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Contributions to the Study of the Rôle of the Double Bond in the Absorption Spectra of Organic Compounds

CHAPTER I

Introduction

It is proposed in this thesis to carry out a systematic study of absorption spectra, in the visible and ultra-violet, of organic compounds. It is intended to determine the nature of the groups responsible for the absorption and to find some interpretation of this complex problem.

The importance of unsaturation in absorption has been revealed since the pioneer investigations. The strong absorption, in the ultra-violet, of some unsaturated compounds has been recorded, in qualitative determinations, by Hartley and Huntington (Phil. Trans. 1879, *170*. 257), Hartley (J. C. S. 1881, *39*, 153), Magini (Nuov. Cim. 1903, *6*, 343; J. Chim. Phys. 1904, *2*, 410), Stewart (J. C. S. 1907, *91*, 199), etc.

In 1913, J. Bielecki and V. Henri determined the quantitative absorption of ultra-violet rays for some acids of the ethylenic series (C. R. 1913, *157*, 372). V. Henri and his collaborators have made a systematic study of the absorption of organic compounds. The most important results are summed up in V. Henri's «Etudes de Photochimie» (1918).

Concerning the absorption of the ethylenic acids (C. R. *loc. cit.*) Bielecki and Henri conclude: «La liaison éthylènique produit dans les acides une éxaltation de l'absorption des rayons ultra-violets ; cette éxaltation est d'autant plus intense que la liaison double se trouve plus rapprochée du groupe carboxyle».

From the numerical results they conclude: «L'influence d'une

liaison éthylènique ne peut pas être exprimée par un coefficient determiné qui interviendrait comme un terme additif dans la valeur de la constánte d'absorption ; l'éxaltation produite par cette liaison doit être exprimée par un certain facteur qui fait varier la valeur de *e* dans un raport determiné... On peut énoncer la loi générale : Lorsqu'on a un corps de formule A. B. C... la constante d'absorption moleculaire *e* est égale à un produit $e = a.b.c... \alpha.\beta.\gamma...$ dans lequel $a, b, c,...$ sont des facteurs correspondant aux différents groupements moléculaires A, B, C,... et, $\alpha, \beta, \gamma...$ sont des facteurs qui indiquent les influences des liaisons, configurations et positions réciproques de ces groupements».

These results of Henri will not for the moment be discussed further, but the importance attributed to the ethylenic linkage even in the earliest quantitative work must be emphasised.

Definitions and Fundamental Absorption Laws

Before proceeding to the exposition and criticism of the different interpretations of absorption phenomena, let us consider certain fundamental notions.

(1) *Absorbing media* are those in which the intensity of the light diminishes when the path of light in these media increases.

(2) *Chromophores* are groups capable of selective absorption

in the region 1800-8000 A. *e.g.* : $>C=C<$. CO, $\overset{C}{\underset{C}{\overset{\|}{|}}}\overset{C}{\underset{C}{\overset{\|}{|}}}$,
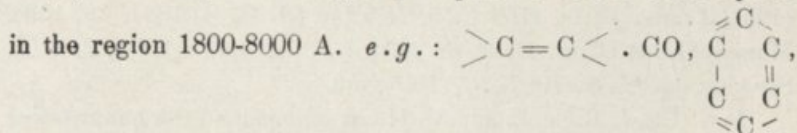
$-N=N-$, etc.

(3) *Auxochromes* are groups that do not in themselves give rise to selective absorption, but when associated with chromophores have a strong influence in the absorption of these, *e.g.*, $:OH$, NH, etc.

(4) *Extinction coefficient* ε of an absorbing medium at a wave-length λ is the inverse of the thickness, expressed in cm., of the medium that reduced the intensity of radiation by 1/10.

(5) *Lambert's Law* — When monochromatic light of intensity I passes through x absorbing layers, the intensity of light is reduced to the fraction $1/n^x$, $1/n$ being the fraction the light

is reduced in each layer. The quantities of light that emerge in the successive layers are $1/n$, $1/n^2$, $1/n^3$, ..., $1/n^x$.

(6) *Beer's Law* — Changes in the concentration of a solution do not modify the absorption phenomena if, in inverse sense, the thickness of the solution traversed by the light is varied proportionally, that is, the absorption of a radiation λ by 0,1 cm. of N. solution is exactly the same as that absorbed by 1 cm. of the N/10 solution, etc.

(7) Hurter and Driffield call *density* the relation $D = \log I_0/I$, in which I_0 is the incident light and I the emergent light. The importance of this notion comes from the fact that the total density of any number of media is equal to the sum of the densities of each medium.

The extinction coefficient may be expressed as a function of the density and the thickness d of the absorbing medium. By definition $\varepsilon = 1/d$. Applying Lambert's law to a medium of thickness d, it follows that: $Id/I_0 = 1/10 = 1/n^d$ $\therefore$ $\varepsilon = \log n$. For a medium of thickness d', it follows that:

$$I/I_0 = 1/n^{d'} \text{ or } \log I/I_0 = - d' \times \log n = - d' . \varepsilon . \therefore$$
$$\therefore \varepsilon = - 1/d' . \log I/I_0 = 1/d' . \log I_0/I .$$

(8) In a solution, according to Beer's Law, the extinction coefficient is proportional to the molecular concentration: $\varepsilon = e. c.$

e is called *molecular extinction coefficient* and is given by the following expression $e = 1/d'c . \log I_0/I$.

General ideas about absorption theory

The absorption and other phenomena such as the dispersion (and perhaps also reflexion and refraction) are explained by the theories of Sellmeier, Ketteler-Helmholtz, Drude, Lorentz, Voigt, Plank and Goldhammer as resonance phenomena between the vibration of the incident wave and vibrators characteristic of molecules, or atomic groups, or isolated atoms, or electrons. The electromagnetic wave supplies energy to the vibrators, which emit this energy modified, producing absorption, dispersion, etc. phenomena.

The absorption in the ultra-violet is explained in the classic

theory (Drude, etc.) as a resonance phenomenon between electromagnetic vibrations and the movement of electrons: with the development of Bohr's theory, the absorption in the ultra-violet is explained nowadays by jumps of certain electrons from normal orbits to others of higher energetic level.

The physical study of emission and absorption spectra has been successful in the case of simple molecules (diatomic molecules). In the case of more complex molecules the degrees of freedom are so many that the calculations are extremely difficult and up to the present progress has been slow.

From the physical point of view, theoretically and experimentally verified in a certain extent, the problem lies in the following state:

(1) The bands in the far infra-red are due to the pure rotation of the molecules. The experimental work of Rubens, Wartenberg and Czerny on hydrogen chloride, and that of Rubens and Hettner on water vapour shew this.

(2) The bands in the near infra-red are due to the vibrations between the atoms that constitute the molecules, with sub-maxima due to the rotational energy of the molecule as a whole. Experimental work of Colby on the hydrogen halides provides evidence for this view.

(3) The bands in the visible and ultra-violet are of electronic origin: the groups and sub-groups into which these bands are resolved are respectively due to vibrational energy (atoms) and rotational energy (molecules or atomic groups).

Ever since the pioneer investigations, physicists and chemists have tried to explain the origin of the absorption bands of organic compounds, both as vapours and in solution in diactinic solvents.

Work of Hartley

Hartley has been the pioneer in absorption investigation and his results although largely qualitative are extremely important.

From his papers the following general conclusions may be taken:

(1) The necessity for the complete study of the absorption of organic compounds, *i. e.* the investigations must include the ultra-violet as well as the visible region.

(2) The division of organic compounds in two groups: compounds that shew selective absorption (absorption bands) and compounds shewing only general absorption.

(3) Hartley established the following law: in the absense of perturbating agents or circumstances the absorption curves of compounds of similar constitution are similar.

This rule opened a large field to chemical research. Determining the absorption curves of organic compounds, Hartley and his collaborators succeeded in definitely establishing the structure of a number of compounds in which the other methods of organic chemistry did not give satisfactory results.

Work of Baly

The first objections to Hartley's law arose from the absorption study of the ethyl acetoacetate.

Baly and his collaborators (J. C. S. 1904, *85*, 1029: 1905, *87*, 766) intended to establish the structure of ethyl acetoacetate and metallic derivatives in which ketonic and enolic forms are possible. The absorption spectra of these compounds were entirely different from those exhibited by the ethyl — β — ethoxycrotonate (fixed ether) and the ethyl ethylacetoacetate (ketonic form). From these results, Baly concluded that the origin of absorption bands cannot be found in any determined structure but in the oscillatory change of linkages involved in a tautomeric equilibrium. This theory has been extended to aromatic compounds, compounds with quinonoid structure, di-ketones, etc., Unfortunately, however, the existence of well marked selective absorption in many compounds for which no tautomeric equilibrium appears to be possible, greatly reduces the value of this theory.

Work of Hantzsch

Hantzsch published in Ber. (1908-1919) a series of papers in which the problem of the ethyl acetoacetate was re-examined, and the absorption of numerous compounds of acidic type in different basic solvents were investigated.

Hantzsch arrived at the following conclusions:

(1) There is a definite correlation between the constitution of compounds and their absorption.

(2) When a compound under different conditions shews different absorption curves, these are due to definite variations in the constitution of the compound.

(3) The selective absorption of the metallic derivatives of compounds of acidic type is due to the reciprocal influence of secondary valencies or residual affinities of the metal and oxygen atoms.

There are many objections to the theory of Hantzsch. Hantzsch himself confesses that in many cases it is impossible to explain the variations of absorption by different constitution formulae. Baly criticised the theory, raising important objections. For instance, there are compounds the constitution of which can be only explained by secondary valencies, which do not shew selective absorption in the visible or ultra-violet. Also, Baly does not find in the theory of Hantzsch the explanation of the similar bands shewn by alkaline solutions of ethyl dimethyl acetoacetate and ethyl acetoacetate, and also to the incipient band of ethyl β — ethoxycrotonate in presence of acid.

Criticising his own work, especially the relation between quinonoid structure and colour, Baly recognised the necessity for a more general theory applicable to the whole spectrum (infra-red, visible and ultra-violet), with a quantitative physical basis. Such a theory should also explain fluorescence and phosphorescence.

Molecular phase theory of Baly

The general theory of absorption spectra of Baly is built up on the following postulates:

(1) A marked correlation exists between selective absorption and the reactivity of compounds, that is, a certain band of absorption is always associated with a definite type of reactivity.

(2) Except in the case of fluorescence or phosphorescence phenomena, the energy absorbed by any compound in the visible or ultra-violet is equal to the energy irradiated in the infra-red.

This postulate implies a relation between the different frequencies in infra-red, visible and ultra-violet.

(3) Each elementary atom possesses one or more frequencies characteristic of the element itself. They are called the elementary atomic frequencies, and are assumed to lie in the far infra-red, (order 2000μ).

(4) When atoms of different elements combine, the resultant molecule possesses a new frequency which is the lowest common multiple of the frequencies of the atoms constituting the molecule. This is called the true molecular frequency. It lies in the near infra-red: order $3 - 10 \, \mu$.

(5) The molecular frequencies in the visible and ultra-violet are regarded as exact integral multiples of a molecular frequency in the near infra-red called the *fundamental infra-red frequency*. The fundamental infra-red frequency is either the true molecular frequency or an exact multiple of this frequency.

The molecular frequencies are the central frequencies of the absorption bands, that is, the frequencies in which the intensity of absorption is maximal, and these frequencies are characteristic of the molecule because they are the only ones that persist at low temperatures.

As a corollary of postulate (5) it follows that the difference between the frequencies of the two consecutive bands in the visible and ultra-violet is equal to the infra-red fundamental frequency which, according to Baly, has been verified experimentally.

(6) Some intra-molecular frequencies are due to specific groups of atoms in the molecule, and the numerical values are given by the lowest common multiples of the elementary atomic frequencies concerned.

(7) The breadth of the absorption bands, observed at ordinary temperatures, is due to the combination of the molecular central frequency with subsidiary frequencies.

The estructure of absorption bands is described by Baly in the following way: a band consists of a series of subgroups symmetrically disposed in relation to the principal subgroup of highest intensity. Each subgroup shews a principal line in which the intensity of absorption is maximal. The frequency differences between two consecutive principal lines are constant and correspond to a characteristic intra-molecular frequency of a specific atomic group. Each subgroup shews a similar structure with differences of frequencies corresponding to elementary atomic frequencies.

