would tend to migrate, since they were adjacent to $>C = 0$ groups. Thus the stereochemical arrangement of the resulting santonic acid would be controlled probably by the inductive dissymmetry effect of the carbon atom 5 on the rest of the molecule.

Now the enantiomorph of santonin is not known but another l-rotatory isomer has been described by Clemo (45) and called β-santonin. It seemed probable that if the configuration of the carbon atom 5 in β-santonin was opposite to that in santonin itself, one might expect that the prolonged action of alkali would yield d-santonic acid.

In point of fact, it was found that the acid obtained was practically insoluble in ether (unlike l-santonic acid) and had a melting point of $163-166^{\circ}$ which was depressed by the addition of either l-santonin or l-santonic acid. It was not the enantiomorph of the latter since $[\alpha]_D^{17} = -103^{\circ}$ in chloroform, c : 2.36 ($[\alpha]_D^{17}$ for l-santonic acid : -75°).

(3) Synthesis.

The complete synthesis of parasantonide involves in fact the synthesis of santonin. Such a synthesis has been described by Paranjape, Phalnikar, Bhide and Nargund (32), who claimed that their product was optically active. If this is true, then this synthesis would not yield the required racemic parasantonide, so would be of little use in the present case. However, considerable doubt has been shed on the reliability of these claims, since it has been found impossible to produce similar asymmetry in analogous compounds (46). This furnished sufficient justification in attempting to reproduce Paranjape's work in the hope that the product would be inactive.(cf. p. 50).

Morrison (47) improved the first stage of the synthesis by replacing sodium amalgam reduction by alkaline hydrogenation using a Raney nickel catalyst. Almost theoretical yields of dihydroresorcinol (IV) could be obtained from resorcinol (III) in this way. The conversion of the former into 3-chloro- Δ^2 -cyclohexene-1-one (V) and the subsequent condensation with methyl malonic ester has been effected by several workers (48) but hydrolysis and attempted lactonisation led to complete decarboxylation with the formation of 3-ethyl- Δ^2 -cyclohexene-1-one (VA).

It seemed likely that this method would not yield fruitful results so it was decided to attempt to synthesise the ketolactone (VI) by an alternative route.

After preliminary methylation of the dihydroresorcinol with diazomethane, a Reformatsky reaction was effected with ethyl α-bromopropionate in the hope that dehydration of the resultant hydroxyester (X) would yield the $\alpha{\cdot}\beta$-unsaturated ester (XI). In actual fact, water was eliminated inside the ring yielding the isomeric $\alpha{\cdot}\beta$-unsaturated ketone (XIV). This structure was established by two facts.

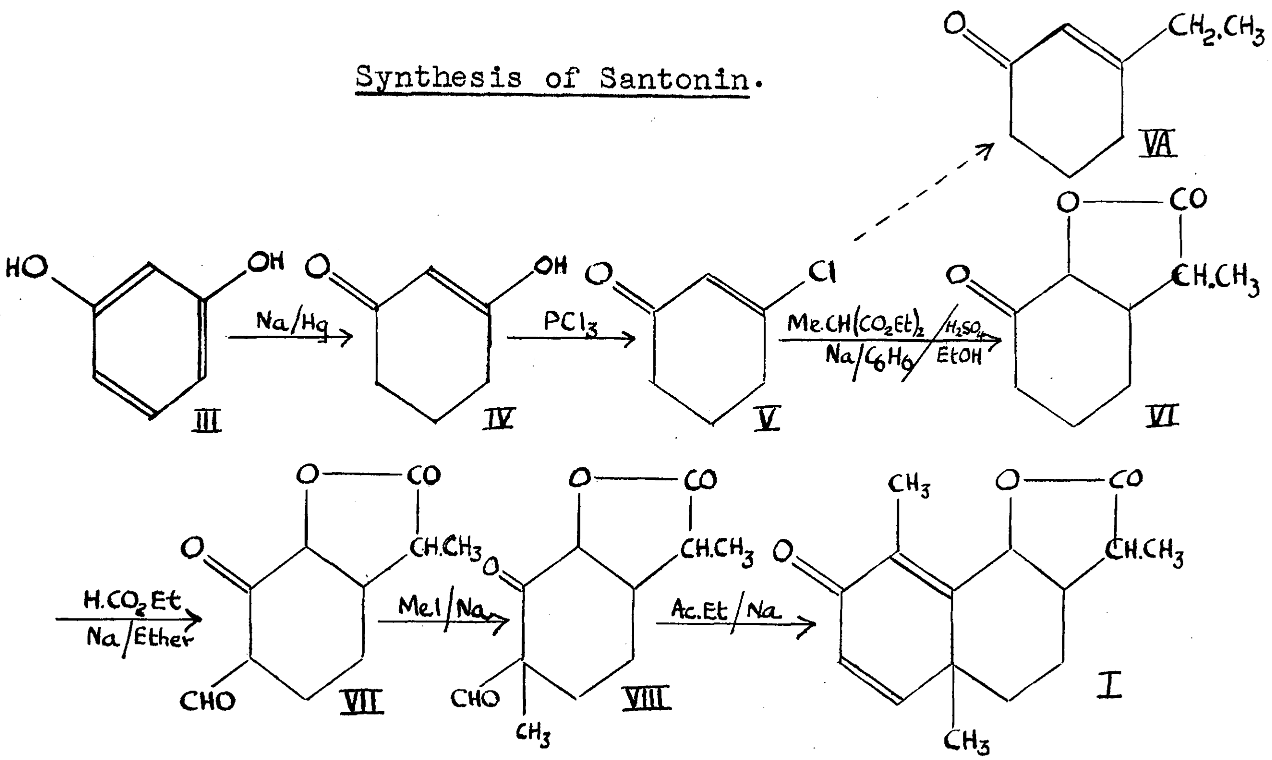
1) It was shown to be identical with a product isolated by Carruthers from the condensation of 3 chloro-Δ^2-cyclohexene-1-one (48) with methyl malonic ester in alcoholic solution.

2) The absorption spectrum of the compound in hexane had two distinct characteristics (Fig.12),

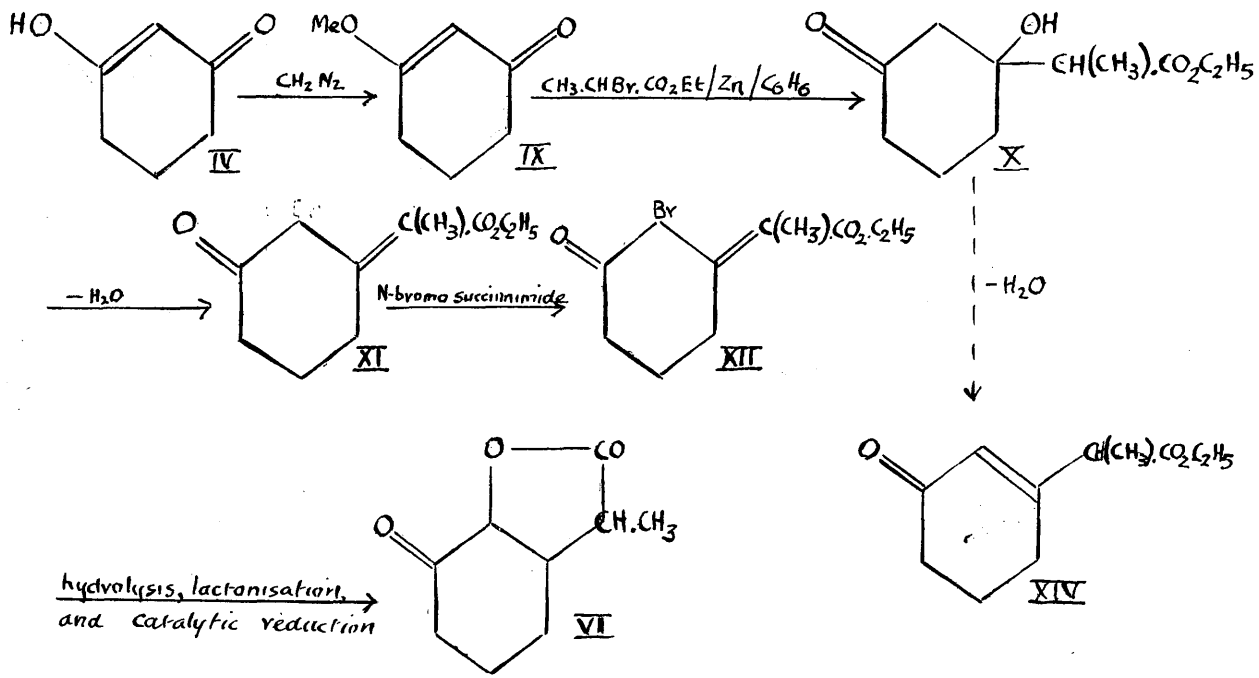
a) an intense band (log ε_{max} = 4) at λ_{max} = 2300 A.,

b) a "step out" corresponding to a weak band (log ε_{max} = 1.5) at λ_{max} = 3200 A.

Synthesis of Santonin.



Alternative Route to VI.



These features indicated the presence of an $\alpha:\beta$ -unsaturated carbonyl group.

An $\alpha:\beta$ -unsaturated ester would exhibit an intense band (log ε_{max} = 4) at about 2100 A, and a weak band at 2500 A. In addition, the carbonyl group would contribute a weak absorption in the 2800-3000 A region. The overall effect would be to produce one intense band at 2100 A which would spread over to the 3000 A region without possessing any perceptible subsidiary bands. An analogous case to this has been examined by Woodward (49).

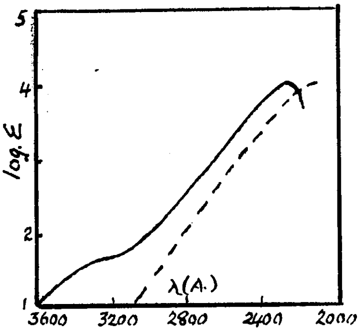


Fig. 12 Absorption Spectrum of Reformatsky product (–) and hypothetical curve for corresponding α-β unsaturated ester (- - -).

Having established the position of the double bond, attempts were made to close the lactone ring by several methods.

1). Addition of bromine to the double bond followed by hydrolysis using alcoholic potash, or boiling water (50).

2). Preparation of the dibromide followed by acetylation and hydrolysis.

3). Oxidation using hydrogen peroxide and a trace of osmium tetroxide (51) followed by hydrolysis.

In none of these cases could a crystalline product be isolated nor a semicarbazone derivative formed.

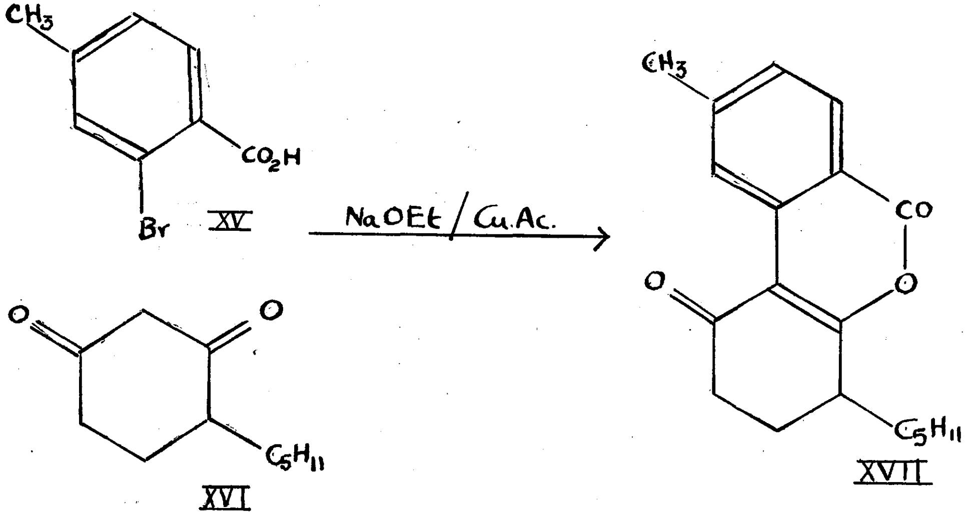
Alternative method of approach. (cf.p.53).

A brief account will be given here of another attempt to synthesise the lactone (VI). This was based on analogy with a synthesis of the pyrone (XVII) by Adams and Baker (52). These authors condensed 4-methyl 2-bromobenzoic acid (XV) with 4 n-amyl dihydroresorcinol (XVI) in the presence of alcoholic sodium ethoxide and a trace of cupric acetate. They obtained a yield of 80% of a mixture of the two possible geometrical isomers. It was proposed to attempt to effect a similar condensation between 1,2 cyclohexanedione (XVIII) and α-bromopropionic acid (XIX).

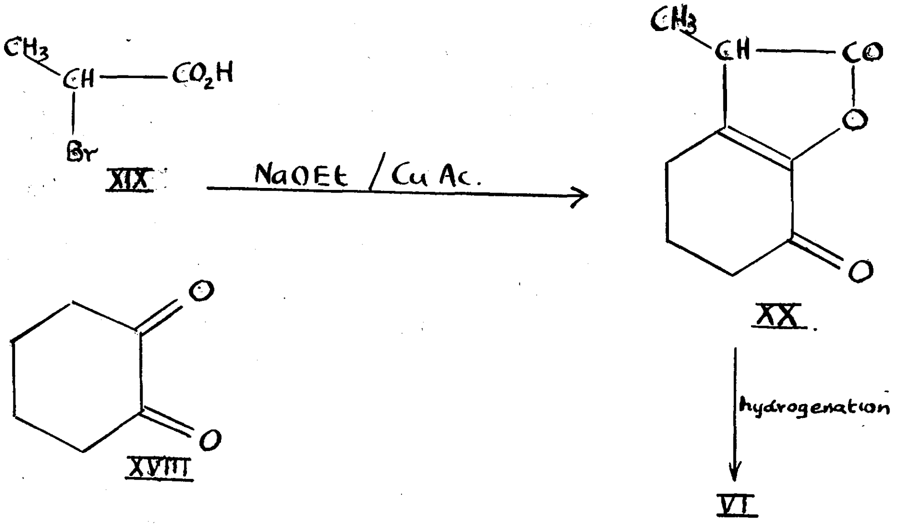
Two organic products were isolated. One was a liquid collected between 85-100°/15 mm. which possessed too low a boiling point to be the required product. The second distilled at 140-150°/3 mm. which partly solidified on standing but gave no ketonic reactions. This latter compound possessed a fairly strong absorption band (ε_{max} = 1300) at approximately 2700 A, suggesting that it was probably benzenoid in character.

While this work was in progress, Cocker and Hornsby (53) published a paper which indicated that $\alpha:\beta$-unsaturated lactones of the type (XX) were highly resistant to catalytic hydrogenation. In view of this fact and also the difficulty in obtaining the required lactone by the above method, the work was discontinued at this stage.

The Condensation of 4-n-amyldihydroresorcinol (XVI) with 4-methyl 2-bromobenzoic acid (XV). (Adams & Baker).



Condensation of 1,2 cyclohexanedione (XVIII) with α-bromopropionic acid (XIX).



EXPERIMENTAL

1. Preparation of Parasantonide.

(a) Preparation of Santonic Acid from Santonin (35).

Powdered barium hydroxide (100 gm.) was refluxed with carbon dioxide free water (100 cc.) for 1 hour in a 500 cc. flask. Santonin (20 gm.) was added and refluxing was continued in the absence of light for 10 hours.

The mixture was then cooled, diluted with water (25 cc.) and shaken with concentrated hydrochloric acid (80 cc.) until acid to litmus. The precipitated santonic acid was then extracted with ether (150 cc.) until the extract was colourless. After evaporation of the ether, the residue was refluxed for ten minutes in alcoholic solution with animal charcoal and subsequently recrystallised from 60% alcohol. M.p. 162-163° (Lit. 163°). Yield 10 gm. (Lit. 55%).

(b) Preparation of Parasantonide from Santonic Acid.

Parasantonide was prepared by a modification of that first employed by Canizzarro and Valente (54).

Santonic acid (10 gm.) was refluxed with glacial acetic acid (50 ml.) for 5 hours. The solution was then treated in five portions, the first of which was transferred to a small distilling flask with the side arm fitting directly into a receiver and the acetic acid was removed under reduced pressure. The apparatus was then filled with nitrogen and the flask heated slowly to between 260° and 300° on a metal bath, with nitrogen bubbling through the viscous mass, which partly distilled. On reducing the pressure, a further amount of material passed into the receiver. The entire distillate was dissolved in ether, washed with dilute sodium carbonate solution, and dried with Na_2SO_4. This procedure was repeated for the other four portions, and the combined amounts of impure parasantonide, obtained on distilling off the ether, were crystallised from ether-light petroleum, and finally from light petroleum alone. M.p. 110° (Lit. 110.5°). About ten crystallisations were necessary so that the yield of crude parasantonide (about 25%) was much reduced.

2. Determination of the Concentration of Parasantonide required for Quantum Efficiency Measurements.

The concentration of parasantonide was conditioned by several factors. No radiation should be transmitted by the solution at the end of the experiment so that 90% of the initial concentration should absorb all the incident radiation. Moreover, the concentration should be as low as possible so that the reaction may be completed in the shortest possible time. If the concentration is too high only those molecules at the surface of the cell nearest to the light source would be affected and thus there would be a greater need for efficient stirring.

The optimum concentration to be employed was found by constructing a Hartley absorption curve (see Fig.13). It will be seen that a 2% solution (1 cm.) is sufficient to absorb the 2650-2537 A group, but transmits a little of the 3342 A line. In order to ensure absorption of this wave length, a 3% solution was used for the 3132-2895 A group.

3. Source of Radiation and Light Filters.

A Hewittic vacuum mercury-vapour lamp running at 4.5 amp. was employed as a source of ultra-violet radiation in all cases. The two different groups of wave lengths were isolated by interposing between lamp and reaction cell various sets of filters (55).

In determining γ with wave lengths within the first band, the infra-red, visible and ultra-violet radiation down to and including the 3342 A line were absorbed by a filter consisting of 215 gm. of nickel sulphate ($NiSO_4$, $7H_2O$) and 60 gm. of cobalt sulphate ($CoSO_4$, $7H_2O$) in 600 ml. aqueous solution. This filter was contained in a 500 ml. fused silica flask, which also acted as a condensing lens.

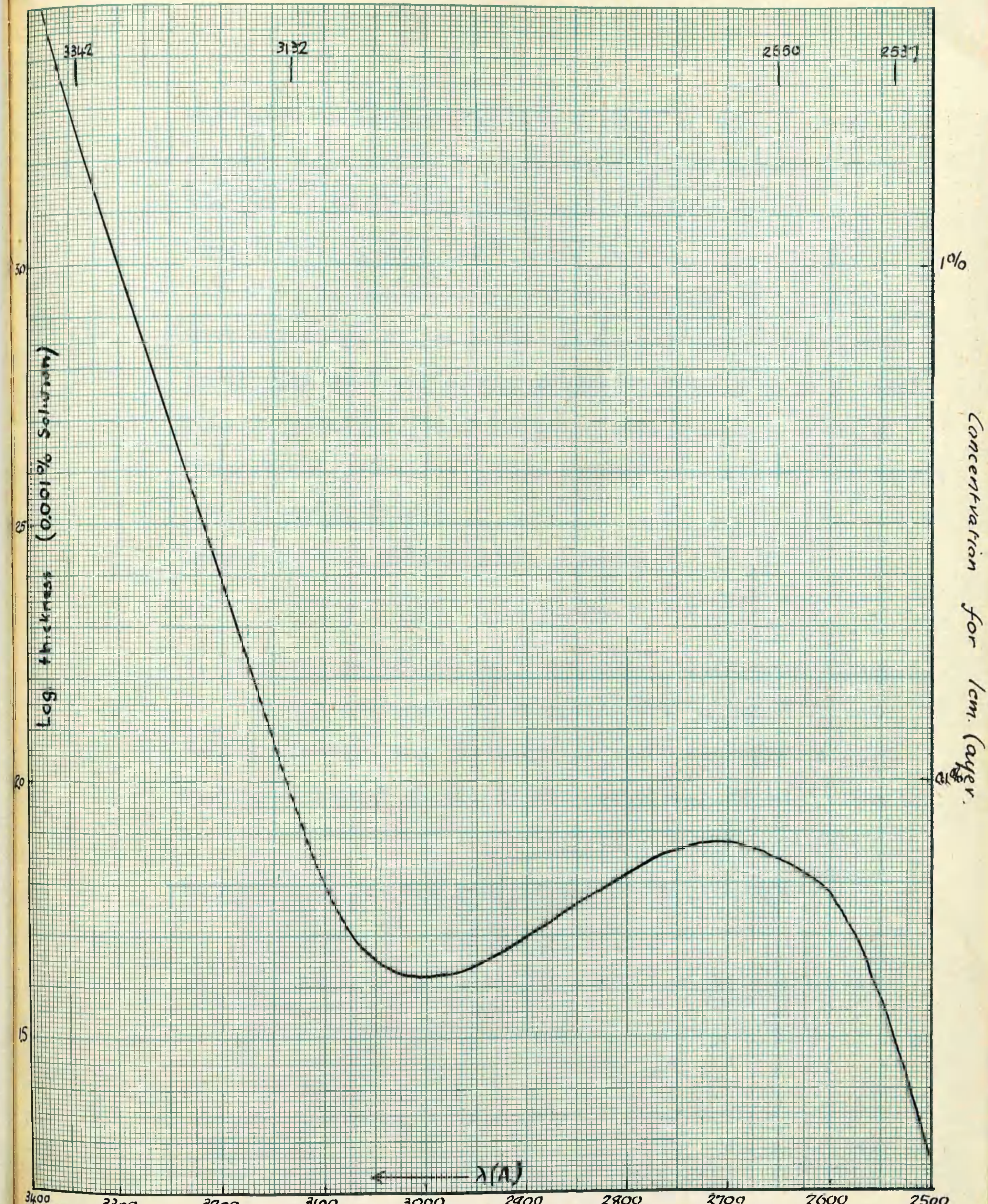


Fig. 13. Absorption Spectrum of Parasantonide in Alcohol (Hartley Method)

When used in conjunction with a sheet of mica (.05 mm. thick), which absorbed ultra-violet light beyond 2800 A, the following mercury lines were transmitted:-
3132 (strong), 3022, 2967, 2920 (weak), 2895 (weak).

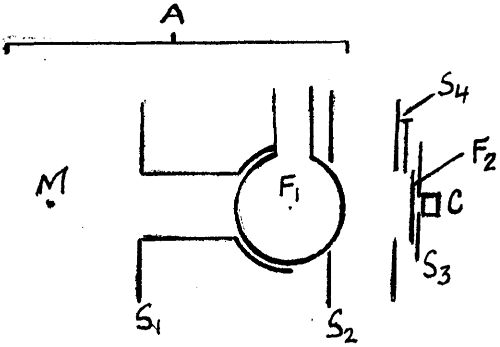
For the second band, a filter combination similar to that suggested by Bowen (55) was used, viz., nickel sulphate (145 gm.) and cobalt sulphate (71.5 gm.) in 1 litre aqueous solution, in conjunction with 3 cm. chlorine at atmospheric pressure. This combination transmitted mainly the following lines:
2655 (strong), 2535-7 (strong), 2482.

4. Standardization of the Thermopile-Galvanometer System.

Energy measurements were made with a large surface Moll thermopile and galvanometer which was calibrated against a Hefner candle by the method suggested by Gerlach(56).

5. Apparatus for the Measurement of Quantum Efficiency in the Ultra-Violet.

(a) Apparatus using 3132-2895 A group of Wave Lengths (Fig.14).



M : Mercury-Vapour lamp.
F_1 : Nickel Sulphate, Cobalt Sulphate filter contained in a 500 ml. fused silica flask.
F_2 : Sheet of Mica.
C : Cell
S_1, S_2, S_3, S_4 : Stops. In S_1 was fitted a cylinder of metal, spherically shaped at the end to fit close to the flask. S_4 is fitted with a shutter.

Radiation from the mercury-vapour lamp was condensed by the 500 ml. fused silica flask containing the solution filter placed 20 cm. from the lamp. The stop S_3 was positioned where a sharp image of the lamp was formed. Behind this stop was fixed a sheet of mica (0.05 mm.), while in front of it was placed the reaction cell. This cell consisted of a fused silica tube of square section (7.5 x 1 x 1 cm.) with side tube for filling. A small piece of glass tubing about 1 cm. long was inserted for stirring and glass ends of good optical quality were cemented in position.

Further blackened stops (S_1, S_2, S_4) were interposed at various points of the apparatus. The section marked A was housed in a black box to minimise the amount of stray light.

Procedure and Calculation of the Energy Absorbed per second.

The intensity of the radiating system was first of all determined.

Before the radiation from the mercury lamp entered the cell it passed through a small rectangular slit (5.5 x 0.5 cm.)

in the brass stop S_3. The measurement of this slit was made precisely since it corresponded to the area of solution irradiated. Fitted into the thermopile was a fused silica window held in position by a black metal disc. A square slit was cut in this disc (1.8 x 1.8 cm.) so that readings could be taken for three positions along the slit S_3. Thus the average of these readings represented the mean intensity of light over an area of 0.9 sq.cm. When the thermopile-galvanometer system was standardised, the silica window was omitted and a stop inserted so that only an area of 0.9 sq.cm. was exposed.

An example is here given of the calculation of the intensity using the 3132-2895 A wave length group.

Deflections recorded for three positions along the slit at commencement of experiment : 9.2, 13.75, 9.6 cm.

Total deflection : 32.55 cm.

Similar measurements made at end of experiment : 9.32, 14.05, 9.5 cm.

Total deflection : 32.87 cm.

Mean total deflection : 32.71 cm.

Deflection when Hefner candle was placed at a distance of 1 metre : 2.88 cm.

Gerlach showed that under these conditions the amount of energy falling on the thermopile was 2.25×10^{-5} cals/per sq.cm. per sec.

Intensity at inner surface of cell when it does not contain any solution : $\frac{32.71 \times 2.25 \times 10^{-5} \times 5.5 \times 0.5}{3 \times 2.88}$ cals. per sec.

A further correction had to be made since in the measurement of the intensity of the mercury lamp, a silica window was used. Thus when a solution filled the cell, one of the quartz-air interfaces was eliminated. The reflections thus were decreased, since those at a quartz-solution surface could be neglected. The losses due to reflection in such a case are usually taken as 4.5% - a value which may be calculated from Fresnel's Reflection Law (57).

Thus the energy absorbed by the solution would be:

$$\frac{32.71 \times 2.25 \times 10^{-5} \times 0.5 \times 5.5 \times 1.045}{3 \times 2.88} \text{ cals. per sec.}$$

and since the period of exposure was 11 hours, the total energy absorbed would be

$$\frac{32.71 \times 2.25 \times 10^{-5} \times 5.5 \times 0.5 \times 1.045 \times 11 \times 3600}{3 \times 2.88} \text{ cals.}$$

= 9.69 cals.

The intensity of the radiating system was determined only after the mercury lamp had attained a condition of constant energy output. This usually occurred after about ½ hour running. Meanwhile 10 ml. of an alcoholic solution of parasantonide had been prepared and weighed.

The cell was also weighed and filled with solution. The weight of the cell was again measured and so the volume of liquid in it could be found.

The rotation of the solution was next determined. Polarimetric measurements were always made at room temperature (17^{o}) with sodium light (5893 A).

The cell was then placed in position behind the stop S_3 and irradiation continued for 11 hours. Periodically the cell was shaken to ensure thorough mixing of the solution. At the conclusion of the experiment, the rotation of the solution was again taken. After the quartz condensing flask had cooled, another reading of the intensity was obtained. This usually differed from the initial measurement by less than 1%, as is indicated in the above calculation.

It was still necessary to determine the rotation after prolonged exposure to the same radiation. However, since the nickel sulphate-cobalt sulphate filter did not appreciably affect the wave lengths of radiation being absorbed by the solution, it was dispensed with and was replaced by a water filter. A fresh solution of parasantonide was prepared with the same concentration as that used in the Quantum Efficiency experiment and was irradiated as before. Polarimetric readings were taken periodically and irradiation continued until no further change in rotation could be observed. The results of this experiment are shown in Table VIII and Fig.15.

Table VIII

α_D for solution during the irradiation with 3132-2895 A.

c : 3.040 gm./100 ml.   l : 0.75 dm.

α_D	18.79°	10.72°	6.78°	3.18°	2.04°	1.68°
Time (hours)	0.0	10.5	18.5	33.5	48.0	62.5
α_D	1.54°	1.48°	1.44°	1.30°	1.28°	1.28°
Time	77.0	92.0	106.5	135.5	150.0	165.0

Table IX

α_D for solution during the irradiation with 2650-2537 A.

c : 1.74 g./100 ml.   l : 0.75 dm.

α_D	10.96°	8.58°	6.73°	3.70°	1.68°	0.30°
Time (hours)	0.0	8.0	16.0	32.0	46.0	57.0
α_D	-0.52°	-1.92°	-2.60°	-3.02°	-3.18°	-3.18°
Time	65.0	89.0	109.0	133.0	149.0	165.0

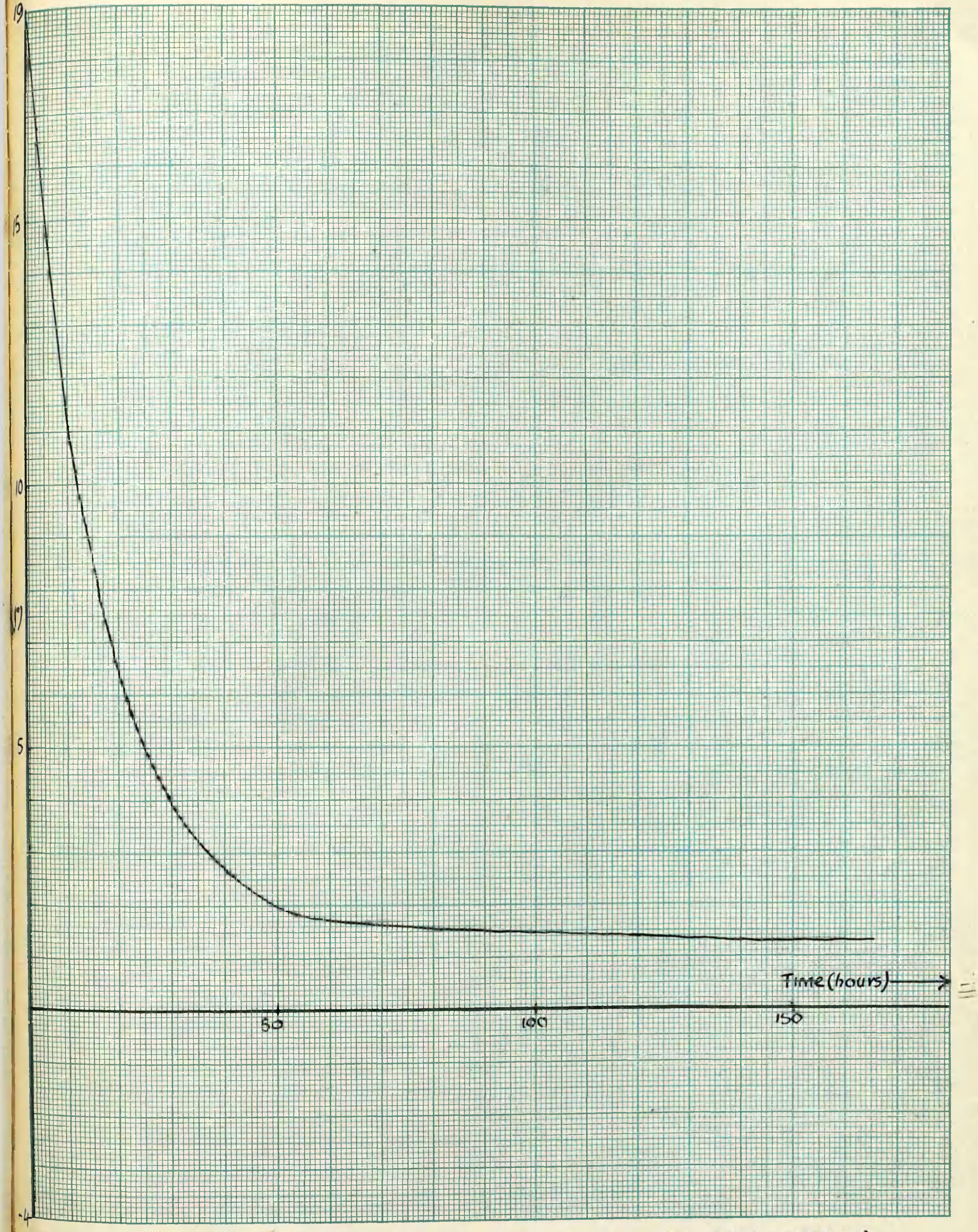


Fig.15 Variation of α_D with time during Irradiation with 3132 - 2895 A.

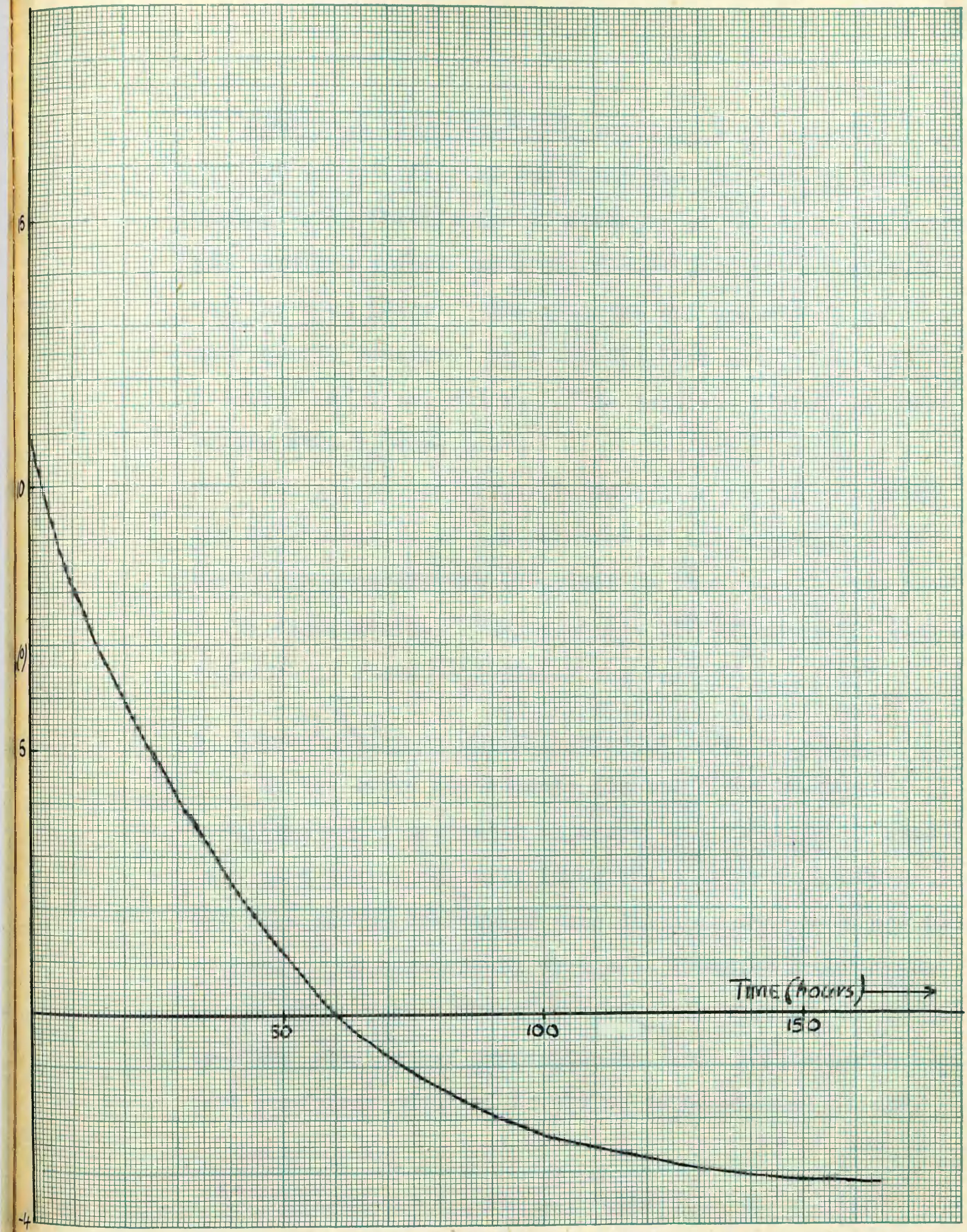


Fig16 Variation of α_D with time during Irradiation with 2650-2537 A.

(b) Apparatus using 2650-2537 group of Wave Lengths.

In essentials, the apparatus was the same as that used above, except that a weaker strength of the solution filter was employed (p.57) and a chlorine filter was substituted for the mica plate. The chlorine was contained (at atmospheric pressure) in a fused silica cell, 8 cm. in diameter and 3 cm. thick. This cell was placed in front of the stop S_4 (see p.57).

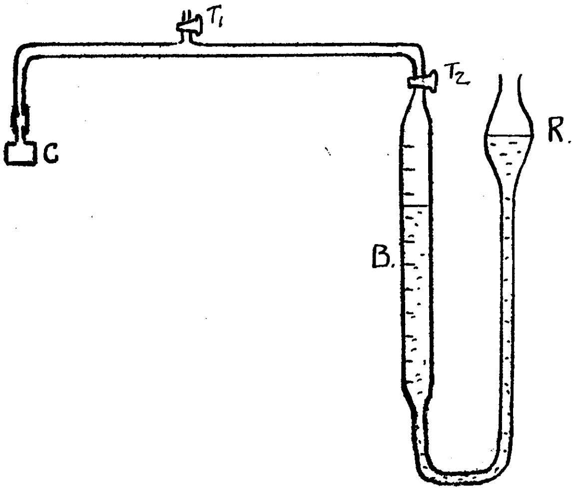
The general procedure, calculation of the intensity and determination of the rotation of the solution after prolonged exposure was identical to that used in the previous experiments. The variation of rotation with time of exposure is shown in Table IX and Fig.16.

6. Investigation of the Existence of Dark Reactions.

In the above experiments (in which the residual rotations after prolonged exposure were determined) readings were taken, not only immediately after irradiation, but also during the period when the solutions were not being exposed. No significant change in rotation could be observed after such a "dark" period. In view of the large specific rotation of parasantonide, this indicated that no dark reactions occurred involving parasantonide itself.

7. The Effect of Oxygen on the Reaction.

An apparatus of the type shown in Fig.17 was used to examine whether oxygen had any effect on the end point of the reaction using the longer set of wave lengths.



C : Cell
B : Burette
R : Reservoir
T_1, T_2: Taps.

Fig.17.

The reaction cell was filled with an alcoholic solution of approximately 0.3 gm. per 100 ml. parasantonide. This alcohol and also the water in the burette were first of all saturated with oxygen. The whole apparatus was then filled with oxygen and the rotation of the solution determined (2.24°). The cell was then exposed to ultra-violet radiation (3132-2895 A), the level of the water in the reservoir being 10 cm. higher than that in the burette. After 16 hours' exposure the rotation was constant at 0.08° and no oxygen had been absorbed. This indicated that oxygen had no effect on the reaction.

8. Measurement of Absorption Spectra.

For all absorption work, a Spekker ultra-violet spectrophotometer (A. Hilger) was employed. As is well known, this instrument consists essentially of two beams (initially of equal intensity) one of which passes through the absorbing solution, while the other has its intensity diminished by a known amount. This is accomplished by a rectangular aperture of variable area. The drum, which controls this area, has a Density ($\log I_0/I$) scale.

9. Measurement of Rotatory Dispersion.

Visual readings were taken with a Hilger polarimeter illuminated with light from a 100 c.p. Pointolite lamp, after it had passed through a Zeiss-Winkel monochromator.

For photographic readings, the ultra-violet polarimeter described by Mitchell and Gordon (58) was employed but a Bellingham-Stanley polariser (half-shadow angle 6°) was substituted for the one previously used.

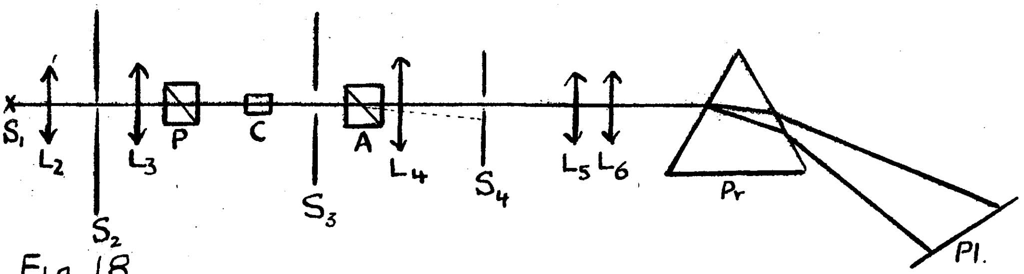


Fig 18

Radiation from an iron arc (3 amps.) is condensed on to a pin hole in a brass stop (S_2) by a lens (L_2). It then passes through another lens (L_3) and the Bellingham and Stanley prism (P) from which it emerges plane polarised. After being transmitted by the optically active medium contained in a 1 cm. quartz cell (C), the light passes through a stop (S_3) and the analyser (A) - a Rochon prism. Finally a lens (L_4) condenses the beam on to the slit of the spectrograph (S_4). Photographs are taken for different settings of the analyser. Thus the wave length, producing a given rotation, may be determined from the equally illuminated portions of the two juxta-posed strips in the spectrogram.

10. Measurement of Circular Dichroism.

As in the case of the Ultra-Violet Polarimeter, description of this apparatus may be found elsewhere, but a brief account will be given here (59).

In essence the method is to compensate for the ellipticity of the solution by polarising the incident radiation with an equal ellipticity of opposite sense. The emergent beam will thus be plane polarised and may be extinguished by means of a Rochon prism.

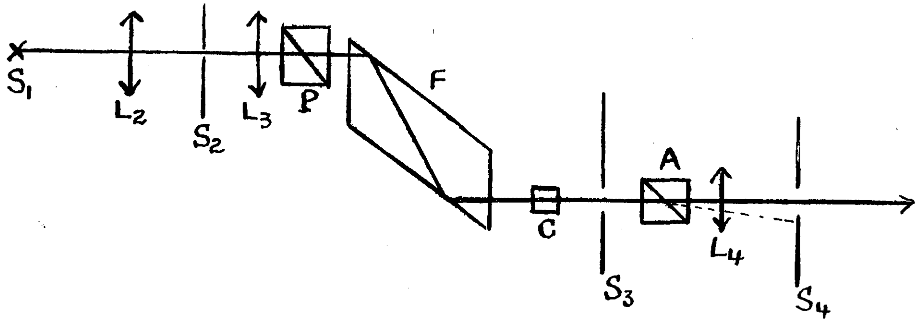


Fig. 19

For these measurements a Fresnel rhomb (F) is interposed between the polariser of the ultra violet polarimeter and the cell. If light falls on one end of this rhomb, plane polarised at an angle to the plane in which it undergoes two reflections, then the emergent light will be elliptically polarised. Since the polariser involves a half shadow angle, the analyser is used, in fact, to match two elliptically polarised rays in a similar way to the matching of two plane polarised beams in the ordinary polarimeter. For simplicity, instead of rotating the Fresnel rhomb, the polariser is rotated, the angle of the latter being used to calculate the circular dichroism given by the formula:

$$\varepsilon_l - \varepsilon_r = \frac{4 \times 0.4343 . \alpha . \pi}{c . l . \times 180}$$

where α is the angle in degrees of polariser,

c : concentration of solution (gm.mols/litre)

l : thickness of layer (cm.).