According to the ideas of Baly, the elementary atomic frequencies are due to shifts of electrons from certain stationary orbits to others, each electronic transition corres-

ponding to a change of energy related with the frequency as
follows: —

$$E/const. = \nu$$

The true molecular frequencies reflect the loss of energy
associated with the combination of atoms to form molecules.
The energy loss in this combination is called the *molecular quan-
tum*, and it is the lowest whole common multiple of the elemen-
tary quanta of the atoms that constitute the molecule.

The atoms do not lose their individuality when in combina-
tion and therefore the absorption spectra of molecules shew not
only the molecular frequencies as also the atomic elementary
frequencies and the intramolecular frequencies.

As has been already stated, in the mechanism of atomic com-
bination each atom loses a determined amount of energy expres-
sed as a whole number of elementary atomic quanta. The loss
of energy is equally shared by the different atoms and the syn-
thesis of the molecule occurs simultaneously with a loss of
energy equal to the molecular quantum. The newly synthesised
molecule is unstable and loses successive molecular quanta.
Each of these states of the molecule, corresponding to the succes-
sive losses of molecular quanta, is one *phase* of the molecule.
Thus, the molecule presents, in different conditions, different pha-
ses differing one from another by whole numbers of molecular
quanta. The different phases exhibit different fundamental fre-
quencies which are integral multiples of the molecular frequency.
Under defined conditions (medium etc.) a molecule exhibits a
definite «phase» which is then stable while the conditions remain
constant. Each molecular phase is characterised in the visible
or ultra-violet by a definite absorption band. A molecule in a
certain phase, if exposed to a suitable source of radiation, chan-
ges to another phase. The molecules very often exhibit different
phases in different solvents. In this way, an explanation of the
variability of the absorption spectra of certain compounds in
different solvents is obtained.

The fluorescence and phosphorescence are explained on the
basis of this theory by assuming that the absorbed quantum may
be emitted either as a whole number of infra-red, visible or
ultra-violet quanta, the integer varying with the wave-length of
the light emitted.

Work of Henri

The work of Henri and his collaborators concerning absorption spectra marks a definite advance in these studies, not only in technique, but also in the interpretation and rationalisation of this branch of spectroscopy.

With the advent of the technique used by Henri and his collaborators a new stage in the development of the subject was reached and even their earlier results are entirely comparable with those of present day methods. The qualitative technique, or better, the semi-quantitative technique of Hartley, has been replaced by the quantitative measurement of the absorbed light. The method of Hartley consisted of measuring the frequencies at which the absorption is complete when the light passes through a solution of fixed thickness and concentration. The concentration of the solution is diminished, the thickness being maintained the same, until the solutions do not exhibit any absorption. The absorption curves were plotted by marking in abscissae the oscillation frequencies of light and in ordinates the thicknesses expressed as a fixed concentration corresponding to the different solutions used, which is legitimate provided Beer's law is valid for the substance studied.

Henri measured quantitatively the light absorbed by the solutions. The absorption of substances in solution was for the first time expressed in molecular extinction coefficients, $e = \log I_0/I /c. d.$ in which. (as has already been stated) I_0/I is the ratio of the incident light to the emergent light, c is the molecular concentration of the substance in diactinic solvent, and d the thickness of the solution expressed in centimeters. Henri has devoted special attention to the choice of a convenient light source. He used a spark between iron-cadmium electrodes which gives a very rich spectrum for $\lambda > 214$ mμ. For shorter wave-lenghts, $\lambda > 193$ mμ, Henri considers very convenient the use of zinc and aluminium electrodes. A high frequency spark between electrodes of aluminium under distilled water was used as a light source giving a continuous spectrum.

Space does not allow a detailed account of the work of Henri, especially in the part concerning infra-red absorption spectra.

Henri and his collaborators carried out a systematic study of

absorption of organic compounds in the infra-red, visible and ultra-violet in order to determine the influence in absorption of CH_2 , CH_3 , OH , CO , CHO , $COOH$, $C:C$, $C\vdots C$, benzenic, naphthalenic, anthracenic, phenanthrenic, etc., groups, existing each one by itself, or two or more simultaneously in the same molecule.

A brief account may be given of the most important conclusions of Henri.

Rule of absorption of saturated acids and alcohols. — When we pass from the acid $C_n H_{2n+1} COOH$ to the acid $C_n H_{2n+1} CH_2 COOH$ or from the alcohol $C_n H_{2n+1} OH$ to the alcohol $C_n H_{2n+1} CH_2 OH$, the absorption curve is displaced to the red, the differences of the frequencies to the same absorption being equal to $\Delta \nu = 20 \cdot 10^{12}$ that it is the characteristic frequency of the CH_2 group. (Subsequent work has not confirmed this generalisation).

Rule of absorption of saturated esters — The ultra-violet absorption of the esters of general formula $C_n H_{2n+1} COOC_p H_{2p+1}$ differs very little from the absorption of the corresponding acid $C_n H_{2n+1} COOH$.

Rule of absorption of the salts of saturated acids — The absorption of the salts of saturated acids is not so intense as that of the corresponding acids.

By comparing the results obtained in the infrared, visible and ultra-violet, V. Henri established the following rules:

(1) The frequencies of the absorption bands in the visible and ultra-violet are whole number multiples of the frequencies of the infra-red bands.

(2) Substances that give rise to several bands in the infra-red exhibit several bands in the ultra-violet, the frequencies of which are equal to the same integral multiple of the frequencies of the infra-red bands. (The above statements can scarcely be justified to-day).

Henri established the following rules concerning the mutual influence of chromophoric groups:

(1) When the molecule of a substance contains two chromophores the substance exhibits the characteristic absorption bands of these chromophores: if the groups are near, the positions of the bands are displaced to the longer wave-lengths, and the intensities are only slightly modified: if the chromophores are sepa-

rated, the positions of the bands are not modified, but the intensities of the absorption increase. (There can be no doubt that this statement contains much truth.)

(2) An atomic group A possesses in the infra-red a certain number of absorption bands with frequencies ν_1, ν_2, ν_3, ... and in the ultra-violet absorption bands with frequencies:

$$\nu' = n \cdot \nu_1 ; \quad \nu'' = n \cdot \nu_2 ; \quad \nu''' = n \cdot \nu_3 ; \quad \ldots$$

n being a whole number. The principal difficulty here depends on the fact that the hypothesis is too elastic to be fruitful.

(3) When in the molecule of a substance a group A occurs together with other groups B, C. D.... this substance exhibits in the infra-red the $\nu_1, \nu_2, \nu_3 \ldots$ bands and in the ultra-violet bands with the frequencies

$$\nu'_1 = (n - r) . \nu_1 ; \quad \nu''_1 = (n - r) . \nu_2 ; \quad \nu'''_1 = (n - r) . \nu_3 ; \quad \ldots$$

in which r is a whole number. Again, the hypothesis is too readily adaptable to any set of data to throw much light on the mechanism of absorption.

(4) The value of r, characterising the displacement of the bands, depends upon the distance of the group A in relation to the other groups and upon the atomic composition of these groups.

Regarding the problem of the relation between the intensity of absorption and the complexity of the molecules, in first place, Henri advanced the following generalisation:

The highest intensity of absorption in the ultra-violet corresponds with the greatest chemical lability.

According to Henri, the influence of B. C. D.... groups upon the absorption coefficient of the atomic group A is different in the infra-red and ultra-violet. In the infra-red the change of the molecular absorption coefficient e is additive: in the ultra-violet, as a first approximation, the absorption coefficient varies in geometric progression with increasing complexity of the molecule.

Starting from these rules, Henri considers it possible to calculate the extinction curves of any compound of known structure if the absorption of the different chromophores that constitute the molecule is known. The following method of calculation is des-

cribed by Henri: Let us consider a molecule constituted by two chromophores, A and B of which the absorptions are known. The absorption curve of a solution that contains equimolecular quantities of two molecules, of which one contains the chromophore A and the other the chromophore B is measured. The extinction curve of the compound that contains A and B is obtained from that of the mixture by multiplying the frequencies of the infra-red bands by a whole number, which gives the displacement to the visible bands of the compound which contains both A and B, in relation to the bands exhibited by the mixture of the molecules that contain separately the two chromophores. The absorption coefficients are multiplied by a second constant.

The modified frequency of the chromophore A is $\nu = \nu_0 + r . \nu_i$ in which ν_0 is the frequency of the chromophore A in the mixture, ν_i is the frequemcy of the infra-red band related to the ultra-violet band, and r is a constant, usually equal to 1, 2, 3, 4, or 5.

The molecular extinction coefficient is given by the expression $e = \alpha . e_0$.

According to Henri, the extinction curves of thousands of compounds may be calculated, the results agreeing very well with experience. In spite of initial successes with relatively simple compounds, it does not appear that Henri's optimism was in any real sense justified.

The work of Victor Henri, although very important, is to be regarded as exploratory rather than definitive; the broad scope of the investigations has to a considerable extent been obtained at the expense of finality in interpretation.

During recent years, Mme Ramart-Lucas and her collaborators have published in the Comptes Rendus and in the Bull. Soc. Chim. de France, a series of papers which on account of the care devoted to purity of compounds and accuracy of observations, we consider to be among the most important and definite contributions to the knowledge concerning absorption phenomena.

Work of Mme Ramart-Lucas

Mme Ramart-Lucas, in a very clear way, defines *transparent groups* and *absorbing groups* or *chromophores*. She assumes the transparency for $\lambda > 1900$ A, of all saturated hydrocarbons, cyclic or acyclic, and considers *transparent* any group which when introduced into any saturated hydrocarbon, does not modify the transparency. *Absorbing groups* or *chromophores*, are those groups which when introduced into any saturated hydrocarbon, give rise to a selectively absorbing molecule. According to these definitions, the groups CH_3, CH_2, and CH are transparent. The halogens sulphur, $-NO$, $-NO_2$, $-NH_2$, $-SH$, $-CN$, $-COOH$, $>C:O$, $>C:S$, $-CH:CH-$, $>C:C<$, etc. are chromophores. The notion of chromophore is generalised to radicals of valency n, these being considered chromophores if united to n monovalent alkyl radicals give rise to coloured molecules, e. g.: benzenic, naphthalenic, anthracenic groups, etc. When the chromophore contains carbon atoms, the saturation of the free valencies by hydrogen atoms gives rise to an absorbing molecule. It is difficult to make a rigid correlation between a chromophore and a specific «colour» (ultra-violet or visible) because the chromophore may give rise to different «colours» in different compounds. The «colour» due to a certain chromophore in a molecule depends not only upon the constitution of the chromophore but also upon the atoms or atomic groups to which the chromophore is linked. For instance, the $>C:O$ group exhibits different «colours» in formaldehyde, acetaldehyde, acetone, formic acid, acetic acid, pinacoline, hexamethyl-acetone.

In contradiction to certain rules advanced by Henri (absorption of the homologous series $C_n H_{2n+1} . COOH$ and $C_n H_{2n+1} . OH$) Mme Ramart-Lucas enunciated the following rules ([1]).

([1]) Resting her conclusions on the investigations of Hantzsch on the saturated fatty acids, on the observations of Ley on the alkylanilines, on those of Rice on the ketones of general formula $CH_3 COCH_2 R$ and on her own work in the collaboration of Mlle Biquard and M. Grunfeld (C. R. 1930, *190*, 1196) on the saturated fatty acids and with M. Hoch (C. R. 1932, *194*, 96) on the alkylphenylketones, on the homologues of methyl stirolene, diphenoxymethane, phenoxybutiric acid, etc.

(1) The CH_3, CH_2, (and CH) groups are transparent in the ultra-violet to all wave-lengths longer than 2000 A.

(2) In a straight chain homologous series containing only a single functional (absorbing) group, the molecular weight does not affect the absorption (the first term of the series is always slightly abnormal).

From these rules an extension may be made to the compounds: —

$A.(CH_2)_n.B$ in which A and B are two functional or absorbing groups. It may be expected that the absorption will be independent of the length of the $(CH_2)_n$ chain, and will depend only on the nature and mutual influence of the A and B groups. Studies of the mutual influence of the two chromophores have been carried out by Mme Ramart-Lucas and her collaborators for several series of compounds of general formula $A.(CH_2)_n.B$, e. g. : $C_6H_5(CH_2)_n.COOH$ esters, amides and nitriles; $(CH_3)_3$ $C_6H_2(CH_2)_n.COOH$; $C_6H_5.O.(CH_2)_n.COOH$; C_6H_5 $(CH_2)_n.CO.CH_3$ etc. From the results of these investigations the following rules have emerged: —

(1) When the chromophores are directly linked $(n = O)$, the absorption differs profoundly from the absorption due to the superposition of the already definite defined «colours» of each of these cromophores in a carbon chain. (This rule is in complete disagreement with the corresponding one enunciated by Henri).