For the measurement of rotations and dichroism, Ilford's Special Rapid plates were usually employed but, in the case of strongly absorbing solutions, the exposures could be reduced by using Zenith plates. Exposures varied from a minute (for transparent mediums) to an hour, depending on the intensity of absorption. This instrument is not sufficiently sensitive to measure rotations or circular dichroism in the strong bands at about 2300 A in parasantonide and the irradiated solutions.

11. Preparation of Dihydroresorcinol (60).

Dihydroresorcinol was prepared from resorcinol by hydrogenation using a Raney nickel catalyst at ordinary temperature and pressure.

Raney nickel (about 25 gm.) was washed into a hydrogenation flask (2 litre) with 50 cc. distilled water. The sodium hydroxide and resorcinol were then dissolved in 100 cc. distilled water and the brown solution immediately added to the hydrogenating flask. Further 50 cc. were used to wash the beaker and wash in the remaining catalyst.

Hydrogenation proceeded at a rate dependant on the quality of the catalyst. Generally when freshly prepared about 400 cc. of hydrogen were absorbed, but after the nickel had been used in two experiments and recovered after each, the rate in the third experiment would be as high as 1000 cc. per hour or more. After about four or five usages, the nickel became inefficient and a fresh amount was prepared. Variation of the concentration of caustic soda also affected the rate of hydrogenation. Towards the completion of the reaction (i.e., absorption of approximately 12 litres at 20° and 750 mm.), the rate of absorption decreased rapidly and eventually ceased.

The catalyst was then filtered from the colourless liquid and made acid to congo red paper by slowly adding concentrated H_2SO_4 from a dropping funnel, stirring continuously and keeping the solution ice-cold. As p_h 3 was approached, the solid gradually separated from the solution and at p_h 3 the liquid was semi-solid. After filtering off, the dihydroresorcinol was dried on a porous plate. It was obtained slightly impure, due to contamination with some sodium sulphate. It could, however, be crystallised from boiling benzene. On crystallisation, the colour tended to change from white to pale yellow.

The yield, which at this stage was about 80%, could be increased to slightly over 90% by extracting the filtrate (from the acidification) with 75 cc. portions of ether, drying the extracts and evaporating the ether.

The product was usually kept in a dessicator as water tended to decompose it. Since it was extremely soluble in water, it was important that the volume of the solution used in the hydrogenation should be as small as possible.

12. Methylation of Dihydroresorcinol.

Diazomethane was prepared by the action of caustic potash on nitrosodimethyl urea (61). It was distilled in ether over caustic potash before use.

Dihydroresorcinol (3.5 gm.) was powdered and added to an ethereal solution of diazomethane (about 4 gm.) in small portions. The solution was kept at a temperature of 20-25° and continually stirred until complete solution was effected. On addition of the solid effervescence occurred owing to liberation of nitrogen. When the reaction was completed, i.e., when all the solid was dissolved (dihydroresorcinol being practically insoluble in ether), the solution was left for an hour. The ether and excess diazomethane were then distilled off, the water bath being kept below 50°, and a yellow liquid residue was obtained. This was used immediately since it decomposed on standing. Unlike dihydroresorcinol, the liquid did not colour ferric chloride purple.

13. Condensation of (O)-Methyl dihydroresorcinol with Ethyl α-bromo-propionate (Reformatsky reaction).

Zinc was used in small turnings, milled from a block of fused arsenic-free metal. Ethyl α-bromo-propionate was prepared by the action of bromine and phosphorus on propionic acid and subsequent esterification with ethyl alcohol (62). The benzene was thiophene-free and was dried over sodium before use. The apparatus was clean and free from moisture. Molecular quantities of all materials were used throughout.

A three necked flask was fitted with dropping funnel, stirrer and condenser. (The stirrer was only required if there was any difficulty in starting the reaction). Zinc (2 gm.) and a small quantity of mercuric chloride were heated gently until fumes of the latter appeared. The benzene (100 cc.), the methyl ether (4 gm.) and bromo-ester (6 gm.) were then run in.

The reaction commenced almost immediately and a precipitate settled out. After allowing the action to proceed for about 10 minutes, the solution was refluxed for about one and a half hours. During this time nearly all the zinc dissolved. Sulphuric acid was added to decompose the zinc complex, and the mixture was extracted with benzene. The extract was washed and dried with sodium sulphate. The benzene was then distilled off on a water bath and the remaining liquid fractionated. At 58-60°/13 mm. some unchanged bromoester distilled while at 130-150°/14 mm. a pale yellow liquid distilled. It seemed to be homogeneous but failed to distil at a steady temperature. Optimum yield 3.5 gm. (50%). This liquid formed a semicarbazone m.p. 124-126°. The results of an analysis are given below and are compared with the theoretical values for compound XIV (p.50).

	Found (%)	Calculated (%)
Carbon	56.96	56.92
Hydrogen	7.46	7.51
Nitrogen	16.73	16.60

14. The Condensation of α-Bromopropionic acid with 1,2 Cyclohexanedione.

The method used for the preparation of 1,2 cyclohexanedione was identical to that described by Rauh (63). No improvement in yield (about 15%) was observed when freshly sublimed selenium dioxide was used as recommended by Kaplan (64). B.p. 85-87°/20 mm. The product - a pale green liquid - was unstable, so was used immediately for the next stage.

The α-bromopropionic acid was prepared in the same way as the corresponding ester (p.71), but instead of esterifying the intermediate acid bromide, water was added. The acid was extracted with ether, dried over calcium chloride and the mixture fractionated. At 104-106°/19 mm., α-bromopropionic acid distilled as a colourless liquid.

1,2-Cyclohexanedione (5 gm.) and α-bromopropionic acid (6.7 gm.) were added to an alcoholic solution of sodium ethoxide (2.3 gm. sodium in 100 cc. solution). After a trace of cupric acetate (0.5 gm.) had been added, the solution was refluxed for 15 hours on a steam bath and then poured into three volumes of water and acidified. The product was extracted with ether but when an attempt was made to wash it with sodium bicarbonate, the aqueous solution became coloured. The alkaline extract was acidified and extracted with ether. Thus two sets of products were obtained, neither of which gave semicarbazones.

When the experiment was repeated, after the first extraction with ether, the extract was dried and after distilling off the solvent, the residual liquid was fractionated.

Two liquids could be separated, one distilled at 85-100°/25 mm., and the other at 140-150°/3 mm. The latter partly solidified but could not be recrystallised owing to its low melting point and resinous impurity.

The first fraction formed a 2,4-dinitrophenylhydrazone, effervesced with sodium bicarbonate, decolourised bromine water and coloured ferric chloride solution brown.

The second fraction did not form a 2,4-dinitrophenylhydrazone, effervesced with bicarbonate, did not decolourise bromine water and did not colour ferric chloride solution.

Both of these products were formed when the condensation was formed under various conditions. The overall yields were very poor (about 15-20%), since the condensation seemed to give mainly resinous products.

SUMMARY.

The remarkable Cotton Effect associated with the 3000 A. absorption band in d-parasantonide is described in the Introductory Section of this Thesis. It was pointed out that if it could be shown that d-parasantonide (in alcoholic solution) was photosensitive within this region and if, in addition, no complicating dark or chain reactions occurred, then it would be expected that r-parasantonide would be well suited for asymmetric photolysis experiments.

It was already realised that d-parasantonide was photosensitive but it was not known with what absorption bands, photolysis was associated (p.13). Preliminary experiments established that parasantonide was in fact photosensitive within the band of circular dichroism at 3000 A, and also indicated that the type of reaction depended on the wave length of the exciting radiation. Thus with radiation within the 3000A band, the rotation fell to a small positive value, while the total radiation from a mercury vapour lamp produced a small negative rotation.

This suggested that the photochemistry in each case should be investigated. Quantum Efficiency measurements gave values of 0.85 for long waves and 0.40 for short waves (Section 1). These results indicated that no chain reactions occurred and that the deviation from unity must be attributed to deactivating processes and not to any inner filter effect due to the accumulation of the reaction products (pp. 32, 35).

It was found impossible to isolate the products of the reaction in a crystalline state, so irradiated solutions were used for absorption, rotatory dispersion and circular dichroism measurements (Section 2). The irradiated solutions in each case, exhibited two bands similar in position to those in parasantonide but much reduced in intensity. There still remained a Cotton Effect, but it was opposite in sense to that in parasantonide. Moreover it was much reduced in intensity and shifted to longer wave lengths.

The marked similarity between the two inverted Cotton Effects suggested that the reactions with different wave lengths were very similar in type, since the differences between the two curves could be accounted for (at least qualitatively) by assuming the same products were present in varying amounts.

In view of the absence of dark and chain reactions, and the destruction by photolysis of the strong Cotton Effect associated with the 3000 A. band, parasantonide has been shown to be well suited for asymmetric photolysis experiments.

The next stage in the work was the preparation of parasantonide in the racemic form. Attempts made in this direction were described in Section 3. The inability of various workers to reproduce the synthesis of santonin reported by some Indian workers was also discussed. Alternative methods of preparing the keto lactone (VI) (which was an intermediate product in the Indians' synthesis) did not yield the required product.

In conclusion, it can be said that, once r-santonin can be produced in quantity, it will be possible to effect the asymmetric photolysis of parasantonide. It is expected that the results obtained will be much larger than has hitherto been recorded in experiments of this kind.

REFERENCES.

(1) cf. Mitchell, "The Cotton Effect", London, 1933, pp.11,17

(2) cf. Lowry, "Optical Rotatory Power", London, 1935, Chap. 2 and 4.

(3) Pasteur, Compt.rend., 78, 1515 (1874).

(4) Curie, J.Phys., 3, 393 (1894),
Mathieu, "La Synthèse Asymétrique", Paris, 1935, p.9.

(5) Fresnel, Oeuvres complètes, Paris, I, 441, 629 (1866).

(6) cf. Lowry, loc.cit., Chap.3.

(7) Fresnel, loc.cit., p.719.

(8) cf. Houston, "A Treatise on Light", London, 1938, 7th ed., p.230.

(9) cf. Houston, loc.cit., p.232.

(10) Grotthus, Ostwald's Klassiker, No.152, p.101;
Draper, Phil.Mag., 19, 195 (1841).

(11) International Critical Tables, (1926), Vol.5, p.359.

(12) Cotton, Ann.chim.phys., 8, 347 (1896).

(13) Kuhn, Trans.Faraday Soc., 26, 299 (1930);
Z.physik.Chem., B.8, 286 (1930).

(14) Einstein, Ann.Phys., 37, 832 (1912); 38, 881 (1913).
J.phys., 3, 277 (1913).

(15) Warburg, Sitz.kgl.preuss.Akad.Wiss., 746 (1911); 644 (1913).
Bodenstein, Z.physik.Chem., 85, 329 (1913).
See also summary in Z.Elektrochem., 26, 54 (1920).

(16) Kuhn and Braun, Naturwissenschaften, 17, 227 (1929).

(17) Kuhn and Knopf, Naturwissenschaften, 18, 183 (1930);
Z.physik.Chem., B.7, 292 (1930).

(18) Mitchell, J.Chem.Soc., 1930, 1829.

(19) Mitchell and Dawson, J.Chem.Soc., 1944, 452.

(20) Karagunis and Drikos, Z.physik.Chem., B.26, 428 (1934).

(21) Davis and Ackermann, J.Am.Chem.Soc., 67, 486 (1945).

(22) Davis and Heggie, J.Am.Chem.Soc., 57, 377, 1622 (1935).

(23) Betti and Lucchi, Atti.X°.congr.intern.chem., 2, 112 (1938); C.A., 33, 7273 (1939).

(24) Ghosh, J.Ind.Chem.Soc., 16, 51 (1939).

(25) Byk, Z.physik.Chem., 49, 641 (1904).

(26) cf. Mitchell, "The Cotton Effect", p.74.

(27) An account of part of this work is given in J.Chem.Soc., 1947, 686.

(28) For a brief survey of the chemistry of santonin and its derivatives, see Schwarzwald, "The Rotatory Dispersion and Circular Dichroism of Some Ketolactones", Thesis, Glasgow University, 1941, p.45.

(29) Nasini, Gazz.chim.ital, 13, 145 (1883).

(30) Mitchell and Schwarzwald, J.Chem.Soc., 1939, 889.

(31) Carnellutti and Nasini, Gazz.chim.ital., 10, 529 (1880).

(32) Paranjape,Phalnikar, Bhide, Nargund, Current Sci., 12, 150 (1943); C.A., 37, 6671 (1943).
Rasayanam I, 233-45 (1943); C.A., 38, 4266 (1944).
Nature, 153, 141 (1944).

(33) Unpublished work.

(34) Clemo, Haworth and Walton, J.Chem.Soc., 1929, 2368; 1930, 1110.

(35) Abkin and Medvedev, J.Gen.Chem.(U.S.S.R.), 4, 1407 (1934) C.A., 29, 3682 (1935).

(36) Wedekind and Engel, J.Prakt.Chem., 139, 118 (1934).

(37) Schwarzwald, loc.cit., p.36.

(38) Woodward, J.Am.Chem.Soc., 63, 1123 (1941); 64, 76 (1942)

(39) Gillam and West, J.Chem.Soc., 1945, 95.

(40) cf. Betti, Trans.Faraday Soc., 26, 338 (1930).
Singh, Trans.Faraday Soc., 26, 347 (1930).

(41) Nasini, Ber., 14, 1512 (1881).

(42) Schwarzwald, loc.cit., p.34.

(43) Weigert, Optische Methoden der Chemie, Leipzig, 1927, p.213.

(44) cf. Lowry, loc.cit., p.405.

(45) Clemo, J.Chem.Soc., 1934, 1343.

(46) O'Gorman, J.Am.Chem.Soc., 66, 1041 (1944).
Cornforth (J.W.), Cornforth (R.H.) and Dewar, Nature, 153, 317 (1944).

(47) Morrison, unpublished work.

(48) Clemo, Cocker and Hornsby, J.Chem.Soc., 1946, 616.
Morrison, loc.cit.
Carruthers, unpublished work.

(49) Woodward, J.Am.Chem.Soc., 63, 2727 (1941).

(50) Weyl, "Die Methoden der Organischen Chemie", Leipzig, 1911, p.772.

(51) Butenandt, Wolz, Dresler and Meinerts, Ber., 71B., 1483 (1938).

(52) Adams and Baker, J.Am.Chem.Soc., 62, 2208 (1940).

(53) Cocker and Hornsby, J.Chem.Soc., 1947, 1157.

(54) Canizzarro and Valente, Gazz.chim.ital., 8, 315 (1878).

(55) Bowen, J.Chem.Soc., 1935, 76.

(56) Gerlach, Physik.Z., 14, 577 (1913).

(57) cf. Houston, loc.cit., p.448.

(58) Mitchell and Gordon, J.Chem.Soc., 1936, 853.

(59) Gordon, "The Cotton Effect as Exhibited by Some Nitro Compounds", Thesis, Glasgow University, 1937, p.34.

(60) Hoffmann-La Roche, French Patent, 767, 619 (1934); C.A., 29, 482 (1935).

(61) Adams, "Organic Reactions", New York, 1942, p.50.

(62) Weinig, Ann., 280, 250 (1894).

(63) Rauh and Smith, J.Org.Chem., 10, 201 (1945).

(64) Kaplan, J.Am.Chem.Soc., 63, 2654 (1941).

The Fluorescence Spectra of Some Polycyclic Aromatic Hydrocarbons.

CONTENTS.

RESULTS

APPENDIX

Introduction.

Many substances exhibit a 'glow' when irradiated with ultra-violet light. If the emission of light ceases when the source of exciting radiation is removed, the phenomenon is known as 'fluorescence'. The present paper is restricted to the fluorescence obtained with solutions of polycyclic aromatic hydrocarbons.

The first important stage in the development of fluorescence spectroscopy was the discovery by Stokes in 1852 that the frequency of the fluorescent emission was always less than or at most equal to that of the exciting radiation(1). In terms of the quantum theory, this statement reveals itself as an application of the Second Law of Thermodynamics to the fluorescent system, i.e., the energy of the fluorescence radiation is never greater than the energy absorbed.

It was not, however, till 1907, that it was realised that fluorescence was not limited to the visible region of the spectrum but, in fact, could be registered in the ultra-violet. Stark(2), who established this fact, even suggested that all compounds which exhibit selective absorption should fluoresce. The fluorescence spectra of benzene, naphthalene and other aromatic compounds were then studied in detail by various workers. Particular mention should be made in this connection of the work done by Henri(3), Ley and Engelhardt(4) and Dickson(5).

A comprehensive survey was made of the fluorescence spectra of aromatic polycyclic hydrocarbons in 1930. About this time, a search was being made for the cancer producing ('carcinogenic') constituent of coal tar. Mayneord, in 1927, demonstrated that fluorescence spectra showed certain correlations with the carcinogenic activity of many tars. Thus Hieger(6) in 1930 recorded the fluorescence spectra of a large number of polycyclic hydrocarbons for comparison with the spectra obtained from carcinogenic tars. He found that various hydrocarbons could be recognised by the characteristic type of banded spectra they possessed. In 1933, Cook, Hewett and Hieger(7) were able to isolate an active hydrocarbon from carcinogenic pitch, which was later shown to be 3:4-benzpyrene(8).

Sannie(9) and Bandow(10) have suggested that several factors such as concentration and impurities produce a large effect on the intensity of fluorescence spectra. The investigations of Mayneord and Roe(11) and Miescher, Almasu and Kläui(12), on the other hand, support the method - the results of Sannie being attributed to the high concentrations used. Hieger(13) pointed out that Sannie's results were probably due to the sensitivity of microphotometer technique employed and that the visual method was justified to a large extent by the results that had been established by its use. Since these important investigations, fluorescence spectrography has been used as an aid to many metabolic studies(14). More recently, extensive investigations of the several factors in influencing fluorescence intensity have been made by Miller and Baumann(15).

During the work described above, the fluorescence spectra of a number of polycyclic aromatic hydrocarbons were made with somewhat greater accuracy than that originally used by Hieger(6). Berenblum and Schoental(16) have recently improved Hieger's technique and have systematically investigated the influence of substitution on the spectrum of hydrocarbons such as anthracene, 3:4-benzpyrene, 1:2-benzanthracene and chrysene. They established that although shifts to the red occurred depending on the position of the substituent and the type of group introduced, the characteristic fluorescence patterns persisted in the derivatives. In the present paper, these researches have been extended further, using an improved technique, all measurements being made, as far as possible, under standard conditions. These conditions were established after due consideration of the various factors which affect fluorescence and which are summarised here.

Physical Factors influencing Fluorescence.

(a) Sharpness of the bands.

The sharpness of the bands depends mainly on the nature of the solvent used. Definition is best in petroleum ether, satisfactory in benzene and ethylalcohol, and poor in chlorine compounds(16). Diffuseness often arises when the fluorescent compound is photosensitive. In particular, many of the polycyclic hydrocarbons may be photo-oxidised to transannular peroxides (e.g., ) so that solvents such as liquid paraffin, in which oxygen has a low solubility, give sharper spectra. Decrease in temperature usually causes an increase in the definition of the bands(17).

(b) Wave-length of the Fluorescence Maxima.

The spectral positions of the maxima are independent of the wave-length of the absorbed radiation(18), but are influenced by the solvent used. In general, high refractive index of the solvent is associated with large shifts to the red(19). Thus the spectrum in benzene solution is shifted to the red by 100 cm^{-1} compared with that in petroleum ether. Liquid paraffin behaves similarly to benzene.

Sannie emphasised the importance of the effects produced by high concentrations on the position of the fluorescence spectrum and, in particular, the shortest wave-length maximum(9). Change in temperature also influences the position of the maxima in some cases(20).

(c) Intensity.

The intensity is strongly influenced by many factors, e.g., the wave-length and intensity of the exciting radiation, temperature(17), the sensitivity of the photographic plate , the viscosity(21) and oxygen-solubility(22) of the solvent, the concentration(22), the dispersion of the spectrograph and the general set-up of the apparatus.

In the present investigations, fluorescence was examined over the range 3300-6000 A. so that the same set-up of apparatus could not be used in all cases. Thus for the visible region, a glass spectrograph was employed which gave a higher dispersion than the quartz one used for the ultra-violet. Moreover, although the 3650 A mercury line was generally preferred as the exciting radiation, shorter and longer wave lengths had to be employed under different circumstances (cf. Table 6). In view of the effect of concentration on the position of the fluorescence, spectra were only recorded in the region where Beer's Law held (i.e., increase in concentration produced a proportional increase in intensity of fluorescence). In the specific case of 1:2-benzanthracene, it was found that increase in the concentration from 6 to 49 γ/cc. produced a shift to the red in the position of the shortest wave length band of less than 2 A. As far as possible petroleum ether was used as solvent, but in some cases benzene or liquid paraffin was employed. The experimental conditions are described in more detail in another part of this paper (p. 36) and are indicated for each specific compound in Table 6.