(2) When the chromophores, without being directly linked are linked to the same carbon atom, they reacquire wholly or in their separate individuality.
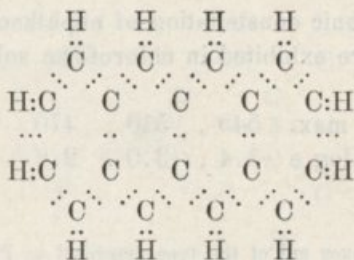
(3) When the chromophores are separated by two or more carbon atoms in a straight chain, they reacquire completely their individual properties. The absorption curves of these compounds agree exactly with those of equimolecular mixtures of substances the chromophores in each of which contain only A or B. This last rule is subject to exceptions in cases where the $(CH_2)_n$ chain is bent around itself to a greater or lesser degree. The first rule greatly limits the validity of Henri's calculations on the absorption curves of molecules containing more than one chromophore, the absorption of each by itself being known. The comparison of glyoxal, diacetyl and acrolein extinction curves whith those of acetone and acetaldehyde provide good examples of the profound

changes in absorption which occur when the two chromophores are directly linked ([1]).

Considering the problem of the relation between absorption and reactivity due to chromopheric groups, Mme Ramart-Lucas criticises the rule of Staudinger which states that «any chemical substitution which displaces the absorption to the visible, diminishes the state of saturation of the molecule» and also the rules suggested by Henri. Mme Ramart-Lucas in the present state of knowledge considers that generalisation cannot go further than statement (based on measurements of reaction velocities) that «a chromophore exhibits the same reactivity in any molecule into which it introduces the same «colour».

Work of D. Radulescu and e Clar

D. Radulescu and his collaborators (Ber. 1931, *64*, 2223 et seq.) studied the absorption of unsaturated hydrocarbons, (*a*) with conjugated double bonds in open chains (crocetin, bixin, carotinoids), (*b*) polycyclic compounds (anthracene, phenanthrene, pyrene, perylene, 2:3 — benzanthracene) and also the diphenyl-polyenes of Kuhn. To interpret the results obtained, Radulescu assumes that the absorption spectra of these compounds are due to complex aggregates of valency electrons, «gemeinschafts--Resonatoren» (shared-Resonators) or «electron constellations». The results obtained with naphthacene and its derivatives (Radulescu and Barbulescu, Z. Physikal Chem., 1929 *B 5*, 177) are particularly interesting and representative. Naphthacene dissolved in CCl_4 presents an electronic constellation of 54 conjugated electrons

$$
\begin{array}{ccccc}
\text{H} & \text{H} & \text{H} & \text{H} & \\
\ddot{\text{C}} & \ddot{\text{C}} & \ddot{\text{C}} & \ddot{\text{C}} & \\
\text{H:C} & \text{C} & \text{C} & \text{C} & \text{C:H} \\
\text{H:C} & \text{C} & \text{C} & \text{C} & \text{C:H} \\
\ddot{\text{C}} & \ddot{\text{C}} & \ddot{\text{C}} & \ddot{\text{C}} & \\
\ddot{\text{H}} & \ddot{\text{H}} & \ddot{\text{H}} & \ddot{\text{H}} &
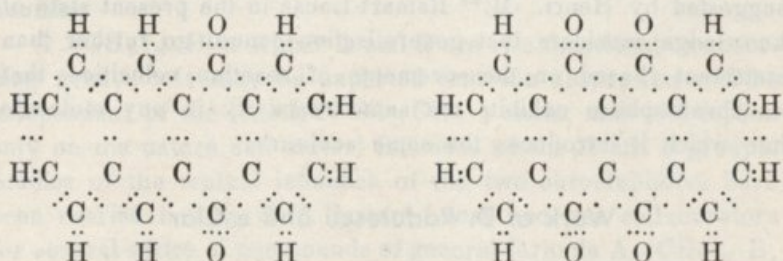\end{array}
$$

([1]) Lifschitz (Zeit. f. Physik. Ch. *95*, 126) has contested theoretically the value of Henri's results on the «a priori» calculations of the absorption of solutions.

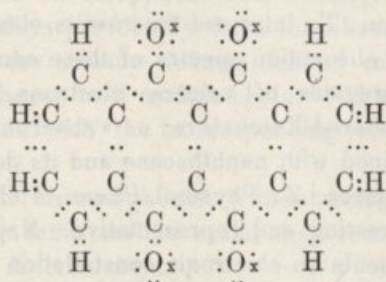The absorption curve in the visible exhibits 3 bands

$$\lambda \text{ max.} \quad 480, \quad 450, \quad 420 \quad ^{m\lambda}$$
$$\log \varepsilon \quad 2.4, \quad 2.3, \quad 2.05$$

The quinones derived from naphthacene, in which the characteristic

```
    H   H   O   H              H   O   O   H
    C   C   C   C              C   C   C   C
H:C   C   C   C   C:H      H:C   C   C   C   C:H

H:C   C   C   C   C:H      H:C   C   C   C   C:H
    C   C   C   C              C   C   C   C
    H   H   O   H              H   O   O   H
```

electronic constellation disappears., shew only continuous general absorption in the visible.

The diquinone halochromic complexes ([1]), in which $X = SO_3$ or $SnCl_4$

```
        H   :O:ˣ   :O:ˣ   H
        C    C      C     C
    H:C    C      C     C   C:H

    H:C    C      C     C   C:H
        C    C      C     C
        H   :O:ˣ   :O:ˣ   H
```

present the electronic constellation of naphthacene: the 3 characteristic maxima are exhibited in chloroform solution

$$\lambda \text{ max.} \quad 545, \quad 510, \quad 470 \quad ^{m\lambda}$$
$$\log \varepsilon \quad 3.4, \quad 3.0, \quad 2.8$$

([1]) These complexes are of the type described by Pfeiffer. The affinity of the oxygen atom is partially saturated by the added molecule: part of the carbon atom affinity becomes free and it is known that a trivalent carbon atom is intensely chromophoric: the carbon atom here is not precisely trivalent: it is in an intermediate state which is the characteristic postulate of Pfeiffer's theory.

Similar behaviour by other compounds of this type corroborates the ideas of Radulescu. In the last example, the displacement of the bands must not be ascribed to changes in the electronic constellation, but to changes of polarity caused by the introduction of the SO_3, $SnCl_4$, etc., groups.

Radulescu also assumes a valency tautomerism for the polycyclic hydrocarbons the phases of which are given by the electronic formulae of J. J. Thomson and the formulae with a bridged link in the *para* position. The tautomeric equilibrium of anthracene is as follows
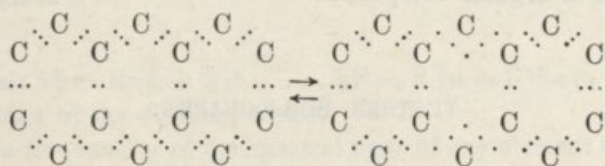
According to Radulescu, the absorption bands in the visible are due to the 'bridged' phase, the electrons of the bridge being controlled by both *meso*-carbons.

E. Clar and his collaborators (Ber. 1930-1932) have investigated the problem of the structure of polycyclic hydrocarbons. In order to explain the differences of *meso*-reactivity of the different hydrocarbons and the differences of absorption, Clar assumes that these hydrocarbons exhibit a type of valency tautomerism which in anthracene for instance is expressed by the equilibrium between the o-quinonoid and the di-radical forms

o-quinonoid form   di-radical form
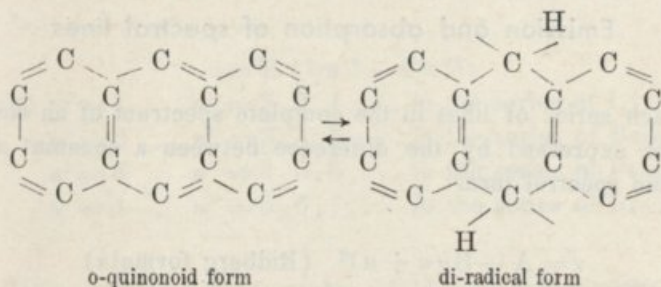
The meso-reactivity and the absorption in the visible are ascribed to the di-radical form which contains unshared electrons

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on the meso-carbons. The hydrocarbons presenting the di-radical form, give addition compounds whith maleic anhydride and exhibit selective absorption in the visible. The addition compounds do not shew the visible bands and the spectra are reduced to the characteristic absorption of the benzenoid and naphthoid groups.

The linear relation between the log e max. of the first bands of the polycyclic hydrocarbons and the reduction potencials of the corresponding quinones appears to throw some light on the problem of the relationship between colour and p-quinonoid structure in organic compounds.

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CHAPTER II

Emission and absorption of spectral lines

Each series of lines in the complete spectrum of an element can be expressed by the difference between a constant and a variable spectral term :

$$\nu = A - B/(n + u)^2 \quad \text{(Ridberg formula)}$$

in which A is the frequency of the convergence limit of the series, B is a constant depending upon the degree of excitation

of the atom, n a variable integer (serial number) and u a constant for the atom concerned.

In the arc spectrum of an element $(B = R = 3.29 \times 10^{15} \text{ sec}^{-1})$ the majority of the lines belong to 4 distinct series:

Principal $\quad u = P \; ; \nu = R\left(1/(1+S)^2 - 1/(n+P)^2\right)$ or $\nu = 1S - nP$

Difuse $\qquad u = D \; ; \nu = R\left(1/(2+P)^2 - 1/(n+D)^2\right)$ or $\nu = 2P - nD$

Sharp $\qquad u = S \; ; \nu = R\left(1/(2+P)^2 - 1/(n+S)^2\right)$ or $\nu = 2P - nS$

Fundamental $u = F \; ; \nu = R\left(1/(3+D)^2 - 1/(n+F)^2\right)$ or $\nu = 3D - nF$
  (Bergmann)

in which $1S = R/(1+S)^2, \ldots, nF = R/(n+F)^2$ are the spectral terms of the different series.

The frequencies of the spectral lines of any element are obtained by subtraction of the terms, these subtractions being regulated by the combination principle of Ritz and its restrictions.

The *combination principle of Ritz* (1908) states that in any spectrum resolved into series, the frequency of any line may be expressed by the difference between two terms and with some exceptions each difference between any pair is the frequency of an observed line.

The possibilities of combination between the terms are limited by the following rules:

(1) Two terms belonging to the same series do not combine.

(2) The S terms only combine with P terms, P terms with S and D terms, D terms with P and F terms.

In the case of the atom of hydrogen, Rydberg's formula is

$$\nu = R \left(1/n'^2 - 1/n''^2\right)$$

with $n' = 1$, $n'' = 2, 3, 4, \ldots$ in the series of Lyman

$\qquad n' = 2$, $n'' = 3, 4, 5, \ldots$ in the series of Balmer

$\qquad n' = 3$, $n'' = 4, 5, 6, \ldots$ in the series of Paschen

$\qquad n' = 4$, $n'' = 5, 6, 7, \ldots$ in the series of Brackett.

Bohr arrived at this formula with his conception of the hydrogen atom in which an electron of mass m and electrical charge $- e$ moves in circular orbits (stationary states) around a nucleus of

positive charge $+ e$, the stationary states being determined by the restriction equation of Bohr

$$m \cdot a^2 \cdot \omega = \text{angular momentum of rotation} = nh/2\pi$$

in which a is the radius of the orbit, ω the angular velocity and h the constant of Planck ($h = 6.55 \ 10^{-27}$ erg. sec.).

Thus, the hydrogen atom in different states of excitation corresponds to a central positive nucleus of charge $+ e$ and an electron of charge $- e$ occupying concentric orbits defined by the quantum number n, each orbit n corresponding to an energy level E_n and a frequency ν_n

$$\nu_n = 2\,A/n^3 h \quad , \quad E_n = A\,(1 - 1/n^2) \quad\quad (A = 2\,\pi^2\,e^4\,m/h^2)$$

Sommerfeld, considering the necessity of elliptical orbits [1] of the electron gave to this two degrees of freedom, the electron being defined by two variables r and θ to which correspond two restriction equations and thus two quantum numbers n_a (azimuthal quantum number) and n_r (radial quantum number) but the total energy of the system is determined by the total quantum number $n = n_a + n_r$, the energy of the levels being equal to

$$E_{n_a,\,n_r} = A\,(1 - 1/(n_a + n_r)^2)$$

and independent of the shape of the orbits (circular or elliptical).

The spectrum of ionised helium may be studied in a similar way, but when the atom contains more than one electron only a qualitative solution of the problem is possible on the basis of these simple assumptions.

The similarity of the spectral terms of any element with the spectra of hydrogen and ionised helium suggests that the essential factor in each stationary state is the orbit of an electron in relation to the atom residue, the transition of this radiating electron from one of these stationary orbits to the others giving rise to the spectral lines. The radiating electron moves in a

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[1] The structure of the spectral lines of hydrogen, the Stark and Zeeman effects, etc., only can be explained by the elliptical orbits of the electron.

spherically symmetrical and central field; its movement is the resultant of two superposed movements, one elliptical and the other a rotation of this ellipse around the centre of force. The system is defined by the total quantum number n and the azimuthal quantum number k. The energy of the system corresponding to the stationary state n_k is $-W_n = -AZ^2/n^{*2} = -RhZ^2/n^{*2}$ in which $n^* = n + \delta$, δ depending only upon the azimuthal quantum number and Z being the number of positive electrical units e in the atomic residue. In this way it is obtained a correspondence between the empirical spectral terms $RZ^2/(n+S)^2$, ... and $RZ^2/(n+\delta)^2$, being evidently $n + S = n + \delta$ [1].

Some important conclusions follow from these results. As δ and thus S, P ... depend only at a first approximation, on the azimuthal quantum number, the terms of a series, e.g. S, correspond to a constant k number, and a varying total quantum number n. Examination of the effective quantum numbers corresponding to the P, ..., F sequences shews that the correction diminishes from the P to the F terms, the F orbits being the closest to those of the hydrogen atom and it is also evident that the k values increase progressively from the S to the F terms, the presumption that S terms correspond to $k = 1$, P terms to $k = 2$, D terms to $k = 3$, and F terms to $k = 4$ being justified. Thus the restriction to the Principle of Combination may be expressed in the quantum theory as only those spectral terms in which the difference of azimuthal quantum numbers is equal to unity $\Delta k = \pm 1$, can combine.

The spectral lines frequently exhibit multiple structures (doublets, triplets, etc.). The multiple spectral terms are usually expressed by the notation of Russel and Saunders (Astrophys. J., 1925, *61*, 38). The complete system of doublets is given by $n^2 S_1$; $n^2 P_1$, $n^2 P_2$; $n^2 D_2$, $n^2 D_3$; $n^2 F_3$, $n^2 F_4$, in which S, P, D, and F characterise the sequences, the multiplicity is indicated by the superior left index, the component of the term by the suffix and the number of the series by the prefix n. The combination of the terms is regulated by the principle of Ritz

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[1] n and $\overline{n}$ are not necessarily the same, because the first is a serial number and the second an empirical value.

and a further restriction which states that only the terms which suffixes are different by O or ± 1 can combine.

To explain the multiple structure of the spectral lines a third quantum number has to be introduced. According to J. Goudsmit and Uhlenbeck (1926) the valency electrons (or more generally the electrons) are not point particles but possess an intrinsic spinning angular momentum equal to half unit of Bohr $1/2 \, (h/2\pi)$. Thus, in any atom with one valency electron, although the atomic residue possesses an angular momentum equal to O, the total angular momentum of the atom is the vectorial sum of the intrinsic angular momentum of the valency electron and the angular momentum of the electronic orbit

$$\overrightarrow{1/2 \, . \, (h/2\pi)} \; + \; \overrightarrow{lh/2\pi} = \overrightarrow{jh/2\pi}$$

in which $l = k - 1$ [1] and j is the new quantum number (inner quantum number). The values of j are limited by $l + s \geq j \geq l - s$ and instead of one energy level corresponding to n_k there are as many as the possible values of j compatible with n and k.

The spectral terms of the elements and ions with one valency electron are *singlet* in the sharp series $(l = O \; ; \; j = \frac{1}{2})$ and doublet in the principal $(l = 1; j = 1/2, 3/2)$, diffuse $(l = 2; j = 3/2, 5/2)$ and fundamental $(l = 3 \; ; \; j = 5/2, \, 7/2)$ series.

The elements or ions with more than one valency electron usually possess spectral terms with different degrees of multiplicity. Each electron in the outer shell is defined by the three quantum numbers n, l, s; in the atom taken as a whole, the angular momenta $lh/2\pi$ of each valency electron are composed together giving a resultant equal to $Lh/2\pi$, and similarly the spinning angular momenta of the electrons give rise to $Sh/2\pi$. From these two values the total angular momentum of the atom is obtained, $jh/2\pi$. Thus the atom as a whole is defined by n, L and S and so are the spectral terms. $L = 0, 1, 2, 3$ gives respectively the sharp, principal, diffuse and fundamental series of terms and S the multiplicity of the lines, being $r =$ multiplicity of the spectral terms $= 2S + 1$.

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[1] l, the linear quantum number has a clear signification in Schrödinger's mechanics.

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CHAPTER III

Emission and absorption band spectra

Band spectra arise from molecules or molecular ions contai-
ning more than one atom.

From the spectroscopic standpoint, the molecules can pos-
sess three types of energy: rotational, vibrational and electronic
energy.

Rotation spectra

The pure rotation bands lie in the far infra-red (100 μ ca)
and are only exhibited by heteropolar molecules, the absorbed
energy being transformed into rotational energy or the emitted
energy being of rotational origin.

The rotation bands in diatomic molecules consist of series
of well defined maxima, the frequencies of which form appro-
ximately an arithmetic progression $\nu = m \cdot b$ or more accura-
tely $\nu = m \cdot b - d \cdot m^3$ (Czerny), in which b and d are constants
(d being very small in relation to b but not negligible) and m
an integer. The pure rotation band of HCl lies between 44
and 120 μ, m varying from 4 to 11 and the values of b and d
being respectively 20.832 cm^{-1} and 2.09 10^{-3} cm^{-1}.

Applying the quantum theory to the rotation of a simple
diatomic molecule, the following expression to the rotational
energy is found:

$$E_r = m^2 h^2 / 8 \pi^2 I$$

in which m is an integer, h the Planck's constant, and I the
moment of inertia.

The new quantum mechanics introduce into the value of the rotational energy the following modification: $E_r = m(m+1)h^2/8\pi^2 I$. The energy levels $h^2/4\pi^2 I$, $3h^2/4\pi^2 I$, $6h^2/4\pi^2 I$, $10h^2/4\pi^2 I$ correspond respectively to values of $m = 0, 1, 2, 3$, and as Δm can only be ± 1 the frequencies of the lines are $\nu = (m+1)h/4\pi^2 I$

$$10\,h^2/4\pi^2 I$$
$$4\,h/4\pi^2 I$$
$$6\,h^2/4\pi^2 I$$
$$3\,h/4\pi^2 I$$
$$3\,h^2/4\pi^2 I$$
$$2\,h/4\pi^2 I$$
$$h^2/4\pi^2 I$$
$$h/4\pi^2 I$$
$$0$$
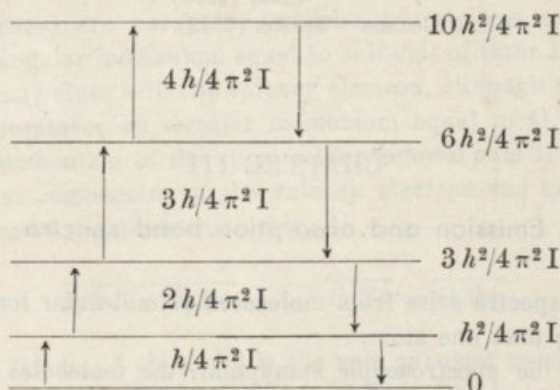
$(m = 0, 1, 2, \ldots)$ which form an arithmetic progression. Therefore the empirical constant b may be identified with $h/4\pi^2 I$, the dm^3 term being a correction which accounts for the increase in the moment of inertia of the molecule when it rotates rapidly.

Vibration-rotation spectra

The rotation-vibration bands lie in the near infra-red and are characterised by a series of sharp submaxima nearly equally spaced on the frequency scale. There is however one striking exception to the constancy of $\Delta\nu$, since an interval of $2\Delta\nu$ occurs in the middle of the band. At the point where maximum might be expected to occur, there is in fact a minimum as though the central frequency were missing.

If ν_r is the frequency of the centre of the band, the frequencies of the sub-maxima are expressed by $\nu = \nu_r \pm bm$ or $\nu = \nu_r \pm bm + cm^2$, ν_r being the interatomic vibration frequency, the other terms, which give the fine structure of the band, corresponding to the rotation of the molecule and being superposed on the atomic vibration which fixes the position of the head of the band.

Applying the quantum theory to a dipole molecule which

rotates as a whole round one of its principal axes, and the atoms of which vibrate linearly whith respect to one another, the total energy corresponding to the stationary state (p, m) is found to be:

$$E_{p,m} = E_p + E_r = p.h.\nu_v + m^2 h^2/8\pi^2 I$$

or, according to the new quantum mechanics,

$$E_{p,m} = (p + \tfrac{1}{2})h\nu_v + m(m+1)h^2/8\pi^2 I$$

If the molecule is heteropolar and the vibrations and the rotations are harmonic, only transitions in which $\Delta p = 0$ or ± 1 and $\Delta m = \pm 1$ are possible and energy may be emitted or absorbed with the frequencies:

$$\nu = \nu_v \pm (m+1)h/4\pi^2 I \quad (m = 0, 1, 2, 3 \ldots)$$

This formula explains the gap in the middle of the band (the second term never can be equal to O) and states that the fine structure in these bands is of the same type found in pure rotation spectra.

Colby found for the vibration-rotation spectrum of HCl

$$\nu = 2886.07 \pm 20.6\,m - 0.301\,m^2 \mp 0.00206\,m^3$$

in which 2886.07 corresponds to ν_v, $\pm 20.6\,m$ to the rotation frequencies, $\mp 0.00206\,m^3$ being a correction corresponding to the changes of the moment of inertia and $-0.301\,m^2$ a correction corresponding to the mutual influence of vibration and rotation and also to the anharmonic nature of the oscillator. (In the near infra-red spectrum of HCl, a series of bands corresponding to transitions in which $\Delta p \neq 1$ have been accurately observed and correlated with anharmonic nature of the oscillator).

Electronic bands

Electronic bands are ascribed to simultaneous changes in the electronic, vibrational and rotational states of the molecules. These bands lie in the infra-red, visible and ultra-violet.

In a molecule, each electronic energy level n is associated with

a certain number of vibrational energy levels ($p = 0, 1, 2, 3 \ldots$) and to each of these correspond rotational energy levels ($m = 0, 1, 2, 3 \ldots$). Thus a great number of lines may be expected due to the combination of all these energy levels.

In a definite state, a molecule is defined by the quantum numbers n, p, m, and the frequency of a line corresponding to the transition n', p', m' to n'', p'', m'' *is*:

$$\nu = \mathrm{E}_{n''} - \mathrm{E}_{n'}/h + \mathrm{E}_{p''} - \mathrm{E}_{p'}/h + \mathrm{E}_{m''} - \mathrm{E}_{m'}/h$$

Let us first study the gross structure of the whole group of bands when the molecule changes from one electronic level to another ($n'p' \longrightarrow n''p''$). The frequencies of the emitted lines are:

$$\nu = \mathrm{E}_{n''} - \mathrm{E}_{n'}/h + \mathrm{E}_{p''} - \mathrm{E}_{p'}/h = \nu_n + \mathrm{E}_{p''} - \mathrm{E}_{p'}/h$$

in which $\mathrm{E}_p = (p + \frac{1}{2}) h \nu_v$ in the harmonic oscillator or $\mathrm{E}_p = (p + \frac{1}{2}) . h \nu (1 - (p + \frac{1}{2}) x \ldots)$ in the anharmonic oscillator, x being an anharmonic factor. Thus for the anharmonic oscillator

$$\nu = \nu_n + p'' \nu''_v (1 - p'' x'') - p' \nu'_v (1 - p' x')$$

As the oscillators are anharmonic, transitions for $p \neq 1$ occur and for $p'' = \mathrm{constant}$

$$\nu = \nu'_n - \beta' p' - \gamma' p'^2$$

in which $p' = 0, 1, 2, 3, \ldots$, $\beta' = \nu'_v$ and $\gamma' = \nu'_v x'$. These values of ν which converge for increasing values of the wave-lengths $\left(\Delta \nu = \beta' - \gamma' (2p' + 1)\right)$ form the Deslandres first progression.