The Wave Mechanical Interpretation of Absorption and Fluorescence.

Before describing the results obtained experimentally, a brief account is here given of the explanation usually accepted to account for the relations between the absorption of light and fluorescence emission(23).

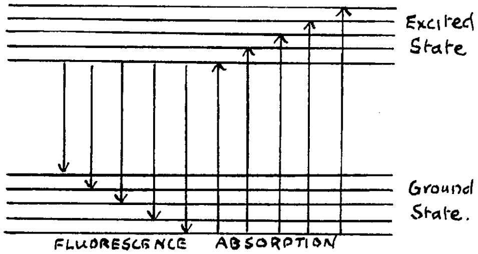


Fig. 1.

Absorption arises when a π -electron passes from the ground state of the molecule to an excited state*. Since simultaneous changes in electronic, vibrational and rotational energies occur, the excited state may thus be regarded as possessing vibrational sub-levels (rotational changes being neglected in view of their small magnitude). Thus in absorption, an electron passes from the lowest vibrational level of the ground state to the various vibrational levels of the excited state. The pattern of vibrational structure, which in general governs the width and symmetry of absorption bands, is determined by the operation of the Franck-Condon principle on the transition involved(24).

A molecule in an excited state will lose its surplus vibrational energy easily by collision with other molecules but may retain the remainder of its energy for a period of

---

* For a further explanation of the part played by π- electrons in visible and ultra violet absorption, see Appendix.

10^{-8} seconds. In the event of this happening the excess energy will be emitted as fluorescence radiation. Thus fluorescence arises when an electron returns from the lowest vibrational level of an excited state to the different sub-levels of the ground state. It is important to note that whereas with absorption the vibrational structure is related to the excited state, the vibrational structure of fluorescence bands correspond to the vibrations of the molecule in the ground state.

Preliminary Observations.

In the present series of compounds investigated, the fluorescence spectra have been compared (wherever possible) with the corresponding absorption spectrum recorded in the literature. A few typical examples are shown in Fig.2*. The fluorescence and absorption spectra were obtained for petroleum ether and alcoholic solutions respectively. In general, it was observed that the fluorescence band of shortest wave length approximately coincided with the longest wave length absorption band. These bands are hereafter termed the 'first fluorescence band' and the 'last absorption band' respectively.

In the case of perylene and 1':2'-naphtha-2:3-fluorene for example, it will be noticed that the fluorescence and absorption spectra are related as mirror images. This relationship, which was first formulated by Lewschin(25) in 1931 as a general characteristic of fluorescence, is exhibited in the case of many compounds (e.g., anthracene, dyes, etc.). The fluorescence spectra of chrysene and 1:2-benzanthracene appear however simpler than their corresponding parts in the absorption spectra. In the case of chrysene, the prominent

---

* Measurements of intensity have not been possible in a large number of cases, as only small amounts of material were available. In view of this, the values of Log. R.I. are only of significance when considering the relative intensities of bands and do not give any indication of the fluorescence power of the compound.

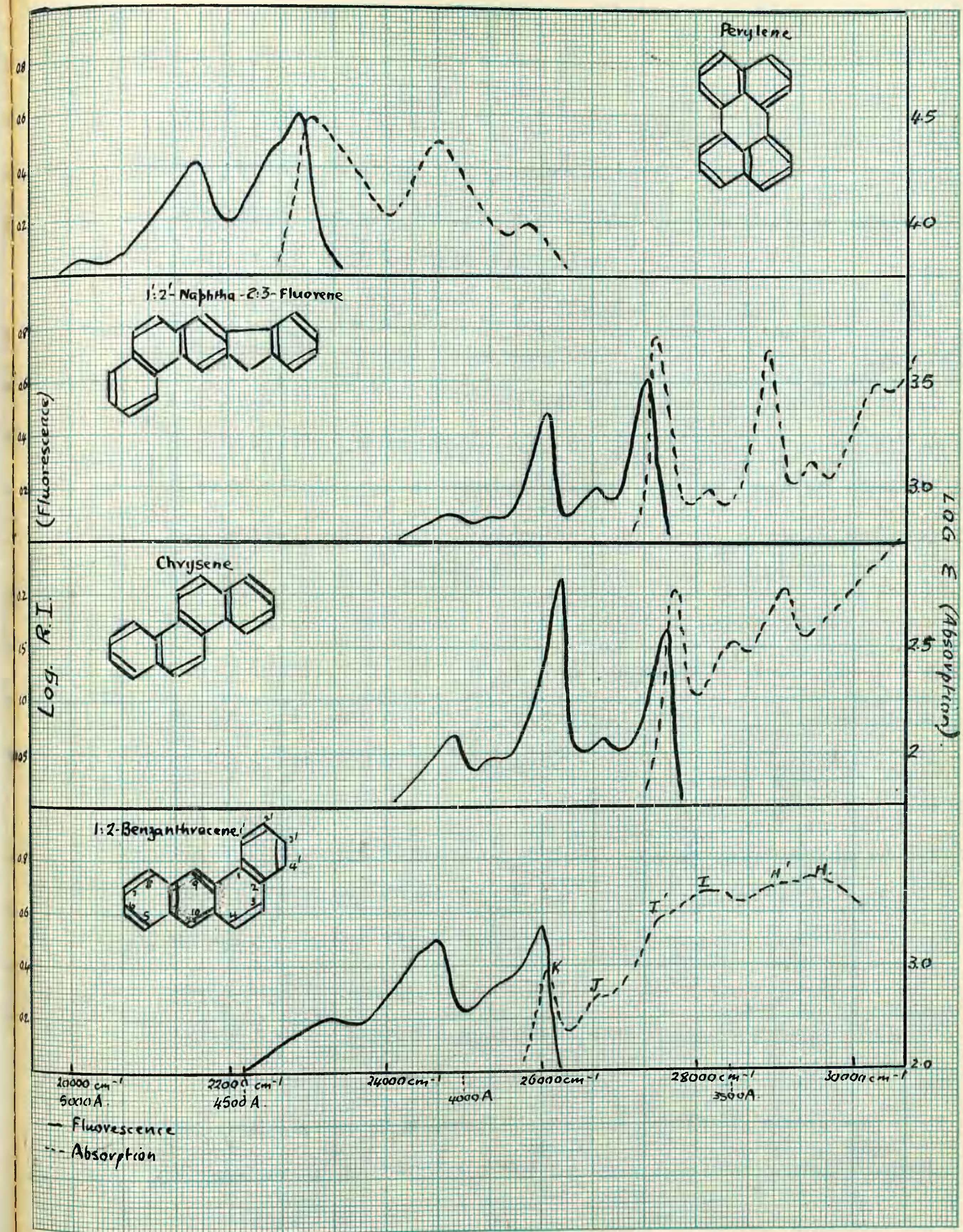


Fig 2: The Fluorescence and Absorption Spectra of Some Polycyclic Aromatic Hydrocarbons.

band at 24800 cm^{-1} has no obvious corresponding band in the absorption spectrum owing to the superimposition of the intense band at 31350 cm^{-1}. The fluorescence spectrum of 1:2-benzanthracene will be discussed later (p. 24).

It is probably true to say that the mirror symmetry relationship can be observed for a fluorescence and absorption spectrum when only one electronic transition is involved. However, even when there does not exist an exact correspondence between fluorescence and absorption spectra use of this idea may still be of help in correlating the different bands in the two spectra (cf. p. 26).

It will be seen from the examples cited in this paper, that benzologues with rings fused in linear condensation and, in general, polycyclic hydrocarbons with only a small proportion of their rings added angularly, have simple fluorescence spectra, which consist of a number of bands spaced at a constant frequency interval, usually diminishing in intensity with increasing wave-lengths. Angular polycyclic hydrocarbons, on the other hand, usually possess spectra comprising two sets of equally spaced bands. More complex types of spectra are exhibited by pyrene and 3:4-benzpyrene (Fig.10).

Owing to the fact that the fluorescence intensity of different compounds varies enormously, it is sometimes difficult to say whether the spectra obtained experimentally

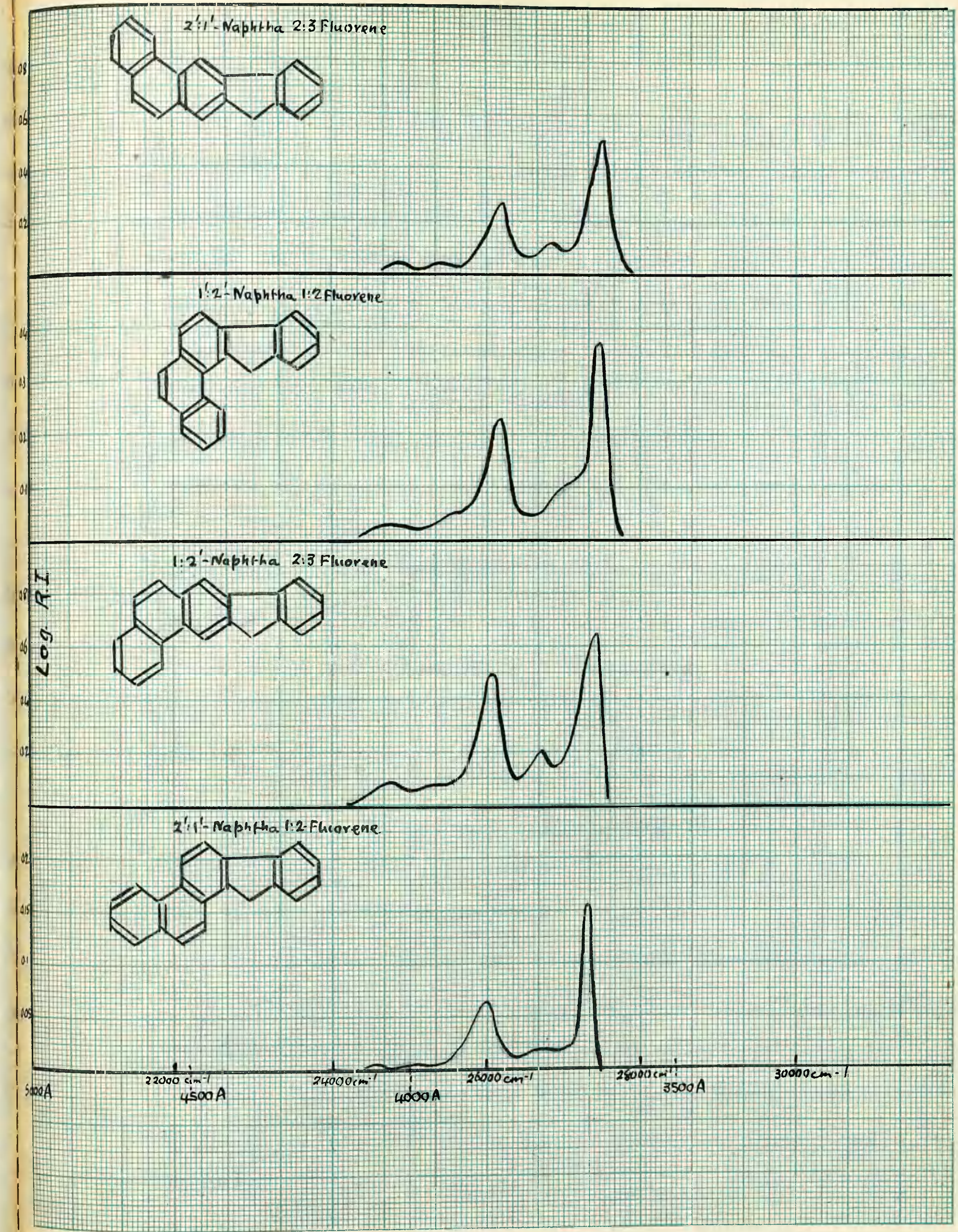


Fig. 3. The Fluorescence Spectra of Some Naphthafluorenes.

of weakly fluorescing substances are characteristic of the pure substance. The fact that compounds of similar structure exhibit similar patterns of fluorescence spectra provides a criterion by which the purity of spectra could be judged. In Fig.3 are shown the fluorescence spectra of four naphthafluorenes. The persistence of a subsidiary set of bands through the whole series of compounds obtained by different methods, indicates the set is a characteristic feature of the spectra of compounds containing the fluorene structure.

The mirror symmetry relationship may be used as an additional criterion of purity, if the absorption spectrum is known and is not too complex. Thus those fluorescence bands which do not correspond to bands in the absorption spectrum may be considered as caused by foreign material.

1. The Fluorescence Spectra of Homocyclic Aromatic Hydrocarbons

(a) Isomeric Tetracyclic Hydrocarbons (Fig.4).

Triphenylene. Long exposures were required for this compound due to its weak fluorescence. This resulted in a rather diffuse spectrum which was probably not characteristic of the pure compound. The first maximum (which was clearly defined) was situated at 3537 A. This value is not far from that of the last absorption maximum at 3500 A. (alcoholic solution)(26).

Chrysene. The main bands are in general agreement with those recorded by several workers(11,12,42,16). Thus the

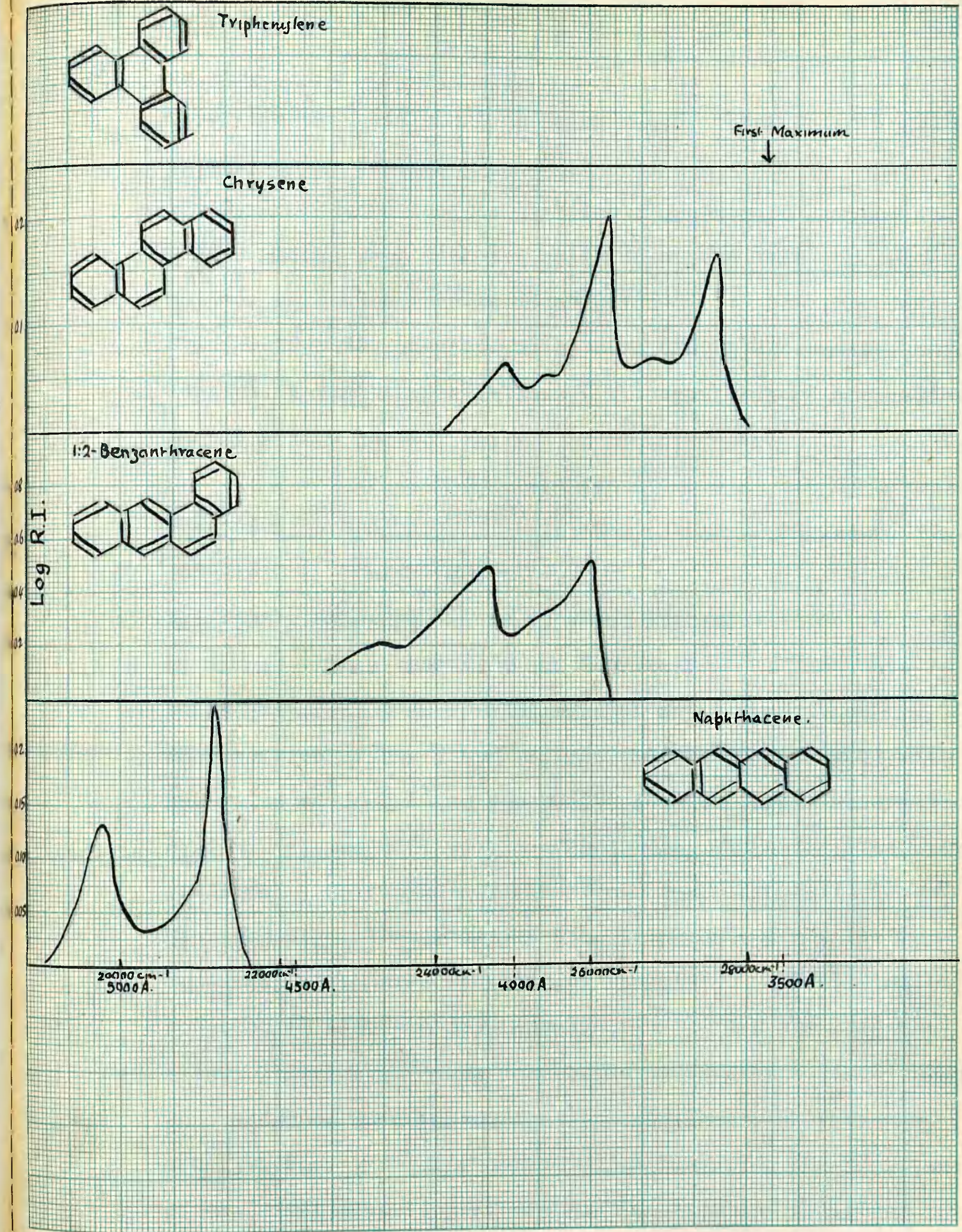
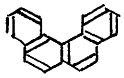


Fig 4. The Fluorescence Spectra of Isomeric Tetracyclic Hydrocarbons.

fluorescence spectrum of chrysene may be represented approximately by the formula $v' : 27650 - 1420\,m - 850\,n$; where $m : 0$, 1 or 2; $n : 0$, or 1. The fluorescence maximum at 3616 A agrees well with the position of the last absorption maximum at 3600 A (alcoholic solution)(27). In this case, the spectrum was recorded using both 3650 A and shorter wave lengths as exciting radiation. The positions of the maxima were the same in each case.

The spectrum of 3:4-benzphenanthrene () according to Chalmers(28) is close to that of chrysene, viz., 3690-4310 A (benzene solution).

<u>1:2-Benzanthracene.</u> This spectrum resembles those recorded by Hieger(6) and Berenblum and Schoental(16). Two sets of bands are present as in chrysene but are merged together. The position of the first maximum (3853 A) agrees well with the value of 3845 A for the position of the last absorption maximum (alcohol)(29). The fundamental vibration frequency (1410 cm^{-1}) is similar to that found for chrysene (1420 cm^{-1}).

<u>Naphthacene.</u> The maxima at 4713 A and 5060 A are not in agreement with those recorded by Ganguly(18) for alcoholic solution at 4750 and 5080 A respectively, but the last absorption maximum(30) has been observed at 4735 A (in benzene). This shift of 20 A to shorter wave lengths is of the same order as that generally noticed when comparing the positions of the first fluorescence maximum in petroleum ether and of

the last absorption maximum in benzene solution.

(b) Isomeric Pentacyclic Hydrocarbons (Fig.5).

3:4:5:6-Dibenzphenanthrene. The fluorescence of this compound was very weak, so, as in the case of triphenylene, long exposures were required, giving a diffuse spectrum. The first maximum lies at 3764 A.

Picene. The fluorescence spectrum of picene is similar in type to that of chrysene and can approximately be represented by the formula $v' = 26420 - 1370\ m - 790\ n$. It agrees well with the spectrum recorded by Hieger(6) and with the absorption spectrum(31). The first fluorescence band (for benzene solution) is at 3785 A, while the last absorption band (for $CHCl_3$) is at 3760 A.

2':3'-Naphtha 1:2-phenanthrene. This fluorescence spectrum comprises three bands, the middle one being the most intense. The first maximum which lies at 3918 A is close to that of the last absorption band (3930Ain benzene). The unequal spacing between the peaks is probably due to the composite nature of each of the bands. Extra purification by chromatography and recrystallisation did not affect this anomaly.

1:2:7:8-Dibenzanthracene. This compound gave a comparatively weak fluorescence. It is doubtful whether it (or the spectrum recorded by Hieger) is characteristic of the pure substance. The position of the first maximum (3942 A.) is in agreement with the last absorption maximum (3950 A for

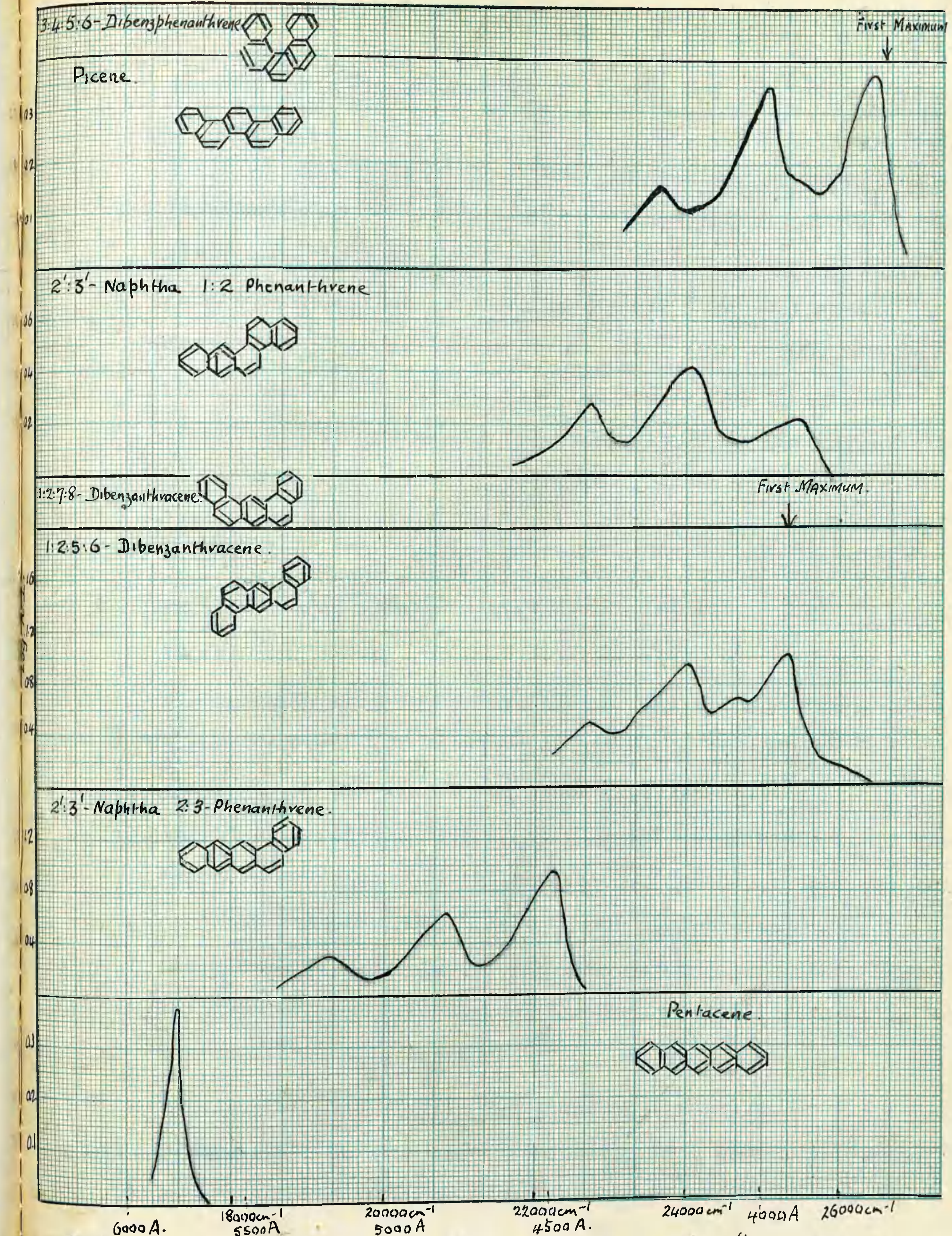


Fig. 5. The Fluorescence Spectra of Isomeric Pentacyclic Hydrocarbons

benzene)(32).