The Deslandres second progression correspond to $p' = \mathrm{constant}$ and $p'' = 0, 1, 2, 3, \ldots$

$$\nu = \nu'_n + \beta'' p'' - \gamma'' p''^2$$

and the lines converge in the direction of the decreasing wave-length $\left(\Delta \nu'' = \beta'' - \gamma'' (2p'' + 1)\right)$.

If the transitions take place for $p'' - p' = \mathrm{constant}$, different sequences for $p'' - p' = 0, 1, 2, \ldots$ are obtained and in each

sequence the sub-maxima frequencies are a quadratic function of p'' or of p', the spacings being in arithmetical progression.

The electronic bands, when observed with a sufficiently high power of dispersion, shew fine lines corresponding to rotational transitions. With the transition $n'p' \longrightarrow n''p''$ may be assoacited quite a large number of rotational transitions giving rise to lines of frequencies

$$\nu = \nu_{n,p} + E_{m''} - E_{m'}/h$$

but in this case the moment of inertia of the molecule instead of being constant as in the pure rotation spectra, varies and the values I' and I'' corresponding to the states m' and m'' have to be considered. For values of $\Delta m = \pm 1$

$$\nu = \nu_{n,p} + B''.m''.(m''+1) - B'm'.(m'+1) \quad (B = h/8\pi^2 I)$$

The R branch of the band corresponds to the transitions $m'' = m \to m' = m - 1$ and the frequencies are

$$\nu = \nu_{n,p} + (B''+B').m + (B''-B').m^2 \quad (m = 1, 2, 3, \ldots)$$

The P branch corresponds to the transitions $m'' = m - 1 \longrightarrow m' = m$ and the frequency values are

$$\nu = \nu_{n,p} - (B''+B').m + (B''-B').m^2$$

The Q or zero branch which corresponds to change in the electronic and vibrational states of the molecule without rotational change is given by

$$\nu = \nu_{n,p} + (B''-B').m'.(m'+1) \quad (m' = 0, 1, 2, 3, \ldots)$$

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CHAPTER IV

Visible and ultra-violet absorption bands of polyatomic organic compounds [1]

The selective absorption of polyatomic organic vapours in the visible and ultra-violet regions is of electronic type, and the number of degrees of freedom is so great as to make a satisfactory analysis very difficult. In solution, the degree of resolution achieved under high dispersion is much inferior to that obtained with vapours, and even with indifferent solvents such as hexane and heptane, the effects of quantised rotational changes are no longer recognisable. With a large number of absorbing substances, dissolved in alcohol or hexane, broad regions of selective absorption are shewn in the visible and ultra-violet, with no indications of resolution into narrower bands, whilst with other substances a number of sub-maxima are shewn, the frequency differences between which are approximately constant. These correspond with inter-atomic vibration frequencies.

Certain groupings, notably the ethenoid linkage, $C = C$, the carbonyl group $C = O$, the azo-grouping $N = N$ are regarded as chromophores in the sense that they give rise to selective absorption in the region $180 - 800 \ m \mu$.

There is no difficulty in conceiving a valency electron in such groupings raised to a higher energy level as a result of the act of absorption. But when the phenyl group or an entity containing several conjugated double bonds gives rise to a special absorption band, difficulties at once arise. It is difficult to localise the act of absorption in a chromophore containing three double bonds and it is necessary to draw a distinction between simple chromophores and complex chromophores. In a *simple chromophore* the electron, which by the act of absorption is raised to a higher level, is simultaneously under the control of two atoms, *e. g.* in the $C = O$, $N = N$, $N - H$, $C = C$, $N = O$ groupings, whereas in a *complex chromophore* such as $C_6 H_5$ and $> C = C - C = O$, the groupings responsible for the band

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[1] Cf. R. A. Morton and A. J. A de Gouveia, J. C. S.,911, 1934.

may contain more than two atoms, although the act of absorption occurs in a simple chromophore within the complex chromophore, the energy level of the electron concerned being determined *before* the act of absorption by the properties of neighbouring atoms or groups.

A complex chromophore may thus be a very large unit, it is a chromophore if the existence in a molecule of the definite large grouping is a condition for the appearance of a particular band. Thus a certain minimum number of conjugated double bonds is necessary for the appearance of the absorption band associated with the visible colour of, for example, carotene.

If the absorption spectra of hydrocarbons are considered, it seems as if all saturated hydrocarbons are transparent, or practically so, in the region $200 - 800 \, m\mu$. Selective absorption in hydrocarbons is therefore due to unsaturation, but whilst ethylene and the butadienes only exhibit selective absorption beyond $225 \, m\mu$ in the direction of the Schumann region, selective absorption occurs at longer and longer wave-lengths as unsaturation is increased, in the order benzene, naphthalene, anthracene, carotene, perylene, to choose only a few hydrocarbons at random.

The chromophore, or the group determining the spectral location of absorption, includes what Radulescu *(loc. cit.)* has termed the «Gemeinschafts-Resonatoren» or the entire «electron constellations». This can only mean that the individual electron, which by the act of absorption is raised to a higher energy level, must initially occupy a specific level, and be maintained in that level as the result of the effect of other centres of unsaturation. A longer or shorter succession of conjugated double bonds determines the normal energy level of a valency electron in a double bond, and although a very large number of levels may be theoretically possible, it is probable that the important ones may not be too numerous for useful classification.

Let us imagine that a series of absorption bands can be identified with the chromophores: —

$$-\,C H = C H -$$
$$-\,C H = C H - C H = C H -$$
$$R\,.\,(C H = C H)_n\,.\,R \text{ etc.}$$
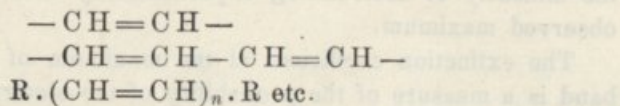
each band should correspond with a particular energy level of a valency electron in the $C = C$ group, and the notation $C = C_\alpha$, $C = C_\beta$, $C = C_\gamma$, $C = C_\delta$, etc. should facilitate description.

In the same way, the statement that a particular absorption band arises only from unsaturation in a molecule containing n conjugated double bonds, may be expressed by $C = C_{(c=c)_n}$ as a description of the chromophore.

Again, acetone has two bands, one at $187\ m\mu$, and another near $275\ m\mu$. Both are due to the carbonyl group, and can be written $C = O_\alpha$, $C = O_\beta$. In mesityl oxide the band due to the carbonyl group is displaced and may be described as $C = O_\gamma$ or $C = O_{c=c}$, intimating that the chromophore contains both the carbonyl and ethenoid groups, but that the act of absorption occurs for an electron under the joint control of C and O but that its initial state is different from that of the corresponding electron in acetone in virtue of an induced effect from the double bond. Mesityl oxide also shews a band near $234\ m\mu$ due to the ethenoid linkage. The chromophore may be written $C = C_{co}$ indicating that the act of absorption occurs at the double bond, the initial state of the electron concerned being different from that of the corresponding electron in ethylene in virtue of an induced effect from the carbonyl group.

On this basis the absorption bands of organic compounds reflect in the first instance, changes in a finite number of electronic energy levels, for a few simple diatomic groupings like $C = O$, $C = C$, $N = N$ etc. The recognition of these different levels is however complicated by the existence of vibrational levels and there are many instances where the actual wave length of maximum absorption in a band resolved into sub groups, represents apparently an electronic frequency plus or minus a vibrational frequency or a simple multiple thereof. In order therefore to arrive at the electronic levels, it is desirable where possible to make allowance for this effect. and in many cases of unresolved broad bands, it is important to realise that the observed frequency of maximum absorption may only be an approximation to the true and theoretically significant electronic frequency, quite apart from the difficulty of determining experimentally with exactitude the observed maximum.

The extinction coefficient at the maximum of an absorption band is a measure of the probability of the electronic transition

concerned taking place. In organic molecules containing only one simple chromophore, there is reason to regard the molecule as distributed over a series of electronic conditions, the valency electron or electrons occupying different levels. Thus the dispersion of acetone indicates an absorption band in the Schumann region connected perhaps with an electronic level related to the ionisation potential, whilst the band observed near 187 $m\mu$ may possibly be connected with a resonance potential. Be that as it may, a statistical distribution of molecules over a series of electronic energy levels must be postulated. These different energy states must not be confused with «electromers» a term best reserved for the type of valency isomerism which is assumed in connection with the octet and similar electronic theories of valency.

If the absorbing molecule contains several simple chromophores together constituting one or more complex chromophores, a whole series of electronic transitions are theoretically possible. Thus the chromophore $(C=C)_{10}$ may be necessary for one absorption band, due to an electron transition of a valency electron in a $C=C$ group influenced by nine other conjugated double bonds, but within that chromophore a second chromophore say $(C=C)_6$ may give rise to another band and another, let us say $(C=C)_4$ may give rise to a third band. The substance may exhibit several absorption bands, each representing the difference between two terms in the $C=C$ spectrum. Carotene $C_{40} H_{56}$ with 13 conjugated double bonds, exhibits maxima at 280, 348 and 462 $m\mu$, each of which must be due finally to a valency electron in a double bond. The obvious possibilities of complexity in electronic levels are not necessarily as alarming as might appear. «In «all molecules where data are available we find a series of energy «levels corresponding at least approximately to the customary «formulæ of line spectra» ... «The energy levels associated with «the valency electrons of molecules agree in all essential aspects «with those associated with the valency electrons of atoms» (R T. Birge, Nature, Feb. 26. 1926, *p.* 301).

CHAPTER V

The technique of absorption spectrophotometry

The present work has been carried out with a Hilger medium quartz spectrograph (E_3) in conjunction with the Hilger sector photometer. Incidentally, the Hilger small quartz spectrograph (E_{37}) fitted with the Spekker ultra-violet photometer (H_{237}) has been used, and occasionally to acquire a rough idea of the absorption spectra of some substances, the Hilger quartz echelon cells have been employed ([1]).

The iron-nickel arc and a nickel-steel spark have been used as sources of light giving spectra very rich in lines and shewing few gaps in the region $200 - 700 \, m\mu$. The high frequency spark between tungsten electrodes immersed in running distilled water, was used as a source of light shewing a continuous spectrum. The effects obtained with the iron-nickel arc and the high frequency spark are illustrated in figs. 4 and 5. The iron-nickel arc was generally used for the study of broad bands, general non-selective absorption and the detection of bands in the far ultra-violet, the continuous light source being especially suitable for the study of highly resolved bands.