<u>1:2:5:6-Dibenzanthracene.</u> This spectrum can be approximately represented by the formula $v' = 25350 - 1420\,m - 700\,n$ and is similar to those of chrysene and picene. Its position is in agreement with that recorded by Hieger(6) and Chalmers(28). The latter gives values of 3940 - 3990, 4040 - 4090, 4180 - 4230, 4290 - 4380, 4440 - 4480 for the maxima in benzene solution. The corresponding values found in the present case (in petroleum ether) are : 3945, 4060, 4175, 4297, 4444 A. The last absorption maximum for alcoholic solution is at 3950 A(33).

<u>2':3'-Naphtha 2:3-phenanthrene.</u> This fluorescence spectrum is essentially of the anthracene - naphthacene type and can be represented by the formula $v' : 22195-1400\,m$. The first fluorescence band appears at 4505 A, while the corresponding absorption band (for benzene solution) is at 4525 A(34).

<u>Pentacene.</u> In view of the great photosensitivity of pentacene, liquid paraffin was used as solvent (cf. p.4) and mercury green light employed as exciting radiation. Although only one band could be photographed, a second band was observed visually at about 6250 A. The position of the first fluorescence maximum at 5770 A agreed with that of the corresponding absorption maximum (5800 A in benzene)(35).

(c) <u>Isomeric Hexacyclic Hydrocarbons</u> (Fig.6).

<u>Fulminine.</u> In this case the formula $v' : 26770 - 1400\,m - 770$ shows that the spectrum is very similar in type to that of

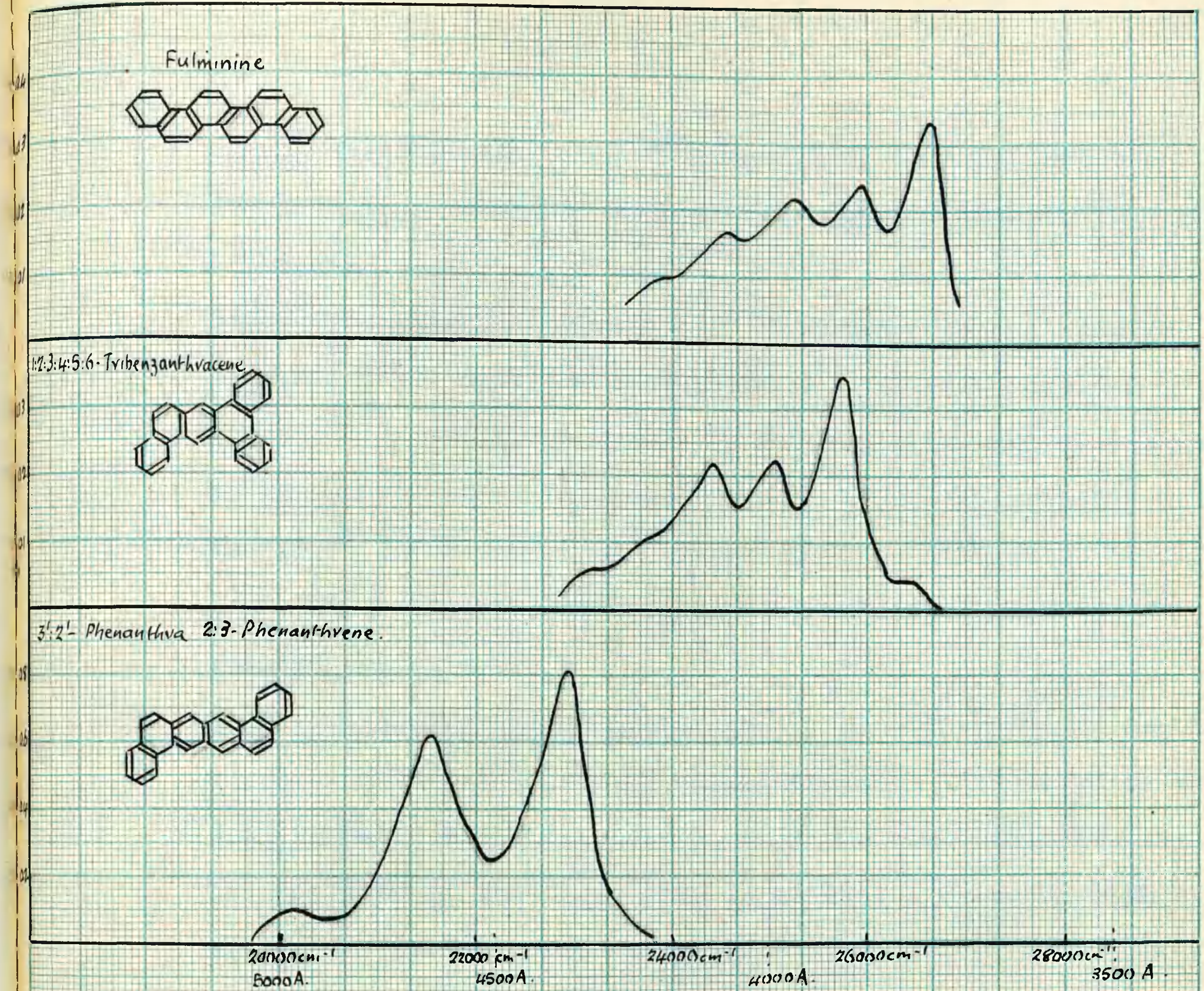


Fig. 6. The Fluorescence Spectra of Isomeric Hexacyclic Hydrocarbons.

picene and chrysene. It is interesting to note that the spectrum is situated at shorter wave lengths than in the case of picene.

1:2:3:4:5:6-Tribenzanthracene. This fluorescence spectrum is similar in position and type to that already recorded by Hieger(6). It is comparable in pattern with that of 1:2:5:6-dibenzanthracene. The small band at 3798 A is probably not the first fluorescence band since the last absorption band (3880 A for benzene)(36) practically coincides with the intense band at 3883 A.

3':2'-Phenanthra-2:3-phenanthrene. This fluorescence spectrum compares well with those of naphthacene and 2':3'-naphtha-2:3-phenanthrene and corresponds to only one electronic transition. The position of the first band is at 4345 A compared with 4375 A for the last absorption band (benzene)(37).

Discussion.

It will be noticed in each case of the above series of isomers, that the straighter the chain of rings, the longer is the wave length of the first fluorescence maximum, paralleling an increase in chemical reactivity. It was thought there might exist a simple relationship which would correlate the chemical reactivity and position of the fluorescence with the structure of the compound.

The greater reactivity of anthracene over that of phenanthrene has been accounted for by the fact that, unlike phenanthrene, the 'Kekulé' structure* for anthracene cannot be constructed using three benzenoid rings (38). One of the rings must be quinonoid. In fact, according to Fries' Rule, the most stable structure of any aromatic compound is likely to be that which contains the maximum number of benzenoid rings or the minimum number of quinonoid rings (39).

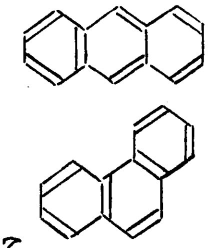
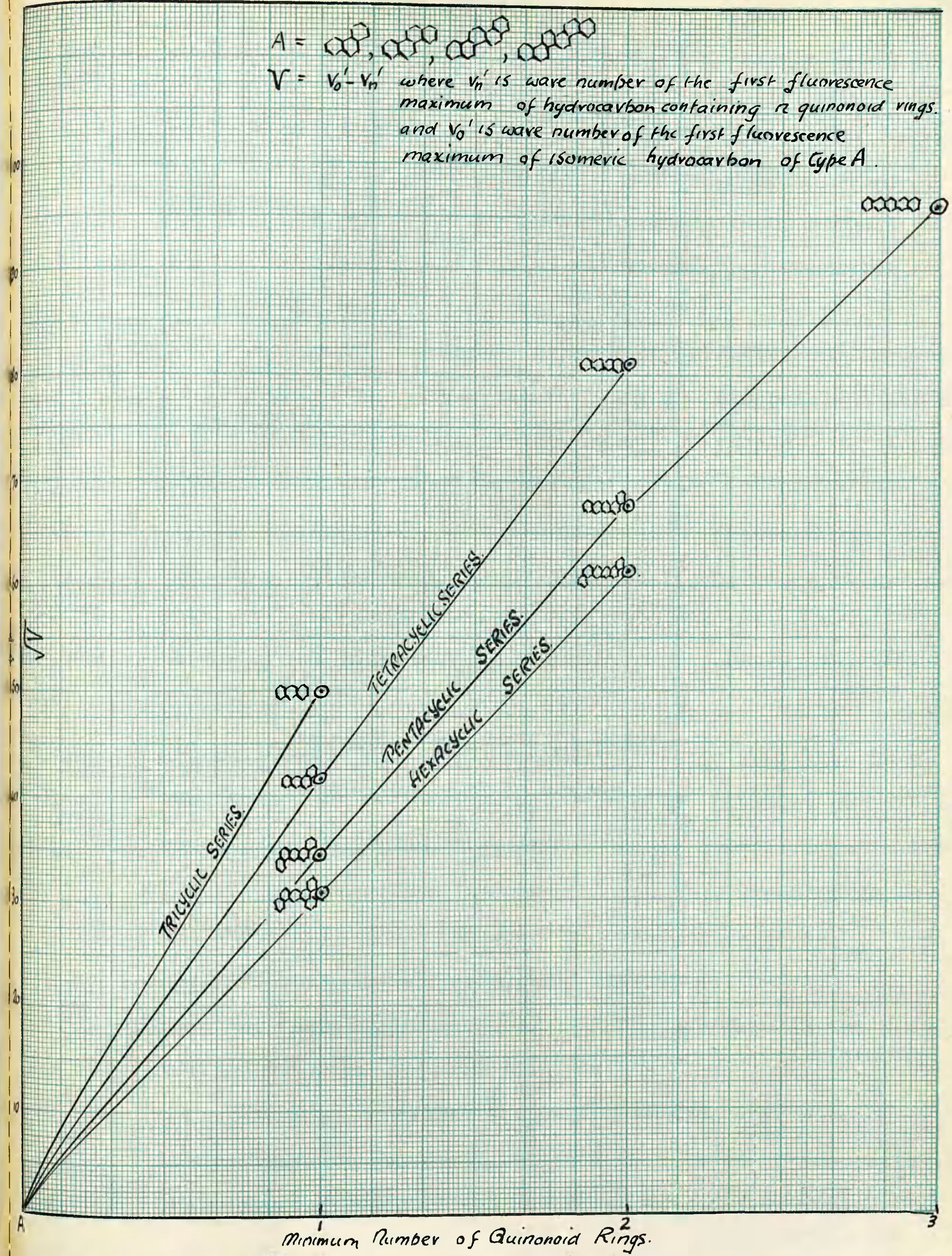


Fig. 7.

It was thought that this simple idea might be extended to correlate the spectral position of the first fluorescence band with chemical structure. It was, in fact, found that if V was the difference in frequency between the first fluorescence bands of the spectra of a given polycyclic compound and of its isomer containing all rings benzenoid, then $\sqrt{V}$ was found to be approximately proportional to the minimum number of quinonoid rings which could be accommodated in a Kekulé structure of the former compound. This relation

---

* In this paper, in order to prevent confusion between 'excited structures' and 'excited electronic states', the terms 'excited' and 'monoexcited' structures have been replaced by 'Kekulé' and 'Dewar' structures respectively. A Kekulé structure comprises alternating single and double bonds, while in a Dewar structure, one of the bonds extends between non-adjacent carbon atoms.



A =

$V = V_0' - V_n'$ where V_n' is wave number of the first fluorescence maximum of hydrocarbon containing n quinonoid rings. and V_0' is wave number of the first fluorescence maximum of isomeric hydrocarbon of type A.

Fig 8. Variation of $\sqrt{V}$ with the number of Quinonoid Rings.

is shown graphically in Fig.8. Chrysene, picene and fulminine were taken as the first members of the respective series. Triphenylene was the only compound which did not conform to this relationship, probably on account of the remarkable symmetry of its structure.

The theory of Resonance provides an alternative method of interpretating reactivity in terms of structure. According to Pauling, the greater the number of possible resonance forms, the greater will be the stabilising resonance energy and the smaller will be the reactivity. Phenanthrene, for example, will be more stable than anthracene since it possesses 5 Kekulé structures compared with 4 in the latter case(40).

In giving an explanation of the spectral position of fluorescence in terms of the Resonance Theory, it is important to realise that resonance will normally stabilise both the ground and excited states. It will, however, be expected that Dewar structures will make a larger contribution to the latter than to the former, so that the stabilisation of the excited state will be greater than the ground state. Since the difference in energy between the two levels will now be reduced, there will be a corresponding increase in the wavelength absorbed.

It might be expected that, to a first approximation, the position of fluorescence would be related to the ratio of the number of Dewar to the number of Kekulé structures.

This connection is in fact found for the simpler polycyclic hydrocarbons and is illustrated for linear addition of benzene rings and the tetracyclic series of isomers (Table 1). In the former case, increase in the number of rings increases both the numbers of Kekulé and Dewar structures and also the ratio of Dewar to Kekulé forms. This corresponds to a progressive shift to longer wave lengths. In Table 1B, the numbers of Kekulé and Dewar structures again increase from naphthacene to triphenylene but this time the ratio of Dewar to Kekulé forms decreases corresponding to a shift to shorter wave lengths. These calculations serve to explain in a qualitative way the experimental results observed, but it would not be expected that considerations of this type would hold so well for hydrocarbons containing 5 rings or more, since the Kekulé forms would probably not make a large contribution to the resonance hybrids.

The most satisfactory way of representing the fluorescence spectra of the above compounds schematically was found to be the correlation of the position of the first fluorescence maximum with the corresponding number of Kekulé structures. This scheme is shown in Fig.9.

The view of the approximate identity of the positions of the first fluorescence maximum and the last absorption band,

Table 1.

The Correlation of the Position of the First Fluorescence. Maximum with the Numbers of Kekulé and Dewar Structures.

Series A.	No. of Kekulé Structures (K)	No. of Dewar Structures (D)	$\frac{D}{K}$	Position of First Fluorescence Max. (cm^{-1})
Benzene	2	3	1.5	(37430)
Naphthalene	3	16	5.3	(31350)
Anthracene	4	48	12	26500
Naphthacene	5	110	22	21220
Pentacene	6	215	35.8	17330

Series B.

Naphthacene	5	110	22	21220
1:2-Benzanthracene	7	112	16	25950
Chrysene	8	117	14.6	27650
Triphenylene	9	117	13	28270

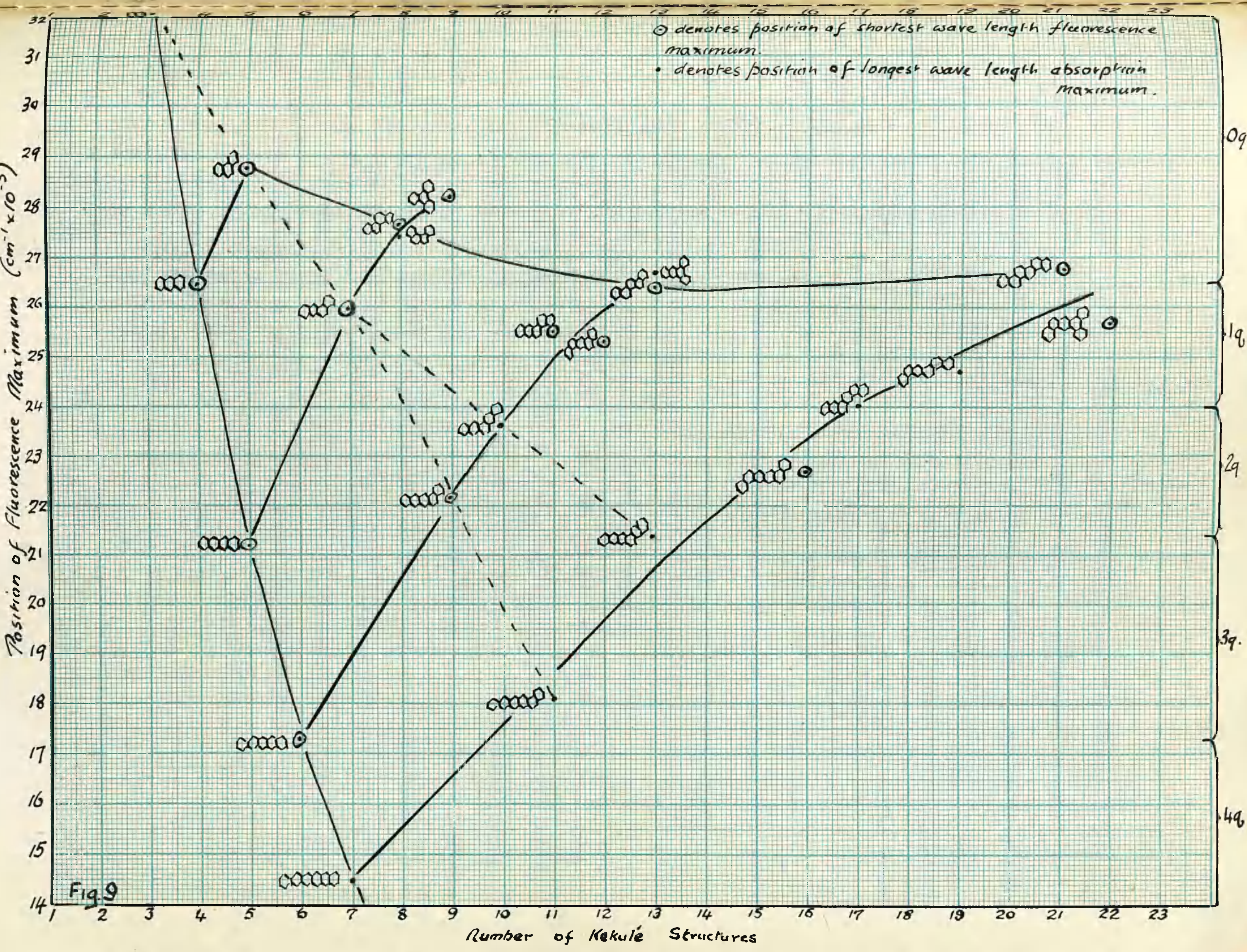


Fig.9

⊙ denotes position of shortest wave length fluorescence maximum.
• denotes position of longest wave length absorption maximum.
Position of Fluorescence Maximum (cm⁻¹ × 10⁻³)
Number of Kekulé Structures
32
31
30
29
28
27
26
25
24
23
22
21
20
19
18
17
16
15
14
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
0q
1q
2q
3q.
4q

the data for the absorption of some compounds were taken from the literature and inserted in this diagram. It will be noticed that although the number of Kekulé structures seems to be only indicative of the position of fluorescence when considered in a series of isomeric hydrocarbons, the number of quinonoid rings seems to define the position within broad limits. These limits are indicated on the right side of the diagram.

Many features of interest arise from an examination of this scheme.

(a) Isomeric compounds lie approximately on a curve running diagonally upwards from left to right.

(b) Benzologues with rings fused linearly lie on a steep curve, i.e., addition of one ring represents an extremely large shift in the spectrum. However, if there already exists a number of rings fused in the 1:2 position of naphthalene, linear condensation produces smaller shifts.

(c) Angular addition of benzenoid rings produces smaller effects than linear addition. With small molecules, angular addition of a ring produces a shift to the red, while with larger molecules the shift is much smaller and even to shorter wave lengths.

(d) More Condensed Structures (Fig.10).