Ilford ordinary plates (H & D. 70) have usually been employed and in certain cases faster and panchromatic plates gave better results. The absorption of the compounds is expressed in molar extinction coefficients: $e = log\,I_0/I\,/c.\,d$. A series of photographs is taken on the same plate, each photograph consisting of a comparison spectrum, that is, a spectrum due to a beam of light which goes only through a cell containing the diactinic solvent, and in close juxtaposition the spectrum due to the beam of light which passes through the solution under study. For each plate the concentration of the solution and the thickness of the cell are maintained constant, the photometer allowing a change of the density ($log\ I_0/I$) from 0.1 to 1.5. The points of equal density are detected, the wave-lengths of these points

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[1] For a complete description of these instruments consult «The practice of absorption spectrophotometry» by F. Twyman (1932) and suplements.
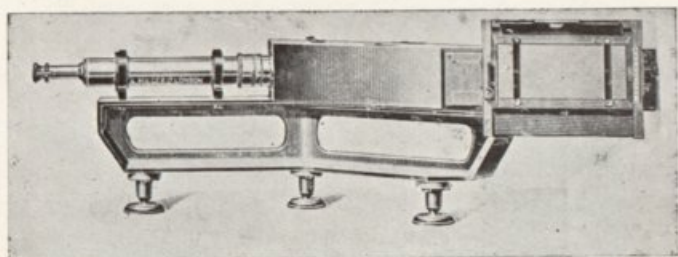
Fig. 1 — Hilger Quartz Spectrograph E₃.
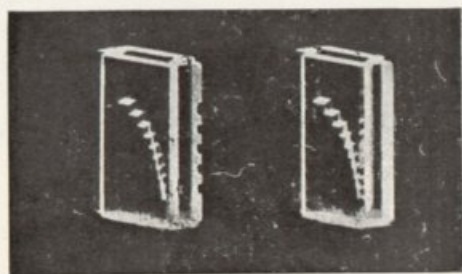
Fig. 2 — Hilger Quartz Echelon Cells.
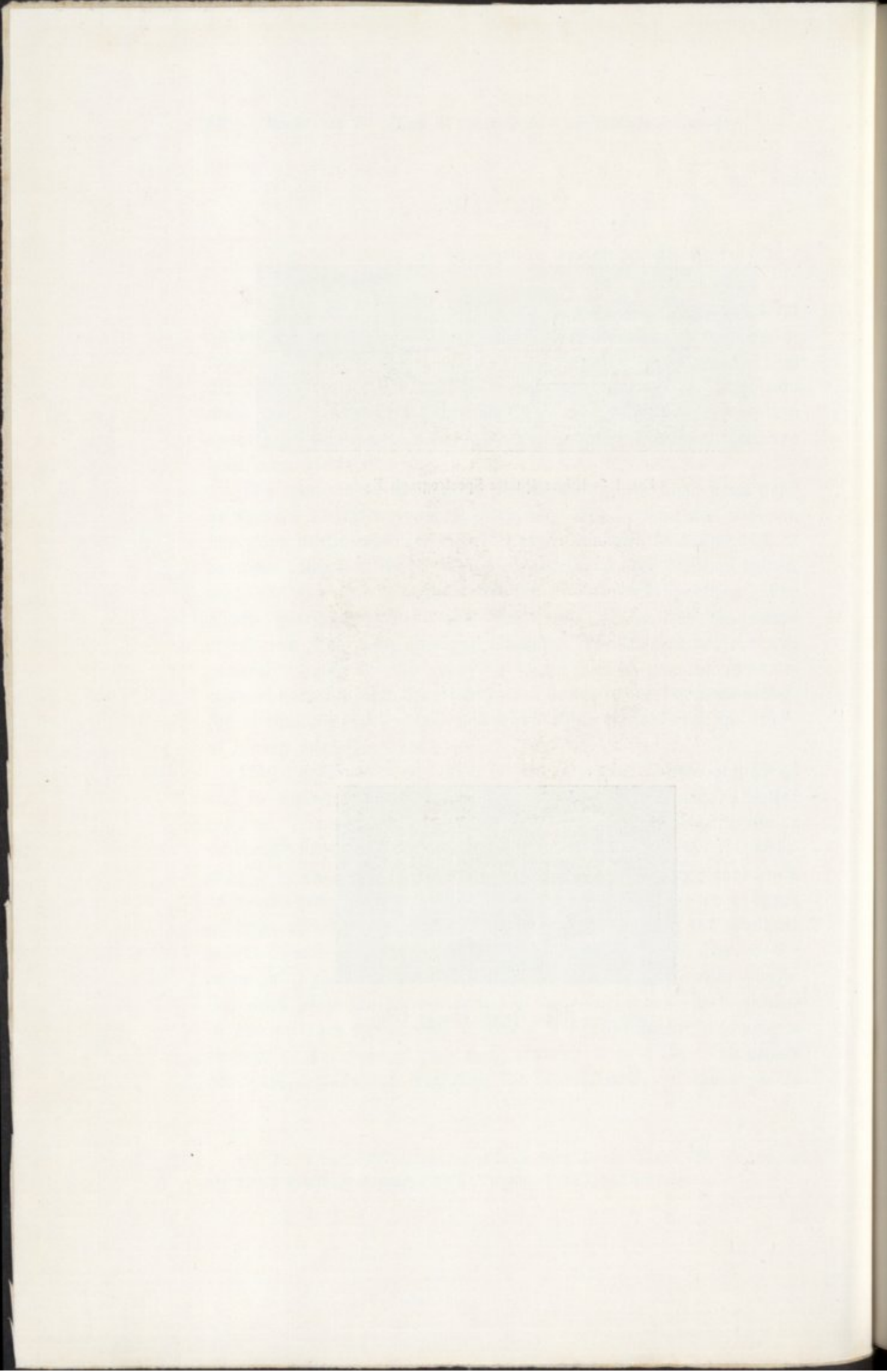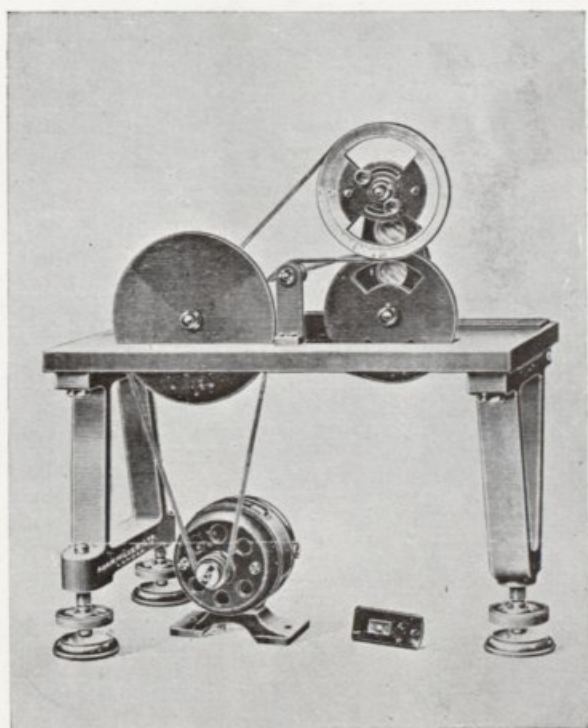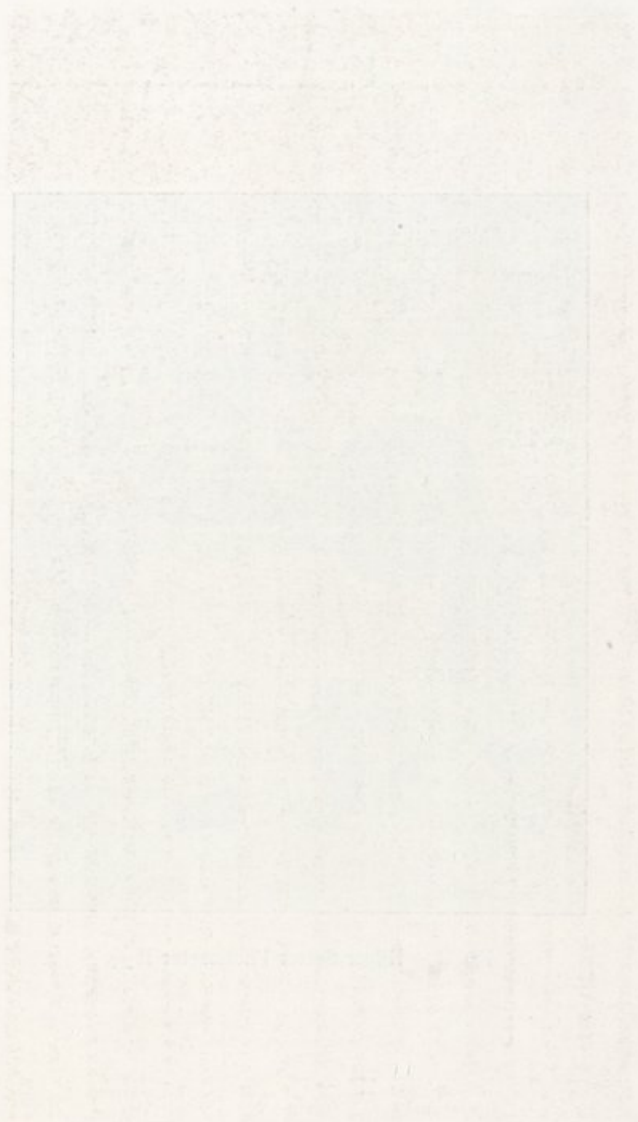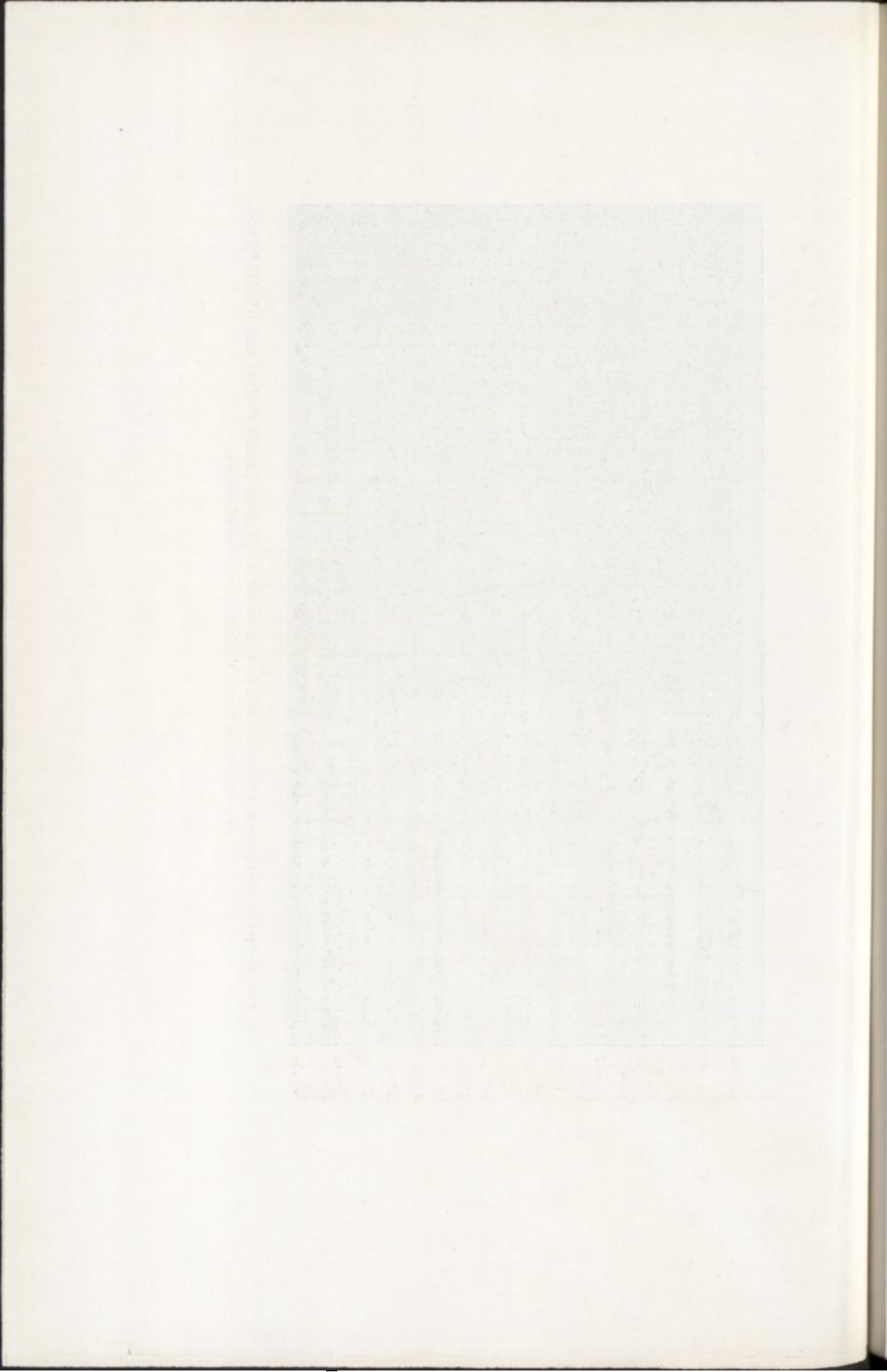
FIG. 3 — Hilger Sector Photometer H$_{237}$.