The spectra recorded in this section are for the most part simple although the compounds themselves are sometimes highly complex. In fact, the most complicated spectra correspond to the most symmetrical molecules such as pyrene and coronene.

Pyrene. It was noticed originally by Hieger that pyrene gave a characteristic spectrum consisting of a number of fine lines in close proximity. Miescher et al.(12) recorded a better spectrum showing 5 peaks similar in type and position to that shown in Fig.10. There is very good agreement between the wave lengths of the maxima obtained from this curve and those recorded by Chalmers(28) for benzene solution. He found maxima at 3730-3750, 3780-3800, 3830-3860, 3890-3920, 3930-3970 A. The corresponding peaks for petroleum ether in Fig.10 are 3725, 3785, 3835, 3880, 3925 A. The corresponding long wave absorption maximum lies at 3710 A (alcohol)(41).

The complexity of the pyrene spectrum suggests that the substance may have been impure. However, two different samples were used, one being obtained from coal tar and the other from petroleum. In each case, rigorous purification by chromatographing, sublimation and recrystallisation was effected but the fluorescence spectra obtained were identical. It must therefore be inferred that the spectrum is probably characteristic of the pure substance.

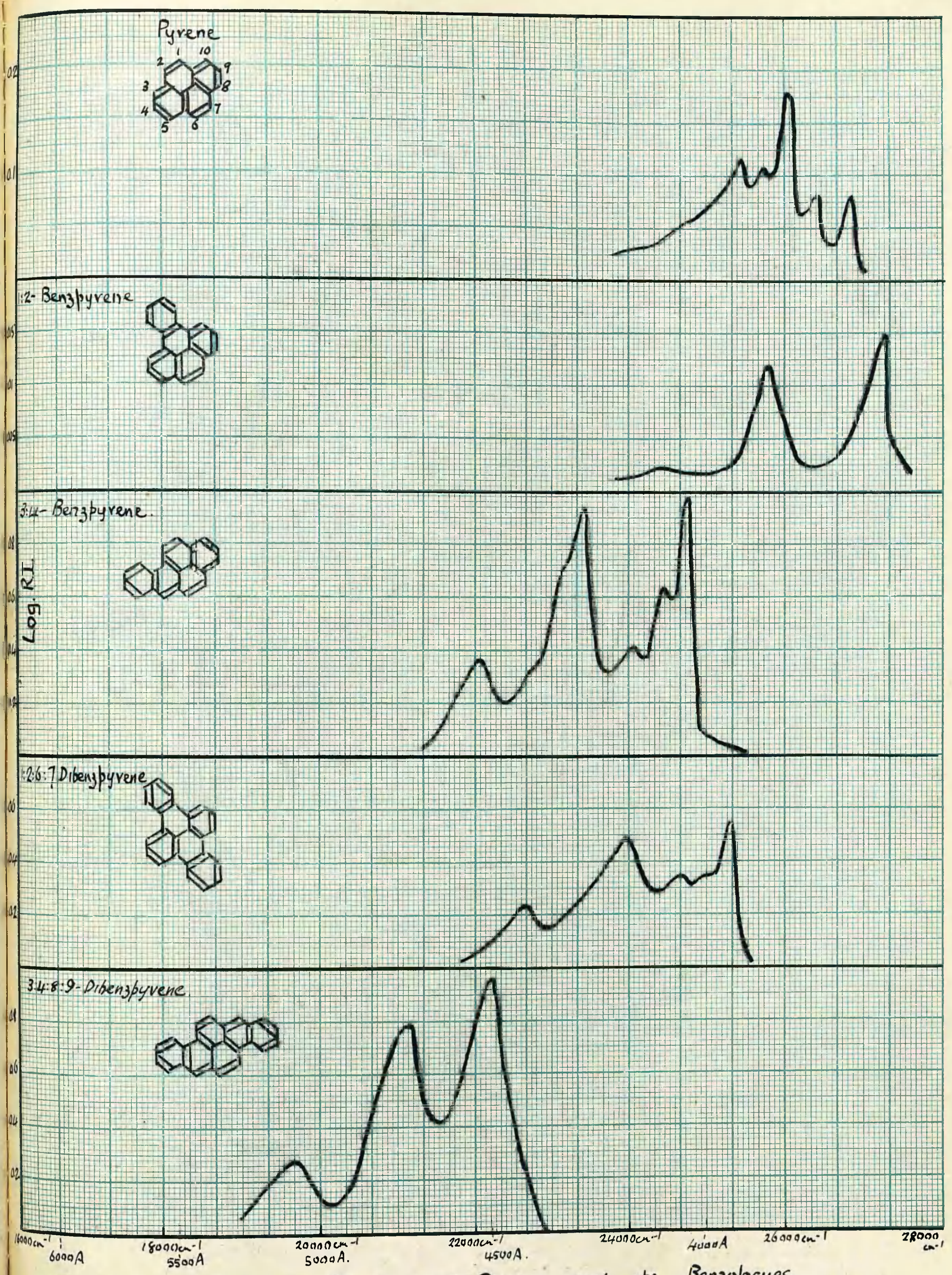


Fig. 10(a). The Fluorescence Spectra of Pyrene and its Benzologues

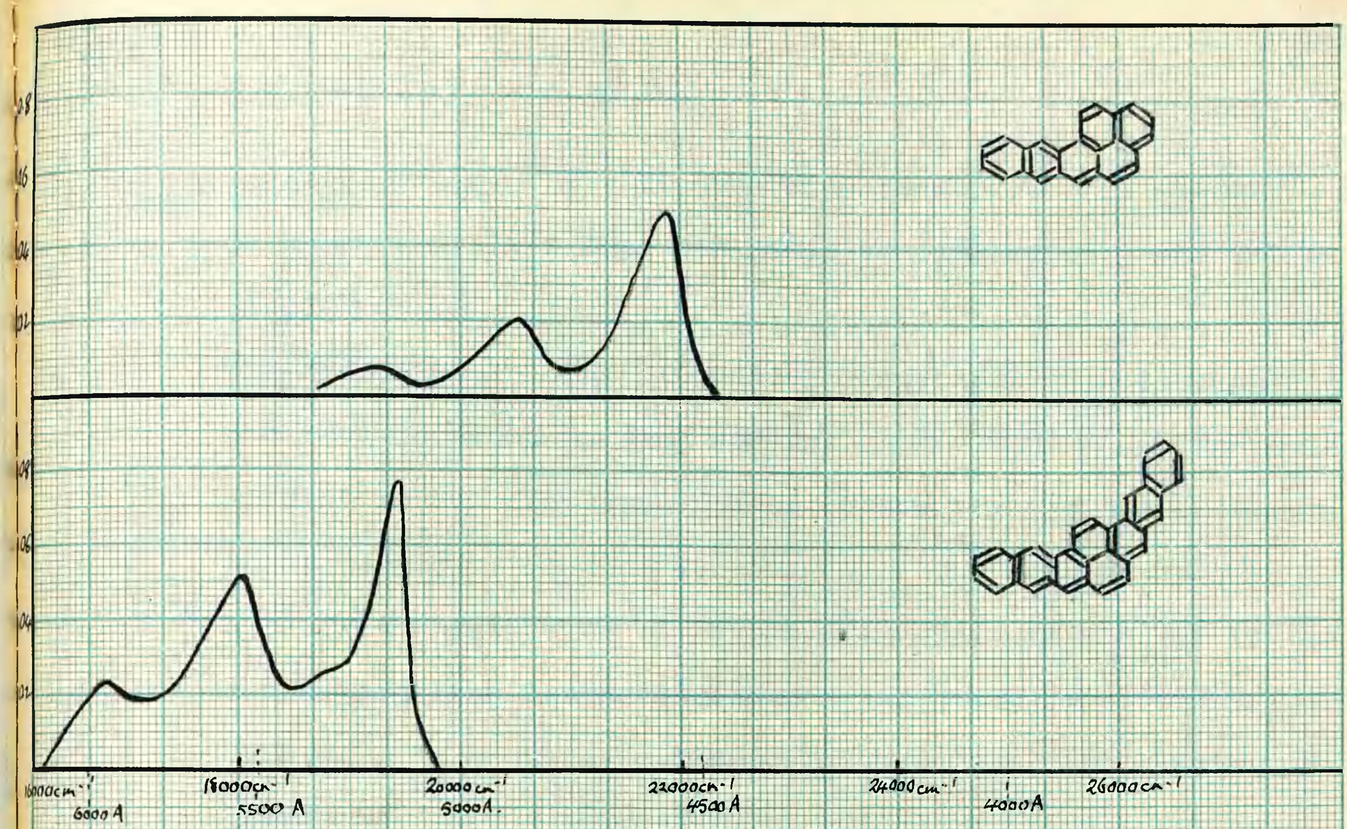


Fig 10(a)(continued)

1:2-Benzpyrene. The fluorescence spectrum of 1:2-benzpyrene is comparatively simple and seems to involve only one set of bands.

3:4-Benzpyrene. The fluorescence spectrum of 3:4-benzpyrene has been recorded by many workers(9,11,12,28,16). The existence of three superimposed sets of bands gives the spectrum its characteristic 'fluted' appearance. The main bands are spaced at a frequency of 1375 cm^{-1}. This is similar to that calculated from Sannie's measurements, i.e., 1360 $cm.^{-1}$ for 0.02 g./l in benzene. The position of the first maximum in hexane was 4040 A compared with 4033 A in the present case. The last absorption maximum appears at 4030 A (alcohol)(43).

Other pyrene derivatives. The spectrum of 1:2:6:7-dibenzpyrene is rather complex, the main set of bands being spaced at 1370 cm^{-1}. However, the spectra of 3:4:8:9-dibenzpyrene and 2':3'-naphtha 3:4-pyrene are much simpler and are similar in type to that of naphthacene. The first fluorescence maxima occur at 4490 and 4565 A, while the corresponding absorption bands lie at 4510 and 4580 A respectively (both values for benzene)(44). In the spectrum of 3:4:9:10-(di 2':3'-naphtha)-pyrene the characteristics of chrysene return, probably due to the increase of emphasis on angulation in the structure. The frequency difference again is about 1390 cm^{-1}.

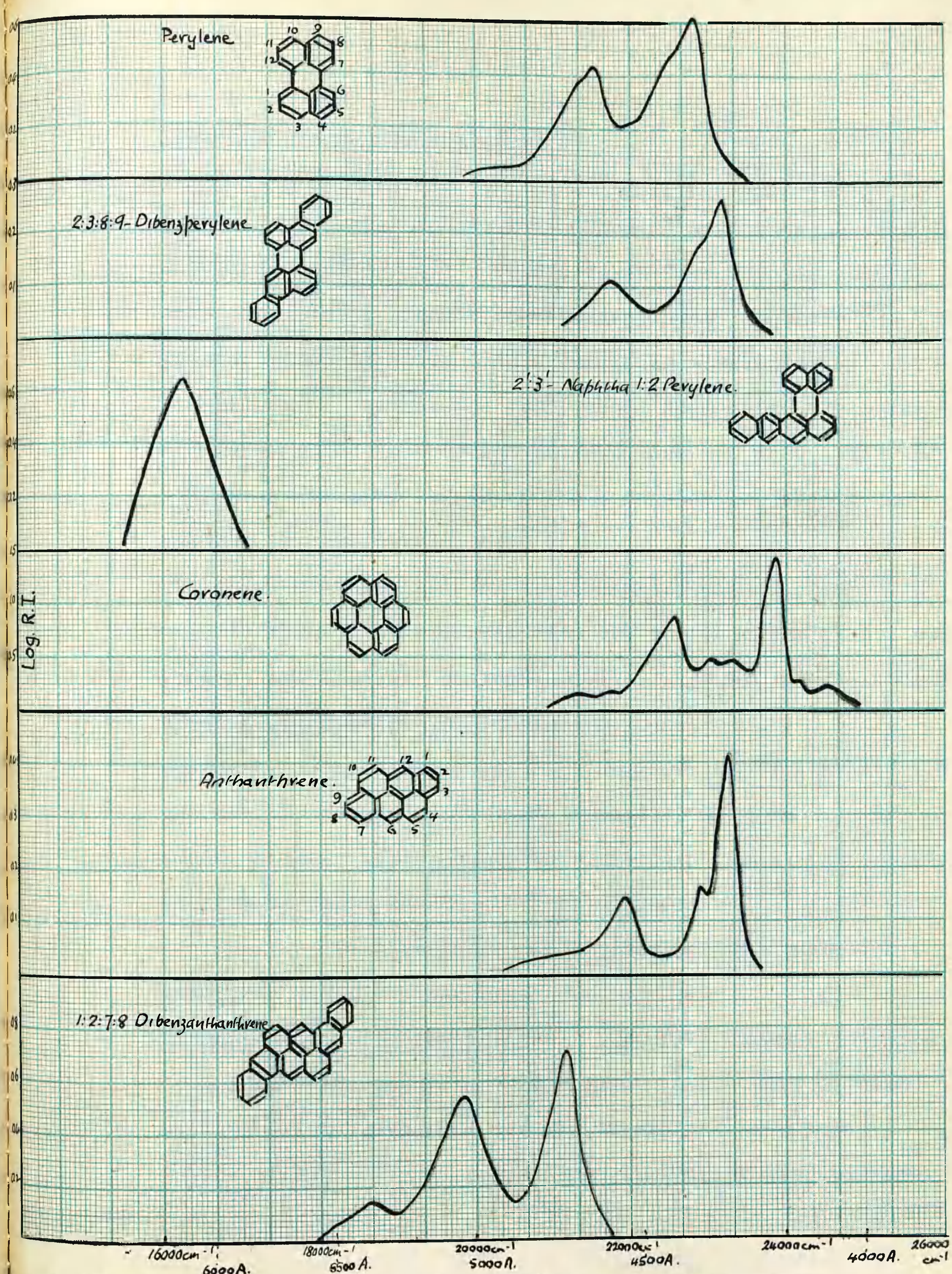


Fig. 10(b). The Fluorescence Spectra of other Condensed-Ring Hydrocarbons.

Perylene and its Derivatives.

The fluorescence spectrum of perylene consists of one main set of bands (spaced at 1360 cm^{-1}) with a suggestion of a weak subsidiary set. Values taken from the literature vary considerably from these observations. Seshan(45) records peaks at 4448, 4762 A for benzene solution, Gangully's(18) values are 4480, 4700, 5000 A for alcoholic solution, while the present observations are 4380, 4644 and 4975 A. The wave length of the corresponding absorption maximum is 4340 A (alcohol)(46).

The spectrum of 2:3:8:9-dibenzperylene is similar in type to that of perylene itself, but the symmetry of the one band recorded in the case of 2':3'-naphtha 1:2-perylene indicates a spectrum of the naphthacene type.

Coronene. The fluorescence spectrum of coronene exhibits one set of strong narrow bands spaced at 1370 cm^{-1}. In addition there are a number of subsidiary bands corresponding to similar bands in the absorption spectrum(47). The main maximum at 4190 A probably corresponds to the absorption maximum at 4200 A (benzene).

Anthanthrene and its derivatives. The fluorescence spectrum of anthanthrene consists of two superimposed sets of bands while its 1:2:7:8-dibenz-derivative exhibits a simple spectrum. The first fluorescence maximum of anthanthrene itself lies at 4300 A, while the corresponding absorption maximum is at 4330 A (benzene)(48).

Discussion.

It is not possible to draw many inferences from such a few examples of each type of condensed structure. It will be seen, however, that the spectral positions of these compounds is to some extent in agreement with their reactivities. For example, coronene is written conventionally with 6 benzenoid rings but the position of the first fluorescence maximum at 23870 cm^{-1}. is situated in the "2-quinonoid" region of Fig. 8 . Perylene, similarly, is usually written with 4 benzenoid rings, but its spectrum lies in the same area. These facts are consistent with the general reactivities of the two compounds. Just as linear addition of benzene rings in the case of naphthalene results in a big shift of the spectrum to the red, whereas angular addition only produces small shift, so 2:3:8:9-dibenzperylene behaves as if it had two quinonoid rings (the same as perylene) while the spectrum of 2':3'-naphtha 1:2-perylene is in the 4-quinonoid region.

It will also be seen that those isomeric compounds possessing the same number of Kekulé structures exhibit fluoresence at similar wave lengths. Thus 2':3'-naphtha 3:4-pyrene and 3:4:8:9-dibenzpyrene exhibit spectra at approximately 4500 A and possess 12 and 13 structures respectively, whereas 1:2:6:7-dibenzpyrene which possesses 20 structures, exhibits a spectrum at much shorter wave lengths (3950 A).

2. The Fluorescence Spectra of 1:2-Benzanthracene Derivatives.

The effect of a number of different substituents in the 5 and 10 positions of 1:2-benzanthracene on the first fluorescence band is shown in Tables 2 and 3. Within the limits of experimental error, no difference could be detected in the effects of various alkyl groups. Substituents containing double bonds conjugated to the aromatic ring effect much larger shifts than alkyl groups owing to the greater ease with which an electron can be removed from the group. The fact that ethoxymethyl- and hydroxymethyl give smaller shifts than the methyl group indicates that a hyperconjugation or charge transfer effect(49) is occurring, which stabilises the excited to a greater extent than the ground state (cf. p. I6).

Methyl Derivatives of 1:2-Benzanthracene.

The fluorescence spectrum of 1:2-benzanthracene in petroleum ether has already been illustrated in Fig.2. Substitution with methyl groups in various positions in

Table 2.

The Effect of Various Substituents in the 10-position of 1:2-Benzanthracene on the fluorescence Spectrum.

	First Fluorescence Position (cm.$^{-1}$)	Maximum Shift
1:2-Benzanthracene	25950	---
10-Ethoxymethyl- "	25700	250
10-Hydroxymethyl-"	25670	280
10-Acetoxymethyl-"	25650	300
10-Methyl- "	25620	330
10-Cyano- "	25180	770

Table 3.

The Effect of Various Substituents in the 5-Position of 1:2-Benzanthracene on the Fluorescence Spectrum.

	First Fluorescence Position (cm.$^{-1}$)	Maximum Shift
1:2-Benzanthracene	25950	--
5-Ethyl- "	25890	60
5-n-Propyl- "	25870	80
5-iso-Propyl-"	25870	80
5-Methyl- "	25850	100
5-Phenyl- "	25670	280
5-Carboxy- "	24930	1020

the molecule does not alter the characteristic shape of the curve but in some cases the bands become rather diffuse (e.g., 9-methyl-). The positions of the first fluorescence maxima for mono and di derivatives are shown in Table 4.

It is interesting to compare the results for mono methyl derivatives with the absorption data recorded by Jones(50). The absorption spectrum of 1:2-benzanthracene for alcoholic solution exhibits a number of peaks in the region 3000 - 3850 A, which seem to fall into two main groups, H', I', K and H, I, J* (see Fig.2). The H and K peaks are taken as the representative members of each group. It will be seen from Table 5 that the displacements for the H and K maxima are not equal for the same derivative. In particular, it will be noticed that substitution in the I' position produces no effect on the H band but shifts the K band quite considerably. Moreover, 10-substitution produces a greater effect on the H maximum than 9-substitution, while with the K band the effect is the opposite.

The behaviour of the first fluorescence maximum is closely similar to that of the K- band. In his discussion of these effects, Jones did not seem to realise the importance of this K band. He mentioned that in the case of I- and 6-methyl

---

* The lettering used here (with the exception of H') is that employed by Jones.

Table 4.

The Effect of the Substitution of Methyl Groups on the First Fluorescence Band of 1:2-Benzanthracene.

(a) Monomethyl Derivatives	Carcinogenicity (61)	First Fluorescence Band	
		Position (cm.$^{-1}$)	Shift
1:2-Benzanthracene	-	25950	---
4-Methyl "	+	25870	80
5-Methyl "	++	25850	100
7-Methyl "	+	25770	180
6-Methyl "	+	25750	200
8-Methyl "	-	25700	250
1'-Methyl "	-	25680	270
3-Methyl "	+	25670	280
10-Methyl "	++	25620	330
9-Methyl "	++	25400	550
(b) Dimethyl Derivatives			
1:2-Benzanthracene	-	25950	---
6:7-Dimethyl "	+	25800	150
3':6-Dimethyl "	-	25780	170
3':7-Dimethyl "	-	25770	180
2':6-Dimethyl "	-	25730	220
2':7-Dimethyl "	-	25570	380
5:6-Dimethyl "	++	25270	680
9:10-Dimethyl "	+++	24670	1280

Table 5.

A Comparison of the Shifts produced in the Absorption and Fluorescence Spectra by the Introduction of Methyl Groups into Various Positions of 1:2-Benzanthracene.

		Absorption Max.* (cm^{-1})(Alcohol)				First Fluorescence Max. (P.8)	
		H Band		K Band			
		Position	Shift	Pos.	Shift	Position	Shift
1:2-Benzanthracene		29330		26010	---	25950	---
4-Methyl	"	29240	90	25970	40	25870	80
5-Methyl	"	28900	430	25910	100	25850	100
7-Methyl	"		0		40**	25770	180
6-Methyl	"		70		100**	25750	200
8-Methyl	"	28900	430	25880	130	25700	250
1'-Methyl	"	29330	0	25810	200	25680	270
10-Methyl	"	28210	1120	25680	330	25620	330
9-Methyl	"	28450	880	25450	560	25400	550

* The values for the absorption maxima in this section were obtained from Jones' values, which were expressed in Angstroms.

** The values of the shifts for 6- and 7-methyl derivatives were taken from the paper of Mayneord and Roe (52).

chrysenes, Brode and Patterson(51) had observed extremely large bathochromic shifts in the absorption spectrum and had attributed them to steric effects, but that no such behaviour occurred in 1:2-benzanthracene. It may well be, however, that the large displacement observed in the K absorption maximum and in the fluorescence maximum of the 9-methyl derivative may be explained by such an effect.