Fig. 4 — Absorption spectrogram of comanic acid in aqueous alkali (12.5 eq. NaOH) obtained with 0.00115 % concentration, 2 mm. thickness, and *iron-nickel arc.*
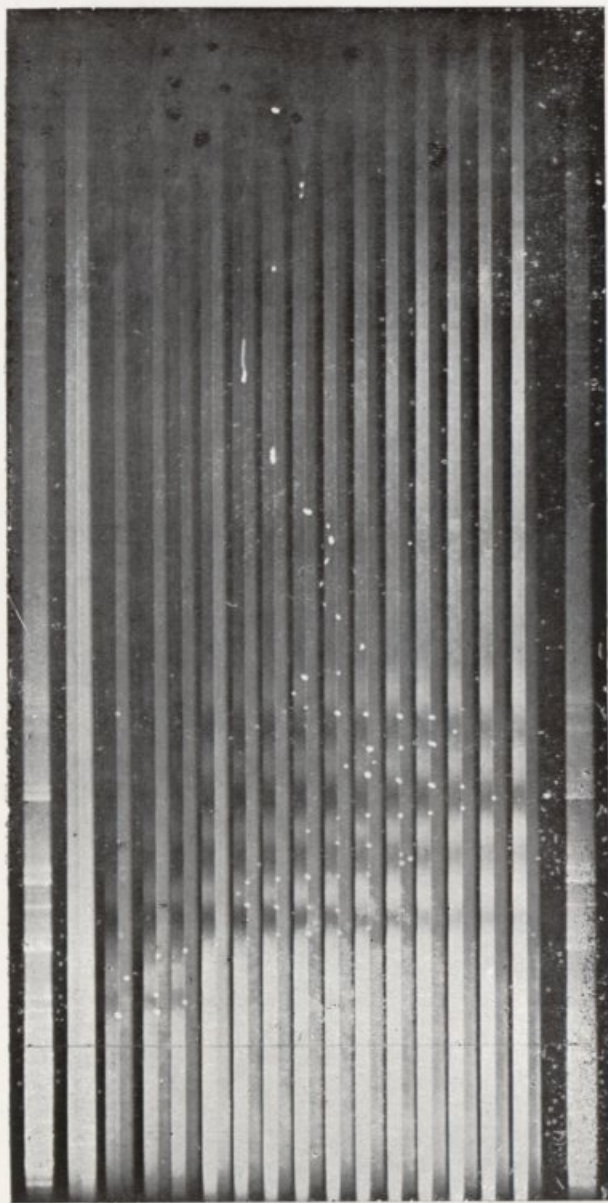
FIG. 5 — Absorption spectrogram of highly unsaturated acids derived from cod liver oil, obtained with the *high frequency spark*. (By the courtesy of Dr. J. R. Elisbury).

determined with a scale, thus providing all the data necessary for the plotting of the extinction curves. In most of our graphs the logarithms of molar extinction coefficients are plotted against the wave-lenghts in $m\mu$.

As solvents, pure hexane and ethyl alcohol (previously treated with sodium) were mainly used, but for some purposes ether, water, aqueous soda, alcoholic sodium ethoxide, etc. have been employed. The comparison of the absorption curves of different substances has so far as possible, always been referred to the same solvent

Special care has been given to the preparation and purification of the different compounds. Only after the physical constants were apparently quite satisfactory (highest and constant melting points, lowest and constant boiling points), were the substances submitted to spectrographic study, and in many cases further purification was controlled by the values of absorption (constancy of intensities and persistency of the different maxima).

Preparation and purification of compounds by different methods proved to be a very helpful process to arrive at definitive extinction curves of substances difficult to obtain in a high degree of purity. The importance of high degree of purity must be emphasised because especially with compounds exhibiting low or medium intensity of absorption, very small traces of a highly absorbing impurity may completely vitiate the results. Difficulties of this character are patent in our absorption work on the hydroderivatives of naphthalene.

CHAPTER VI

Ultra-violet absorption spectra of indene and certain of its derivatives [1]

INDENE
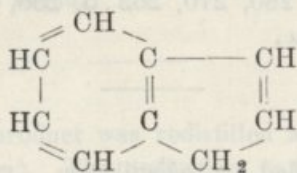
Previous Work

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[1] Cf. R. A. Morton and A. J. A. de Gouveia, J. C. S., 913, 1934.

The results obtained by different workers on the absorption spectrum of indene shew certain divergencies. Thus Stobbe and Farber (Ber. 1924,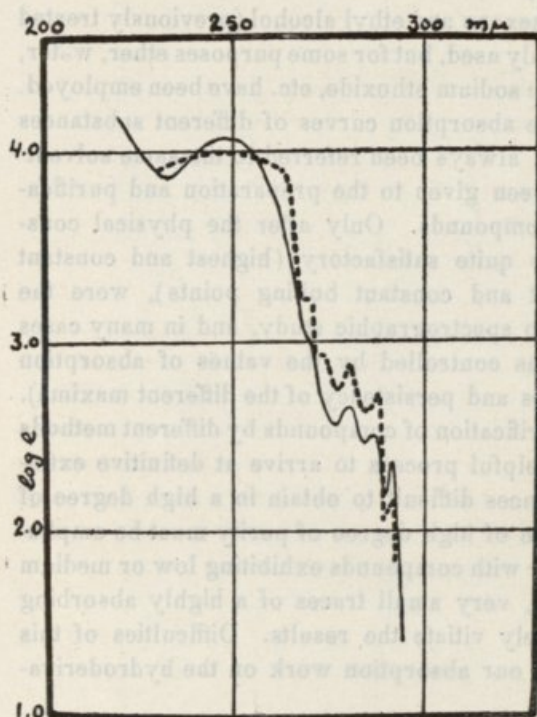 *57*, 1838) and Stobbe and Zschoch (*ibid.*, 1927, *60*, 457) record a weak maximum at 281 $m\mu$ together with much higher absorption towards shorter wave-lengths, whilst Charlampowiczowna and Marchlewski (Bull. Acad. Pol. Sci. A, 1930, 376) find a broad unresolved band in alcoholic solutions with $\lambda_{max} = 249.4$ $m\mu$, and $\epsilon_{max} = 10,900$ but instead of a maximum at 281 $m\mu$ their curve merely flattens out in the region 270—280 $m\mu$. On the other hand, Schwartz (Arch. physique biol. chim. Physique Corps organisés, 1931, *9*, 131,

Fig. 6 — Extinction curves of indene.
—— in alcohol
···· in hexane

Centr. 1932, I, 643) examined indene in hexane and observed a maximum at 250 $m\mu$ with a high extinction coefficient. Maxima were also found at 280, 270, 262.5, 256, (250 intense), 242, 234 (?), and 220 $m\mu$.

———

Indene was purified by redistillation.

The main absorption of the solutions of indene in alcohol and in hexane is on short wave side of 270 $m\mu$, the extinction coefficient reaching a maximum value of about 10,000 near 250 $m\mu$.

In alcoholic solutions the maximum of this band lies at 249 $m\mu$ (log e 4.07) and there is a minimum at 232.5 $m\mu$ (log e 3.86). In hexane the band flattens at 240 — 255 $m\mu$ and the minimum is not evident.

Over the region 292 — 262 $m\mu$, indene exhibits weak and somewhat ill-defined narrow bands, but the spacing of the maxima shews that the wave number separations of ca 460 and 920 cm^{-1} which represent vibrational frequencies appearing regularly in the spectra of hydrocarbons, are also characteristic of indene (Table I)
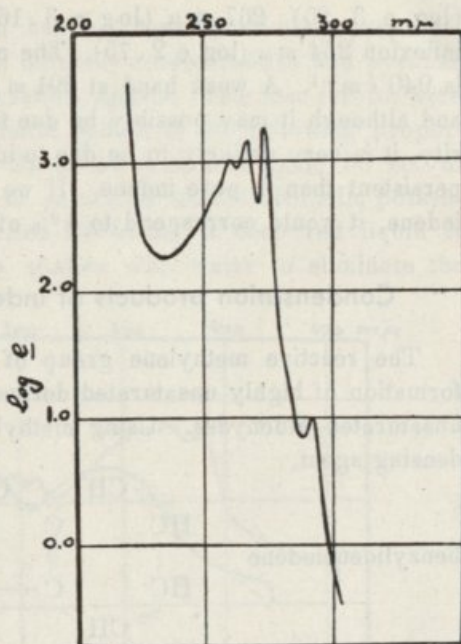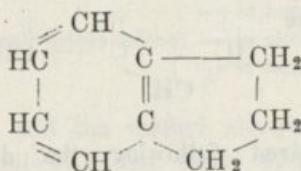

Fig. 7 — Extinction curve of hydrindene in hexane.

HYDRINDENE

$$
\begin{array}{c}
\text{CH} \\
\text{HC} \quad\quad \text{C} \text{----} \text{CH}_2 \\
| \quad\quad\quad || \quad\quad\quad | \\
\text{HC} \quad\quad \text{C} \quad\quad \text{CH}_2 \\
\text{CH} \quad\quad \text{CH}_2
\end{array}
$$

Previous Work

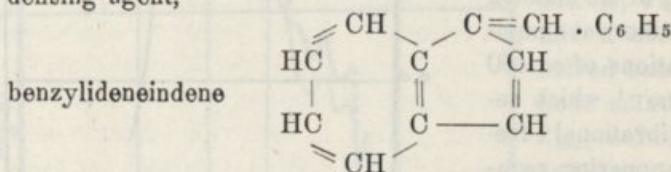Little or no information concerning the absorption spectrum of hydrindene can be found.

The Kahlbáum product was redistilled at reduced pressure (*b. p.* 64°/7 — 8 mm). The extinction curve (fig. 7) is very similar to that characteristic of a wide range of benzene derivatives among which may be mentioned xylenes. The band over the region 275 — 240 $m\mu$ is resolved in sub-maxima 273.6 $m\mu$
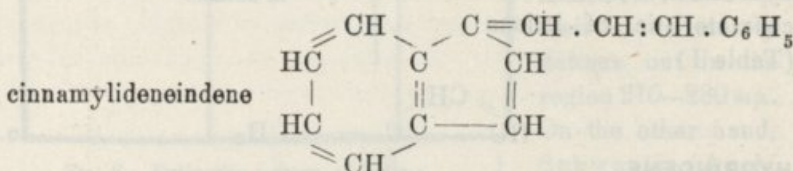
(log e 3.25), 267 $m\mu$ (log e 3.16), 260 $m\mu$ (log e 3.00), inflexion 254 $m\mu$ (log e 2.75). The mean vibrational frequency is 940 cm^{-1}. A weak band at 291 $m\mu$ ($e_{max}=10$) appears also, and although it may possibly be due to a small quantity of impurity, it is very unlikely to be due to indene, as it is already more persistent than in pure indene. If we could ascribe this band to indene, it would correspond to 4% of indene in the hydrindene.

Condensation products of indene with aldehydes

The reactive methylene group of indene permits the ready formation of highly unsaturated derivatives by condensation with unsaturated aldehydes. Using methyl alcoholic potash as condensing agent,
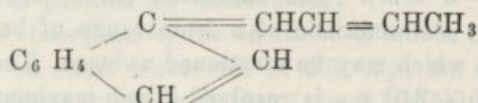
benzylideneindene

$$
\begin{array}{ccc}
& CH & C = CH . C_6 H_5 \\
HC & C & CH \\
| & \| & \| \\
HC & C \text{——} CH \\
& CH
\end{array}
$$

and

cinnamylideneindene

$$
\begin{array}{ccc}
& CH & C = CH . CH:CH . C_6 H_5 \\
HC & C & CH \\
| & \| & \| \\
HC & C \text{——} CH \\
& CH
\end{array}
$$

have been prepared following the directions of Thiele (Ber, 1900, *33*, 3398).

Benzylideneindene was recrystallised from alcohol and heptane as gold plates, *m. p.* 88°: cinnamylideneindene was recrystallised from ethyl acetate in bright gold red needles, *m. p.* 190°.