Apart from the behaviour of 9-substitution, there are other anomalous features about the results which should be mentioned. One might expect substitution in the 3 and 4 positions would produce the same shift. In actual fact, the shift for 4-methyl is negligible while that for 3-methyl is quite appreciable. Similarly 8-substitution produces a much larger effect than substitution in the 5 position. According to the calculations of Pullman(53), the electron densities on the 3 and 4 positions are almost identical (0.204 compared with 0.200), while the densities on positions 5 and 8 are also similar (0.198 and 0.196). It does not therefore seem likely that the bathochromic shifts are related directly to the various electron densities in the various positions of the molecule.

A method of vector addition such as that suggested by Conrad-Billroth(54) is difficult to apply in the present case, since the molecule is not symmetrical. A similar difficulty is encountered in interpreting the results qualitatively in terms of the Lewis-Calvin-Jones theory(55). According to this theory the long wave band of anthracene is associated with a development of an electric moment along the shorter axis of the molecule (i.e., parallel to the direction of the electric vector) (cf., p. 52). In an unsymmetrical molecule, such as 1:2-benzanthracene, one cannot say with certainty what the orientation of the vector will be.

One of the purposes of this research was to investigate whether any relation existed between the fluorescence spectra and carcinogenicity. It is known that only slight modifications of structure may make a compound extremely potent as a cancer producing agent. Thus 1:2-benzanthracene is not carcinogenic, but 9:10-dimethyl 1:2-benzanthracene is one of the most powerful carcinogenic compounds known. It will be seen from Table 4 that no relation seems to hold between fluorescence and carcinogenicity.

Lastly, the importance of examining the fluorescence spectrum in addition to the absorption spectrum is manifest in the case of 1:2-benzanthracene and its derivatives. The fluorescence spectrum is much less complicated than the corresponding part of the absorption spectrum. Moreover, those peaks which are prominent in fluorescence correspond to submerged bands in absorption. Conversely, the prominent maxima in absorption appear as subsidiary maxima in fluorescence

3. The Fluorescence Spectra of Some Aza-compounds.

From what has already been said, it will be realised that the properties of the fluorescence spectrum are very similar to those of the corresponding part of the absorption curve. Thus all the empirical rules which govern the behaviour of these bands such as those described by Clar(56) will hold in a similar way for the corresponding fluorescence spectra.

Thus it was not surprising to find that the introduction of a nitrogen atom into a homocyclic aromatic ring did not appreciably alter the position of the spectrum(57). Quantitative measurements made in the cases of chrysene and pyrene revealed that the introduction of nitrogen increased the intensity of fluorescence about ten fold. This, also, is in conformity with the behaviour of absorption spectra in similar circumstances.

In Fig.11 the spectra of a number of aza-compounds are compared with those of the analogous homocyclic hydrocarbons. In all the cases examined, introduction of nitrogen does not appreciably alter the position of the spectrum and the type of spectrum is retained in the spectra of chrysene and 1:2:5:6-dibenzanthracene. Introduction of nitrogen into

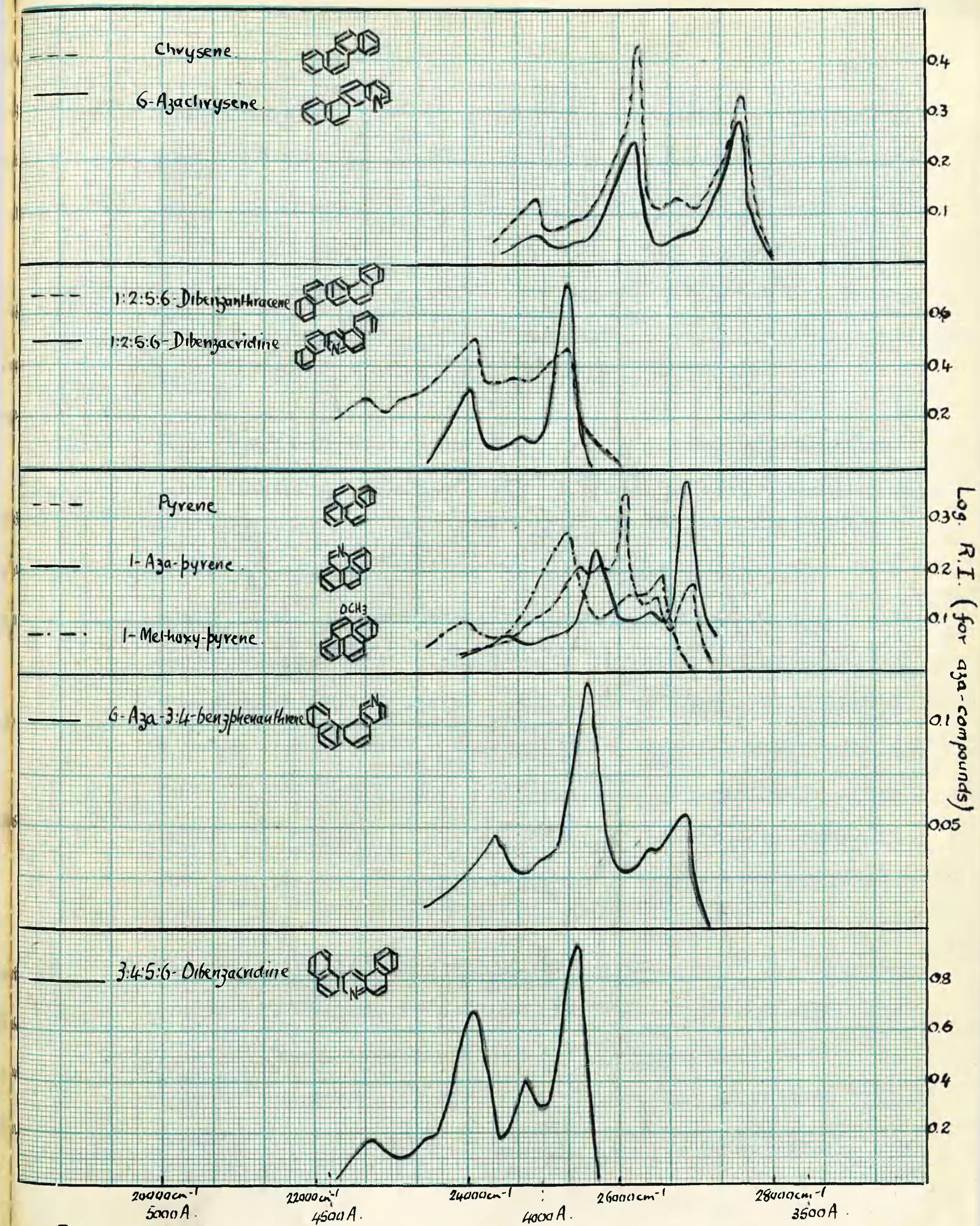


Fig 11. The Fluorescence Spectra of Aza-compounds.

pyrene causes a simplification of the pattern of the spectrum analogous to that produced by the substitution of a methoxy group in the same position. This suggests that the complex spectrum of pyrene is probably due to the characteristic symmetry of the molecule. The spectra of 6-aza 3:4-benzphenanthrene and 3:4:5:6-dibenzacridine are similar in position to those of the corresponding hydrocarbons (pp. II,I2).

4. The Fluorescence Spectra of Some Alicyclic Compounds.

It was of interest to know whether fluorescence spectrography may be used as an aid in the identification of the aromatic structure present in an alicyclic compound. It would be expected that the examination of hydrogenated polycyclic hydrocarbons might provide the most satisfactory approach to this problem. However, in most cases, the hydrogenated product is weakly fluorescent compared with the parent hydrocarbon, and since complete separation from the latter is difficult, the spectrum is sometimes contaminated, both compounds being represented. The spectrum of 1':2':3':4'-tetrahydrobenzpyrene is shown in Fig.12 compared with 1-azapyrene. The latter compound was chosen since its spectrum occurs at the same wave length as that of pyrene without exhibiting those features which are probably peculiar to the symmetrical pyrene itself. The shift to longer wave lengths is characteristic of an additional hydrogenated ring. The

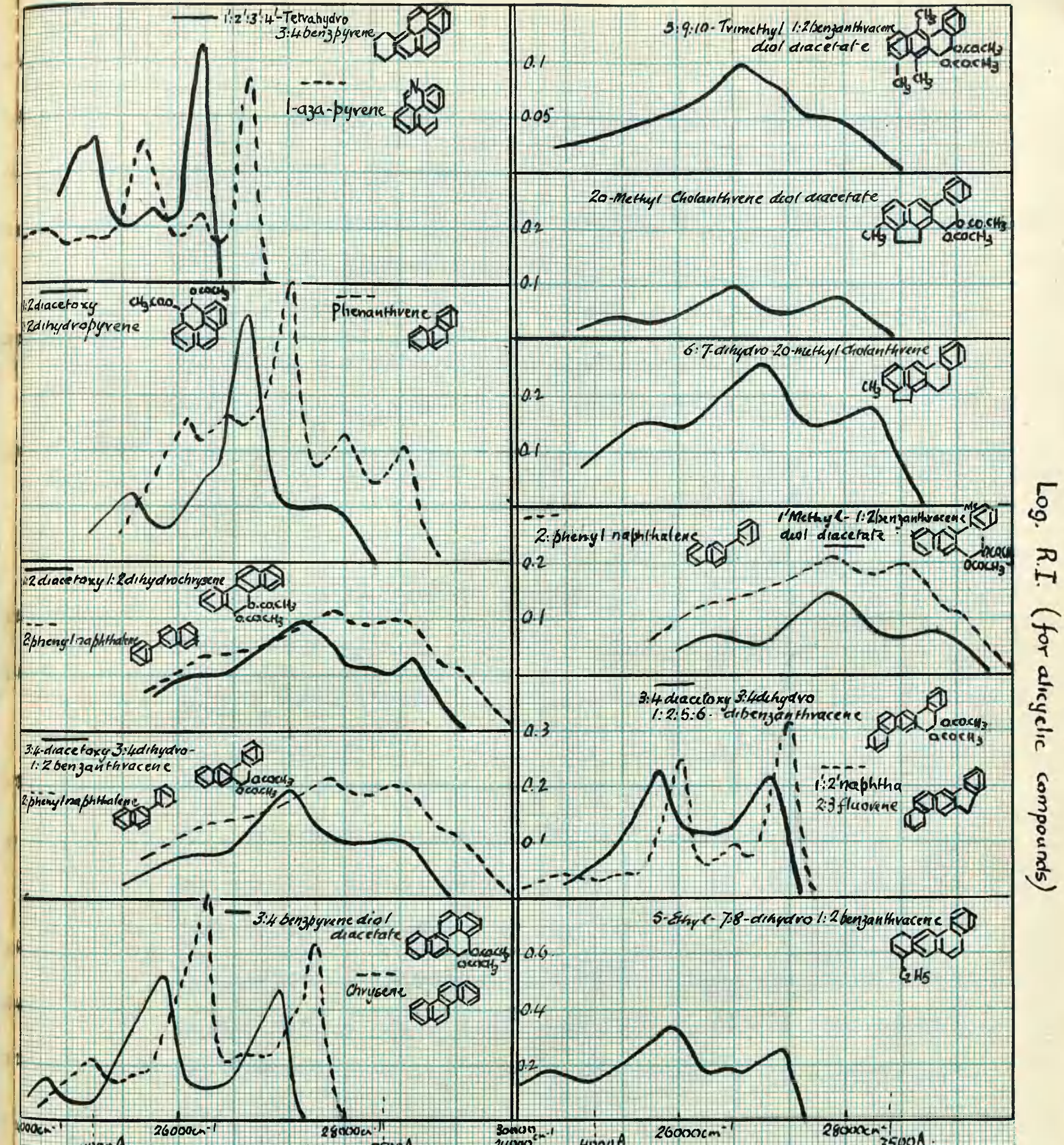


Fig 12. The Fluorescence Spectra of Alicyclic Compounds.

fourth band of the spectrum is due to contamination with 3:4-benzpyrene itself. It will however be noticed that the general structure of the remaining part of the curve is very similar to that of azapyrene.

A more satisfactory method of pursuing this problem was found in the examination of the diacetates of diols of polycyclic compounds synthesised by Cook and Schoental(58). These compounds have the added advantage that they could be easily separated from the parent hydrocarbons.

The fluorescence spectrum of 1:2-diacetoxy-1:2-dihydropyrene will be seen to exhibit the main characteristics of phenanthrene but is shifted to the red by about 500 cm^{-1}. Such a shift seems to be characteristic of the introduction of an additional hydrogenated ring containing two acetate groups. The spectra of 1:2-diacetoxy 1:2-dihydrochrysene and 3:4-diacetoxy 3:4-dihydro 1:2-benzanthracene are both similar to that of 2-phenyl naphthalene, if allowance is made for the expected shift to the red. In all these cases the structures of the diols have been known from chemical evidence. In the case of 3:4-benzpyrene diol diacetate, the structure was not fully established. The presence of a chrysene residual aromatic structure was indicated from the fluorescence spectrum and confirmed that the diol was formed in the 6:7-positions. If the 1:2-diol had been produced, the residual structure would have been that of 1:2-benzanthracene, the fluorescence spectrum of which lies at much longer wave lengths. The fluorescence spectrum in this case indicates which of a number of structures is likely to be the correct one.

The diacetate of 5:9:10-trimethyl 1:2-benzanthracene diol possesses a spectrum shifted to longer wave lengths compared with that of 3:4-diacetoxy 3:4-dihydro 1:2-benzanthracene owing to the larger number of substituents. This spectrum is similar to that of the diacetate of 20-methyl cholanthrene diol with which it has great similarities in structure and both are compatible with the structures suggested for these compounds. The spectrum of 6:7-dihydro 20-methyl cholanthrene is shifted to shorter wave lengths as would be expected.

The spectrum of the diacetate of 1' methyl 1:2-benzanthracene diol does not seem to fit into the general scheme, as it is not shifted to longer wave lengths than that of 2-phenyl naphthalene. It is tentatively suggested that the effect of the methyl group in that position in conjunction with any strain present in the hydrogenated ring, may prevent the benzene ring from being coplanar with the naphthalene structure so that its effect is much reduced.

Comparison is also made between the fluorescence spectra of 3:4-diacetoxy-3:4-dihydro 1:2:5:6-dibenzanthracene[*] and that of 1':2'-naphtha 2:3-fluorene. The shift to the red is not so large in this case since the methylene bridge is already represented in the latter compound. The spectrum of 5-ethyl 7:8-dihydro 1:2-benzanthracene is also of interest since it lies between the spectra of 1:2-benzanthracene and phenanthrene as would be expected from its structure.

---

[*] The structure of this compound has been definitely established by Schoental. Chromic acid oxidation of the diacetate gave the known 1:2:5:6-dibenzanthracene 3:4-quinone (59).

Experimental.

A. Fluorescence Spectra in the 3300-4000A Region.

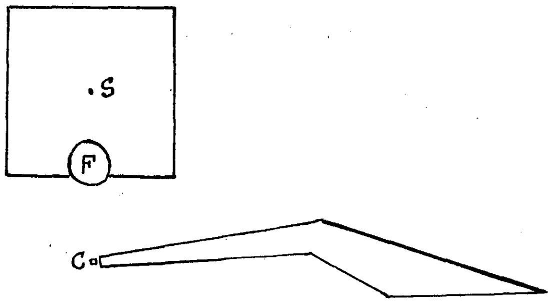


Fig. 13.

Radiation from a mercury vapour lamp S (Kelvin, Bottomley and Baird) contained in a black box, was condensed by a 500 ml. quartz flask containing a 10% solution of nickel sulphate ($NiSO_4 \cdot 7H_2O$). This filter absorbed the 3650 and 4047 A mercury lines, excitation being mainly effected by the 2537-2650 A group. A reduced image of the lamp was formed about 5 mm. from the slit of a Hilger medium quartz spectrograph (Slit : 0.1 mm.) which was inclined at 80° to the path of the light. At the slit of the spectrograph was placed a quartz cell (7 x 1 x 1 cm.) containing the solution to be examined.

Procedure: Solutions of the fluorescing substance were made up in petroleum ether (60/80) wherever possible and the concentrations adjusted visually so that no appreciable quenching occurred. Each solution was then exposed for 5 minutes, a number of spectra being registered on the same (Special Rapid) plate. In order to ensure that no shift of the plate took place in the holder, mercury spectra were recorded between each of the fluorescence spectrograms. The plate was then developed using a standardised technique (p. 39).

The positions of the bands were measured using a Hilger microphotometer (slit : 0.2 mm.). The plate was initially oriented in the holder so that the mercury spectra on either side of the spectra were correctly aligned. Measurements were then taken every 0.5 mm. from the ultra-violet edge of one of the mercury lines (either 3342 or 3650 A) until the whole spectrum had been traversed. For accurate determinations, readings were taken every 0.05 mm. near the heads of the bands. From a distance-frequency calibration table, the heads of the bands could thus be found.

In order to measure the relative intensity of the bands, a reading was initially taken of an unexposed part of the plate. The resistance in series with the photo cell was adjusted so that this reading corresponded to the maximum deflection on the scale (50 cm.). Readings were then taken as before and the logarithm of these values subtracted from $\log_{10}50$. Intensity curves were obtained by plotting this different ($\log_{10}$R.I.) against wave numbers.

The curve of chrysene shown in Fig. 4 was obtained with this set-up, using a concentration of 13.3 γ /cc.

B. Fluorescence Spectra in the 3700-4500 A region.

In this case, radiation from a Mazda Compact Source Mercury Lamp (250 watt) was condensed by two quartz lenses (f : 6" and 8") and passed through a Wood's filter. An image about 3 mm. in height was formed close to the spectrograph which was oriented at 80° to the path of the beam as above. Panchromatic plates were used in this case with exposures of 3 minutes. The procedure was the same as that described in Section A. The curve of 1:2-benzanthracene shown in Fig.4 was obtained with this set-up using a concentration of 24.5 γ/cc.

C. Fluorescence Spectra in the 4000 - 6500 A region.

In this set-up, a Hilger medium glass spectrograph replaced the quartz one used above. Green and yellow mercury light were used in the cases of pentacene and 2':3'-naphtha 1:2-perylene respectively by replacing the Wood's filter by other suitable glass filters.

The procedure varied slightly, since a wave length scale was imprinted above and below each spectrogram. Microphotometer readings were taken every 20 A. For accurate readings, the distance of the head of the band from a line on the scale had to be determined and the wave length found thereafter by interpolation.

The curve of 1:2-benzanthracene obtained using a concentration of 98 γ / cc. was the same as that shown in Fig. 4 .

Intensity Measurements.

Intensity measurements were made in some cases by matching the intensity of spectrograms produced by the compound and a standard solution of 3:4-benzpyrene. The ratio of the concentrations required to give the same photographic density was taken as an inverse measure of the relative intensity of the fluorescence.

The Development Process.

(a) For Panchromatic Plates

Developing Solution

Metol	4 g.
Na_2SO_3 (cryst.)	300 g.
Hydroquinone	16 g.
Na_2CO_3 (cryst.)	200 g.
NaBr	4 g.
Water up to	2 l.

One part of this solution was diluted with two parts of water and the plate developed for three minutes at 18°C in total darkness.

(b) For Special Rapid Plates

Solution A

Hydroquinone	36 g.
Na_2SO_3 (cryst.)	200 g.
Citric acid	14 g.
KBr	9 g.
Water up to	2 l.

Solution B : 18% solution of NaOH.

One part of each of these solutions was mixed with two parts of water and the plate developed at 18°C for three minutes in red light.

Fixing in each case was effected by a solution containing 500 g. Hypo, and 50 g. potassium metabisulphite in 2 litres. After ten minutes in this solution the plate was washed for one hour and dried.

Table 6.

The Fluorescence Spectra of Polycyclic Aromatic Hydrocarbons: Maxima in Wave Numbers (cm^{-1})

	Source	Solvent	Exciting Radiation	Positions of Fluorescence Maxima (cm^{-1}).
Fig.3				
2':1'-Naphtha 2:3-fluorene	(d)	P.	25	27580,26170,24800; 26870,25400.
1':2'-Naphtha 1:2-fluorene	(a)	P.	25	27500,26120,24730; 26930.
1':2'-Naphtha 2:3-fluorene	(a)	P.	25	27420, 26000,24620; 26700,25330.
2':1'-Naphtha 1:2-fluorene	(d)	P.	36	27300,25930,24500; 26630.
Fig.4				
Triphenylene	(a)	P.	25	28270
Chrysene	(a)	P.	25	27650,26230,24800; 26800,25330.
1:2-Benzanthracene	(a)	P.	36	25950,24530,23130.
Naphthacene	(b, f)	P.	36	21220,19760.
Fig.5				
3:4:5:6-Dibenzphenanthrene	(a)	P.	25	26570.
Picene	(a,b)	B.	36	26420,25030,23680; 25600,24270.
2':3'-Naphtha 1:2-phenanthrene	(b)	P.	36	25525,23990,22695.
1:2:7:8-Dibenzanthracene	(a,d)	P.	36	25370.
1:2:5:6-Dibenzanthracene	(a)	P.	36	25350,23950,22500; 24630,23270.
2':3'-Naphtha 2:3-phenanthrene	(a)	P.	36	22195,20800,19400.
Pentacene	(b)	Par.	54	17300,16000(?)

	Source	Solvent	Exciting Radiation	Positions of Fluorescenc Maxima (cm^{-1}).
<u>Fig.6</u>				
Fulminine	(b)	B.	36	26770,25370. 26000,24630.
1:2:3:4:5:6-Tribenzanthracene	(a)	P.	36	25750,24370,22900; (26330),25070,23730.
3':2'-Phenanthra 2:3-phenanthrene	(a)	B.	36	23020,21500,20065
<u>Fig.10</u>				
Pyrene	(a,c)	P.	25	26850,26430,26070, 25770,25470.
1:2-Benzpyrene	(a)	P.	25	27250,25750.
3:4-Benzpyrene	(a)	P.	36	24795,23420,22050; 24500,23200; 24100,22880.
1:2:6:7-Dibenzpyrene	(b)	P.	36	25280,23880,22550. 24800.
3:4:8:9-Dibenzpyrene	(a)	P.	36	22270,20950,19430.
2':3'-Naphtha 3:4-pyrene	(b)	P.	36	21900,20500,19130.
3:4:9:10(Di-2':3'-Naphtha)-pyrene	(b)	P.	36	19400,18000,16730. 18670
<u>Fig.10</u>				
Perylene	(a)	P.	36	22830,21530,20100.
2:3:8:9-Dibenzperylene	(b)	P.	36	23120,21660.
2':3'-Naphtha 1:2-perylene	(b)	Par.	57	16270.
Coronene	(f)	P.	36	23870,22500,21230. (principal bands only)
Anthanthrene	(a)	P.	36	23270,21930 22900.
1:2:7:8-Dibenzanthanthrene	(b)	B.	36	21180,19845,18605.

Fig.11	Source	Solvent	Exciting Radiation	Positions of Fluorescence Maxima (cm^{-1}).
6-Aza-chrysene	(a)	P.	25	27670,26200,24770; 26870,25430.
1:2:5:6-Dibenzacridine	(a)	P.	25	25350,23970; 24700.
1-Azapyrene	(a)	P.	25	26900,25530,24270; 26270,24930.
1-Methoxy pyrene	(a)	P.	36	26530,25250,23920; 26230.
6-Aza-3:4-benzphenanthrene	(a)	P.	25	26830,25560,24330; 26330,25000.
3:4:5:6-Dibenzacridine	(a)	P.	36	25480,24100,22770; 24800,23470.
Fig.12				
1':2':3':4'-Tetrahydro-benzpyrene	(a)	P.	25	26330,25030. 25700.
1:2-Diacetoxy-1:2-dihydropyrene	(e)	B.	25	27930,26870,25500.
Phenanthrene	(e)	P.	25	28800,27430,26070; 28000,26600.
1:2-Diacetoxy-1:2-dihydro-chrysene	(e)	B.	25	28900,27500,26170; 28400,26830,25400.
3:4-Diacetoxy-3:4-dihydro-1:2-benzanthracene	(e)	B.	25	28670,27350,26150.
2-Phenyl naphthalene	(e)	P.	25	29230,27900,26430; 28660.
3:4-Benzpyrene diol diacetate	(e)	B.	25	27230,25830,24420.
5:9:10-Trimethyl 1:2-benzanthracene diol diacetate	(e)	B.	25	27870,26880.
20-Methyl cholanthrene diol diacetate	(e)	B.	25	27970,26660,25300.
6:7-Dihydro 20-methyl cholanthrene	(a)	P.	25	28370,27000,25600.
1'-Methyl 1:2-benzanthracene diol diacetate	(e)	B.	25	29070,27700,26500.
3:4-Diacetoxy-3:4-dihydro-1:2:5:6-dibenzanthracene	(e)	B.	25	27070,25700,24300; 26500.
5-Ethyl 7:8-dihydro 1:2-benzanthracene	(a)	P.	36	27270,25870,24470.

Table 7.

The Fluorescence Spectra of 1:2-Benzanthracene Derivatives: Maxima (cm^{-1}).

All measurements were made for petroleum ether solutions using 3650 A as the exciting radiation and a quartz spectrograph.

A. Methyl Derivatives	Source	Fluorescence Maxima (cm^{-1})		
1' Methyl 1:2-benzanthracene	(a)	25680	24330	22970
3 Methyl- "	(a)	25670	24270	22900
4 Methyl- "	(a)	25870	24450	23030
5 Methyl- "	(a)	25850	24430	23030
6 Methyl- "	(a)	25750	24330	
7 Methyl- "	(a)	25770	24330	22930
8 Methyl- "	(a)	25700	24270	22900
9 Methyl- "	(a)	25400	24000	
10 Methyl- "	(a)	25620	24230	22870
2':6 Dimethyl "	(a)	25730	24300	22930
2':7 Dimethyl "	(a)	25570	24150	22770
3':6 Dimethyl "	(a)	25780	24330	23000
3':7 Dimethyl "	(a)	25770	24330	22930
5:6 Dimethyl "	(a)	25270		
6:7 Dimethyl "	(a)	25800	24350	23000
9:10 Dimethyl "	(a)	24670		
B. Other Substituents				
5 Ethyl "	(a)	25890	24500	23030
5-n-Propyl "	(a)	25870	24500	23030
5-iso-Propyl "	(a)	25870	24470	23030
5 Phenyl "	(a)	25670	24260	
5 Carboxy "	(a)	24930		
10 Acetoxymethyl "	(a)	25650	24300	22870
10 Ethoxymethyl "	(a)	25700	24330	22910
10 Hydroxymethyl "	(a)	25670	24300	22900
10 Cyano "	(c)	25180	23830	22500

Specimens were provided by

(a) Professor J.W. Cook,
(b) Dr. E. Clar,
(c) Dr. G.M. Badger,
(d) Miss E.M.F. Stevenson,
(e) Dr. R. Schoental,
(f) Professor J.M. Robertson.

P : petroleum ether,
B : benzene,
Par : liquid paraffin.

25 : 2537-2650 A;
36 : 3650 A;
54 : 5461 A;
57 : 5770 A.

The glass spectrograph was employed when the position of the first maximum was less than 25000 cm^{-1} (4000 A).

The accuracy of measurement of the peaks depended on the sharpness of the band, but in general was approximately ±100 cm^{-1} for the quartz spectrograph and ±70 cm^{-1} for the glass one.

The maxima are grouped into sets (i.e., peaks spaced at approximately a constant frequency interval). This was not done in the case of pyrene owing to the complexity of the spectrum.

SUMMARY.

The fluorescence spectra of a number of polycyclic aromatic hydrocarbons and their derivatives have been investigated and the results obtained, correlated with the corresponding absorption spectrum, when the latter was known. In general, the behaviour of the fluorescence spectrum parallels that of the longest wave length band system of the absorption spectrum. The shortest wave length fluorescence maximum for petroleum ether solution was found in most cases to be shifted approximately 15 A to the red or 15 A to the blue, when compared with the corresponding longest wave absorption maximum for alcohol or benzene solution respectively. As a consequence of this, it was not surprising to find that the introduction of a nitrogen atom into a homocyclic ring did not appreciably alter the position of the spectrum (p.31) since the absorption spectra of homocyclic and the corresponding aza-compounds, in general, occur at approximately the same wave length.

In a number of cases, the mirror symmetry relationship held between the fluorescence band and the corresponding region of the absorption curve but sometimes the latter consisted of more overlapping sets of bands than the former. The case of 1:2-benzanthracene is an example where the main maxima of the fluorescence spectrum correspond to weak maxima in absorption and vice versa (p.26). This fact indicated that an investigation of the fluorescence spectrum should be made in cases where the absorption spectrum is complex, since it is probable that the results obtained may help in the elucidation of the latter.

In order to attempt to correlate the position of fluorescence in the spectrum with chemical reactivity and structure, the fluorescence spectra of a number of isomeric tetra-, penta- and hexa-cyclic hydrocarbons were investigated. The spectral position of the shortest wave length absorption band was found to be dependent (within broad limits) on the number of quinonoid rings which could be accommodated in a 'Kekulé'* structure for the molecule. The results were also interpreted in terms of the Resonance Theory and it was found that, to a first approximation, the position of fluorescence could be correlated with the ratio of the number of 'Dewar'* structures to the number of 'Kekulé' structures (p.16). The fluorescence spectra of a number of more condensed structures (e.g., pyrene, coronene, etc.) were also recorded, but only a few of each type of compound were available. However, as far as possible, the correlation of fluorescence and reactivity

---

*The meaning assigned to the terms 'Kekulé' and 'Dewar' structures in this paper is given in a footnote, p.15.

with structure was discussed. More data on these types of compounds will have to be obtained before wider generalisations (of the kind described above) can be made.

The influence of substitution on the position of the fluorescence spectrum of 1:2-benzanthracene was investigated (p.24). The shifts obtained seemed to depend on the character of the substituent and the position of substitution. The agreement between the shifts of the fluorescence spectrum and the longest wave absorption maximum of 9 monomethyl derivatives was good. No theoretical interpretation of the results was, however, possible.

Alicyclic compounds were found to exhibit spectra similar to those of the aromatic structures present in the compounds (Section 4). This indicated that the study of the fluorescence spectrum of an alicyclic compound might reveal which of a number of possible structures is probably the correct one. It is known that the absorption spectrum of such a compound may give valuable information in this connection, but in view of the simplicity of the technique and the small quantities of material required, fluorescence spectrography provides a useful additional weapon to tackle such a problem.

APPENDIX

The Wave Mechanical Theory of Absorption of Electromagnetic Radiation(60).

According to Wave Mechanics, when the movement of an electron is restricted in space by the operation of an electrical field, then the electron must be treated as a wave, the amplitude of which is known as the wave function ψ. The variation of ψ in space is given by the well known Schrödinger wave equation. Corresponding to each solution of this equation, there is a fixed value of the total energy of the electron. Thus, in the case of a planetary electron in an atom, the 'quantisation' of possible energy levels arises as a direct consequence of this type of treatment.

The picture of electrons rotating in orbits is now replaced by that of standing wave surfaces with antinodes where the electron is most likely to be situated. Thus if n is the 'quantum number', s orbits are regarded as wave surfaces with n spherical nodes (one of which lies at infinity) and p orbits as wave surfaces with one planar node through the nucleus and (n-1) dumb-bell shaped nodes (with one at infinity) (Fig.14)

On either side of each node, the wave function is opposite in phase and continually oscillates

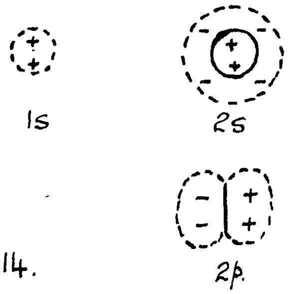


Fig.14.

backwards and forwards. In the case of a planar node (which is directed in space) oscillation gives rise to a fluctuating 'dipole moment'. Such dipole moments are important in connection with the absorption of electromagnetic radiation.

If plane polarised radiation falls on, say, a hydrogen atom, the wave function of the electron in the atom will be set into oscillation by the electric vector (Fig.15).

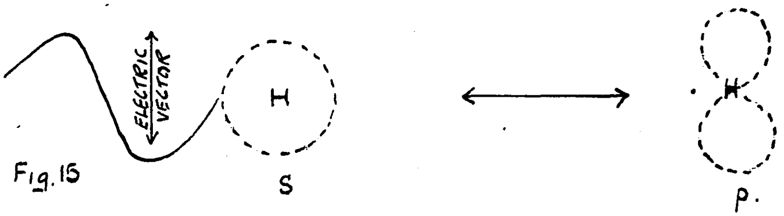


Fig. 15

Two conditions, however, must be satisfied before absorption will occur. 1) The frequency of the radiation must correspond to the difference in energy between two orbitals.

2) A 'dipole moment of transition' must be developed, i.e., the orbital of higher energy must possess one nodal plane in addition to those nodes present in the other orbital. For maximum absorption to occur, the electric vector must be oriented at 90° to this new nodal plane. Thus the 1s ⟷ 2p transition is permitted, but the 1s ⟷ 2s transition is forbidden since the extra node in the 2_p orbital is a planar one, while the corresponding node in the 2s orbital is spherical.

Rigorous wave mechanical treatment of molecules has only been possible in the case of hydrogen. However, various approximate methods of calculation have been used for more complicated molecules and useful results have been obtained. Approximate molecular orbitals are constructed by combining atomic orbitals. Thus the combination of two s atomic orbitals produces a σ molecular orbital, while two p atomic orbitals give rise to a π molecular orbital. Further classification of these orbitals is made as follows:-

σ_g	No nodal planes
σ_u	1 Nodal plane at 90° to the chemical link
π_u	1 Nodal plane containing the molecular axis
π_g.	2 Nodal planes: one containing the molecular axis and the other at 90° to it.

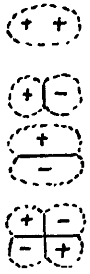


Fig.16.

Thus the transitions $\sigma_g \leftrightarrow \pi_g$, $\sigma_u \leftrightarrow \pi_u$ are forbidden; all the others are 'permitted'.

All C-C and C-H links are of the σ_g type and absorb in the far ultra-violet because of the high energy required to excite one electron to the next highest orbital (σ_u in this case). Thus in general transitions involving σ electrons lie in the far ultra-violet. In the case of ethylene, however, only three of the bonds on each carbon atom are of a σ_g character, the extra link is formed by the interaction of two p orbitals in phase, giving rise to a π_u orbital. Thus a 'double bond' may be regarded as a combination of σ_g and a π_u orbital. It is this latter orbital which produces absorption at 1750 A. In this case an electron passes from a π_u to a π_g orbital.

In the case of benzene, in addition to the two possible orbitals corresponding to the π_u and π_g orbitals of ethylene (1 and 6 in Fig.17), there are also four intermediate possibilities (2,3,4 and 5). The absorption of benzene at 2600 A is attributed to the passing of an electron from orbital 2 or 3 to 4 or 5. This transition is forbidden by the above considerations but becomes permitted when associated with the unsymmetrical vibration corresponding to the lengthening and shortening of the hexagonal atomic skeleton along one direction, Fig.18. The long wave absorption bands of naphthalene and anthracene correspond to similar transitions.

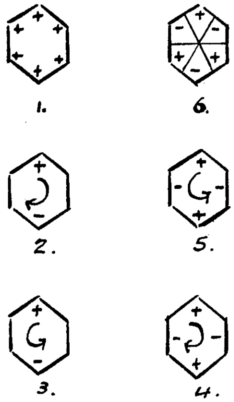


Fig.17.

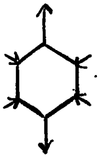


Fig.18

REFERENCES.

(1) Stokes, Phil.Trans., 142, 463 (1852); 143, 385 (1853).

(2) Stark, Physik. Z., 8, 81 (1907).

(3) Henri, J.phys.radium, 3, 181 (1922).

(4) Ley and Engelhardt, Ber., 41, 2988 (1908); Z.physik.Chem., 74, 1 (1910).

(5) Dickson, Z.wiss.Phot., 10, 166, 181 (1911).

(6) Hieger, Biochem.J., 24, 505 (1930).

(7) Cook, Hewett and Hieger, J.Chem.Soc., 1933, 395.

(8) Cook and Hewett, J.Chem.Soc., 1933, 398.

(9) Sannié, Biochem.J., 30, 704 (1936).

(10) Bandow, Biochem.Z., 295, 154 (1937).

(11) Mayneord and Roe, Biochem.J., 30, 707 (1936).

(12) Miescher, Almasy and Kläui, Biochem.Z., 287, 189 (1936).

(13) Hieger, Am.J.Cancer, 29, 709 (1937).

(14) e.g., Chalmers and Peacock, Biochem.J., 30, 1242 (1936).
Peacock, Brit.J.Exp.Path., 17, 164 (1936).
Berenblum and Kendall, Biochem.J., 30, 429 (1936).
Chalmers, Biochem.J., 32, 271 (1938).
Chalmers, Biochem.J., 34, 678 (1940).
Berenblum and Schoental, Biochem.J., 36, 92 (1942).
Berenblum, Crowfoot, Holiday and Schoental, Cancer Research, 3, 151 (1943).
Doniach, Mottram and Weigert, Brit.J.Exp.Path., 24, 1 (1943).

(15) Miller and Baumann, Cancer Research, 3, 223 (1943).

(16) Berenblum and Schoental, J.Chem.Soc., 1946, 1017.

(17) cf. Mayneord and Roe, Proc.Roy.Soc. (London), A.158, 647 (1937).

(18) cf. Ganguly, Indian J.Phys., 18, 347 (1944).

(19) cf. Samburgsky and Wolfsohn, Trans.Faraday Soc., <u>36</u>, 427 (1940).
Seshan, Trans.Faraday Soc., <u>32</u>, 689 (1936).

(20) cf. Bowen, Quarterly Reviews (Chem.Soc.), <u>I</u>, 1 (1947).

(21) cf. Bowen, "Chemical Aspects of Light", London, 2nd Ed., 1946, p.169.

(22) Bowen and Norton, Trans.Faraday Soc., <u>35</u>, 44 (1939).
Miller and Baumann (loc.cit.).
Weil-Malherbe, Cancer Research, <u>4</u>, 102 (1944).

(23) cf. Bowen, Trans.Faraday Soc., <u>35</u>, 15 (1939).

(24) cf. Bowen, "Chemical Aspects of Light", p.122.

(25) Lewschin, Z.Physik., <u>72</u>, 368, 382 (1931).

(26) Clar and Lombardi, Ber., <u>65</u>, 1414 (1932).

(27) Clar and Lombardi, loc.cit., p.1412.
Mayneord and Roe, Proc.Roy.Soc.(London), A.<u>152</u>, 319 (1935).

(28) Chalmers, Biochem.J., <u>35</u>, 1276 (1941).

(29) Clar, Ber., <u>65</u>, 507 (1932)
Mayneord and Roe, Proc.Roy.Soc.(London), A.<u>152</u>, 312 (1935).
Jones, J.Am.Chem.Soc., <u>62</u>, 148 (1940).

(30) Clar, loc.cit., p.506.

(31) Mayneord and Roe, Proc.Roy.Soc.(London), A.<u>152</u>, 319 (1935).

(32) Clar, "Aromatische Kohlenwasserstoffe", Berlin, 1941,p.147.

(33) Clar and Lombardi, Gazz.chim.ital., <u>62</u>, 541 (1932).
Mayneord and Roe, Proc.Roy.Soc.(London), A.<u>152</u>, 320 (1935).

(34) Clar, Ber., <u>65</u>, 1417 (1932).

(35) Clar, Ber., <u>69</u>, 608 (1936).

(36) Clar, "Aromatische Kohlenwasserstoffe", p.148.

(37) Clar, "Aromatische Kohlenwasserstoffe", p.179.

(38) Cook, Annual Reports (Chem.Soc.), <u>39</u>, 162 (1942).

(39) cf. Fieser and Fieser, "Organic Chemistry", Boston, 1944, p.760.

(40) Pauling, "The Nature of the Chemical Bond", New York, 2nd Ed., 1942, p.140.

(41) Clar, Ber., 69, 1677 (1936).
Mayneord and Roe, Proc.Roy.Soc.(London), A.152, 322 (1935).

(42) Titeica, Bull.soc.roumaine phys., 37, No.66,7 (1936).
C.A. 31, 1699 (1937).

(43) Mayneord and Roe, Proc.Roy.Soc.(London), A.152, 323 (1935).

(44) Clar, Ber., 69, 1677, 1679 (1936).

(45) Seshan, Trans.Faraday Soc., 32, 689 (1936).

(46) Clar, Ber., 65, 848 (1932).

(47) Clar, "Aromatische Kohlenwasserstoffe", p.264.
cf. also Patterson, J.Am.Chem.Soc., 64, 1485 (1942).

(48) Clar, Ber., 73, 604 (1940).

(49) cf. Price, Chem.Rev., 41, 257 (1947).

(50) Jones, Chem.Rev., 32, 11 (1943);
J.Am.Chem.Soc., 62, 148 (1941).

(51) Brode and Patterson, J.Am.Chem.Soc., 63, 3252 (1941).

(52) Mayneord and Roe, Proc.Roy.Soc.(London), A.152, 313, (1935).

(53) Pullman (A) Thèses, Paris, 1946, p.33
Pullman (A) and Pullman (B), Rev.Sci., Paris, 84, 145 (1946)

(54) Conrad-Billroth, Ber., 20, 222,227 (1933); 33, 133 (1936).

(55) Jones, Chem.Rev., 32, 1 (1943),
J.Am.Chem.Soc., 67, 2127 (1945).

(56) Clar, "Aromatische Kohlenwasserstoffe"

(57) Braude, Annual Reports (Chem.Soc.), 42, 129 (1945).

(58) Cook and Schoental, J.Chem.Soc., 1948, 170.

(59) Cook, J. Chem. Soc. , 1933,1592.

ACKNOWLEDGMENTS

The author wishes to express his grateful appreciation to Dr. S.T.R.S. Mitchell for suggesting the photochemical problem and for his constant guidance and encouragement.

The author also wishes to thank Dr. R. Schoental for indicating the need for fluorescence spectrographic investigations and for her assistance and valuable criticism during this work.

Thanks are also due to Professor J.W. Cook, F.R.S. for kindly supplying a large number of specimens of polycyclic aromatic hydrocarbons and to Dr. E. Clar, Dr. G.M. Badger, Professor J.M. Robertson, F.R.S., and Miss E.M.F. Stevenson for other specimens.

The author is indebted to the Carnegie Trustees for the award of a Scholarship held during the time this work was carried out.

Thanks are also due to Mr. J.M.L. Cameron for several microanalyses and to Mr. R. McCulloch for technical assistance.