Though not entirely successful, as we could not separate any crystals from the product of reaction, we have prepared the condensation product of indene with crotonaldehyde. As condensation product we may expect a compound of formula

$$
C_6 H_4
\begin{array}{c}
C = CHCH = CHCH_3 \\
CH \\
CH
\end{array},
$$

crotonylideneindene, which has not been previously prepared. Methyl alcoholic potash in different concentrations and pyridine have been tried as condensation agents. The best results were obtained with methyl alcoholic potash in the following proportions: 34,8 g of indene, 21 g. of crotonaldehyde, 30 cc. of methyl alcohol and 3 cc. of saturated methyl alcoholic potash. Under these conditions, after 24 hours, a deep red liquid is obtained. This liquid was shaken with water to eliminate the
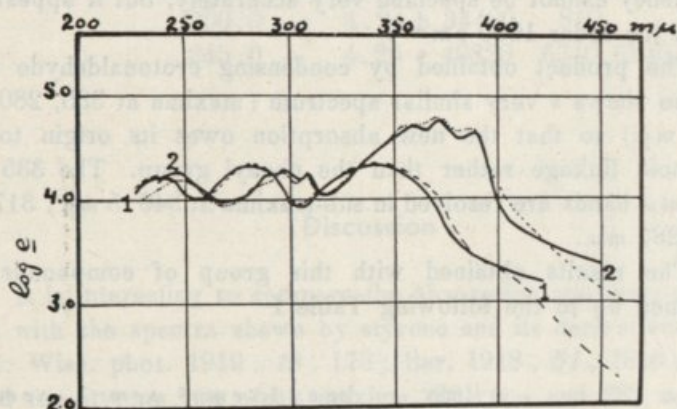

Fig. 8 — Extinction curves of
    (1) Benzylidene indene :   —— in alcohol
                         ···· in hexane
    (2) Cinnamylidene indene : —— in alcohol
                         ···· in hexane.

potassium hydroxide and the methyl alcohol. The water was decanted and the yellowish red liquid extracted with petrol ether. The petrol ether was distilled at normal pressure and the unchanged crotonaldehyde and indene distilled at reduced pressure (5 mm). We obtained as residue a very thick red liquid from which we could not separate any crystals. The absorption spectra of the petrol ether extract and of the last residue have been investigated.

————

The extinction curves of benzylideneindene in hexane and alcohol shew three broad unresolved bands of high intensity λ max 340 $m\mu$, 280 $m\mu$ and 238 $m\mu$, spaced some 6000 cm^{-1} apart.

The effect of an additional conjugated double bond as in cinnamylideneindene, is to displace the bands of benzylideneindene, some $20\text{-}30\ m\mu$ in direction of longer wavelengths, and in addition the bands are partially resolved. The principal maxima are at $371\ m\mu$, $297\ m\mu$ and $245\ m\mu$. The third band at $245\ m\mu$ is unresolved and is more intense than in indene itself. The three bands are all of high intensity and the separations of $6720\ cm^{-1}$ and $7150\ cm^{-1}$ are of the same order. The vibrational frequency cannot be specified very accurately, but it appears to be of the order $1000\ cm^{-1}$.

The product obtained by condensing crotonaldehyde with indene shews a very similar spectrum (maxima at 335, 280 and $252\ m\mu$) so that the new absorption owes its origin to the ethenoid linkage rather than the phenyl group. The 335 and $280\ m\mu$ bands are resolved in sub-maxima at $349.5\ m\mu$, $317\ m\mu$ and $287\ m\mu$.

The results obtained with this group of compounds are summed up in the following Table I

	λ max		log e	$1/\lambda\ cm^{-1}$	$\Delta\ cm^{-1}$ (vibr.)	$\Delta\ cm^{-1}$ (broad bands)
Hydrindene	273.6 $m\mu$		3.25	36550		
(in hexane)	267	—	3.16	37450	900	
	260	—	3.00	38460	1010	
inf.	254	—	2.75	39370	910	
	291 ?	—	1.00	34360		
Indene	291.5	—	2.21	34300 a	440	
(in hexane)	287.8	—	2.73	34740	960	6350 (b — a)
	280.1	—	2.90	35700	860	
	273.5	—	2.94	36560	480	
	270.0	—	3.23	37040	1130	
inf.	262	—	3.85	38170	2480	
	246	—	4.00	40650 b		
Indene	290.8	—	2.37	34390 a		
(in alcohol)	286.5	—	2.50	34910	520	5770 (b — a)
	279.5	—	2.65	35770	860	
	249.0	--	4.06	40160 b	4390	

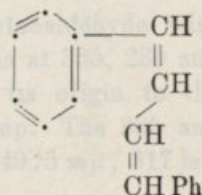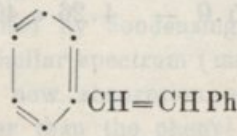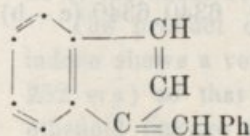|					
Benzylidene-	340.0 —	4.34	29410 a		6300 (b — a)
indene	280.0 —	4.33	35710 b		6310 (c — b)
in hexane	238.0 —	4.22	42020 c		
Cinnamylidene -	388.0 —	4.66	25770		
indene	371.0 —	4.77	26950	1180	
in hexane	358.5 —	4.72 a	27890	940	
	308.5 —	4.26	32420		6590 (b — a)
	297.0 —	4.30	33670	1250	
	290.0 —	4.24 b	34480	810	
	245.0 —	4.26 c	40820	6340 6340 (c — b)

Discussion

It is interesting to compare the absorption spectrum of inde-
ne with the spectra shewn by styrene and its derivatives. Ley
(Z. Wiss. phot. 1919 , *18* , 178; Ber. 1918 , *51* , 1810) obser-
ved for styrene two weak maxima, 291 $m\mu$ and 282 $m\mu$ with
an intense maximum at 246 $m\mu$; α — methyl styrene shewed an
inflexion at 280·290 $m\mu$ whilst β-methyl styrene gave a band at
293 $m\mu$, an inflexion near 277 $m\mu$ and a strong maximum at
246 $m\mu$. Using quantitative methods, Ramart-Lucas and Ama-
gat (Bull. Soc. Chim. 1932, *51*, 965) record a practically cons-
tant curve for the compounds $C_6H_5 . CH = CH . CH_3, C_6H_5 .$
$CH = CH(CH_2)_n . CH_3$ up to $n = 7$.

Styrene			Methyl Styrene		
λ max.		log e	λ max.		log e
291	$m\mu$	2.55	288.8	$m\mu$	2.6
281.5	—	2.67	277.7	—	2.7
243.5	—	4.07	246	—	4.0

whereas allyl benzene and compounds $C_6H_5 . (CH_2)_n . CH = CH_2$
are spectroscopically indistinguishable from ethyl benzene and in
fact resemble hydrindene. It is thus obvious that the resolved
absorption of low intensity in the region 275 — 295 $m\mu$ together
with the intense unresolved band near 240·250 $m\mu$ is common to

indene and to the styrenes so that the group $C_6H_5.C=C.$ has its own characteristic spectrum quite different from that of the phenyl group. Ring closure exerts but little influence on the absorption beyond perhaps slightly increasing the resolution into component maxima near $280-290\ m\mu$. The double bond in the five membered ring of indene therefore functions similarly to a true ethenoid linkage.

The absorption spectrum of benzylideneindene may be compared with those of stilbene and diphenyl-butadiene.

CH
CH
C = CH Ph

CH = CH Ph

CH
CH
CH
CH Ph

λ max 340, 280, 228 $m\mu$

λ max 323, 294 $m\mu$

λ max 320 $m\mu$

log e 4.3, 4.3, 4.2

log e 4.45, 4.55 (Castille Bull. Sci. Acad, Roy. Belge, 1926, *12* 498).

log e 3.15 (Radulescu and Barbulescu, Ber. 1931, *64*.2225).

λ max 322, 288, 222 $m\mu$ log e 4.1, 4.3, 4.1 (Ramart-Lucas and Amagat, loc. cit).

λ max 346.5, 328.4, 312.5 $m\mu$ log e 4.7, 4.68, 4.6 (Castille, loc. cit.).

Both stilbene and diphenyl-butadiene shew a very broad absorption band extending from 250-350 $m\mu$ approximately. The absense of a well-defined band with a maximum at 280 $m\mu$ in diphenyl-butadiene is not evidence of the absence of the corresponding chromophoric group, because the absorption curve is so unusually broad as to indicate that the observed curve is really a summation curve. In benzylideneindene, the separate bands which are fused together in stilbene and diphenyl-butadiene are quite clearly shewn. Confirmation of the 280 $m\mu$ band is obtained from the data of Stobbe and Reuss (Ber. 1912, *15*, 3496) on $\alpha\gamma$-butadienyl benzene which shews a single unresolved intense band at 282 $m\mu$. Radulescu (loc. cit.) records for diphenyl-hexatriene high absorption in the near ultra-violet, with

sub-maxima at 373 , 355 , and 335 $m\mu$, whilst the corresponding values for cinnamylideneindene are 388 , 371 and 358 . 5 $m\mu$.

In all these compounds the act of absorption concerns all electrons belonging to the $- C = C -$ group either in the ring or as a true ethenoid linkage.

The absorption curve will naturally be influenced by vibrational frequencies, but the fundamental cromophore is a double bond. This simple chromophore forms a part of complex chromophores in which double bonds are conjugated. The following chromophores are thus possible:

(1) $- C = C -$ (2) $- C = C . C = C -$ (3) $C_6 H_5 -$

(4) $C_6 H_5 . C = C -$ (5) $C_6 H_5 - C = C - C = C -$

and (6) $C_6 H_5 . (C H : C H)_2 . C_6 H_5$.

(1) and (2) give rise to absorption on the short wave side of 230 $m\mu$ only. (3) gives rise to absorption near 260-270 $m\mu$ of log e 2.6 whilst (4) gives rise to two types of absorption one of log e ca 4 at 250 $m\mu$ and another of log e ca 2.5 at 270-290 $m\mu$; (5) gives rise to a band of high intensity near 280 $m\mu$ whilst (6) occasions three bands.

Now this notion of complex chromophores would be greatly enhanced in value if it could be stated at which double bond the different acts of absorption occur.

A notation to express such localisation may be suggested: considering chromophore (4) there are obviously two alternatives at least:

$$\text{(a)} \quad Ph . \overset{*}{C} : C . \qquad \text{(b)} \quad \overset{*}{Ph} . C : C .$$
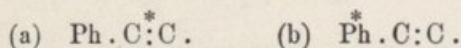
but further consideration of this aspect of the problem may be deferred, pending the accumulation of further evidence of hydroaromatic hydrocarbons, but it is plausible to suggest that the bands at $270 - 290$ $m\mu$ of indene are due to (*b*) since log e 2.5 (*ca*) is shewn in benzenoid compounds like toluene and tetralin.

Summary

(1) The absorption spectra in alcohol and hexane of hydrindene, indene, benzylideneindene, cinnamylideneindene were investigated.

(2) The extinction curve of hydrindene is of benzenoid type

(similar to xylenes, allyl benzene and compounds $C_6H_5.(CH_2)_n.$ $CH=CH_2$, etc.). The chromophore is therefore located in the benzene ring and is only slightly influenced by the five membered ring.

(3) The absorption spectrum of indene is very similar to that of styrene and alkyl derivatives $C_6H_5.CH=CH.(CH_2)_n.CH_3$. The absorption is due to the complex chromophore Ph.C:C. some evidence being obtained concerning the mechanism of absorption. It is assumed that the band over the region $292-262$ $m\mu$ is produced by an absorbing electron of the benzene ring under the influence of the conjugated ethylenic linkage; the unresolved, intense 249 $m\mu$ band is due to an absorbing electron from the ethylenic linkage influenced by the benzene ring.

(4) The vibrational frequencies 460 cm^{-1} and 920 cm^{-1} appear in the spectrum of indene; the 940 cm^{-1} in hydrindene.

(5) Three regions of absorption are exhibited by benzylideneindene, cinnamylideneindene, and crotonylideneindene separatde by $6000-7000$ cm^{-1}. The separations of these regions are of the same order as those of certain highly unsaturated compounds (*e.g.* carotene, lycopene, etc.).

(6) Correspondence between different regions of absorption and different chromophores is inferred.

CHAPTER VII

Ultra-violet absorption spectra of naphthalene alkyl-naphthalenes, hydro-naphthalenes, and related compounds [1]

NAPHTHALENE

Early work on naphthalene (cf. Baly and Tuck, J. C. S. 1908, *93*, 1902) was hampered by the lack of a light source

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[1] Cf. R. A. Morton and A. J. A. de Gouveia, J. C. S., 916, 1934.

shewing a continuous spectrum and by the semiquantitative methods then in use for determining intensities of absorption. It is not surprising therefore that maxima were only observed at 320, 311 and 270 $m\mu$. Henri and Steiner (C. R. 1922, *175*, 421) obtained a very much better resolution of the spectral absorption of naphthalene dissolved in hexane, and found a large number of narrow bands resembling those observed in naphthalene vapour. De Laszlo (Z. physikal Chem. 1925, *118*, 369) confirmed and extended the work of Henri and Steiner. S. Kimura (Mem. Coll. Sci. Kyoto, 1931, *14*, 303) examined alcoholic solutions of naphthalene, but his results are not in agreement with earlier work, particularly with respect to extinction coefficients. Kimura's paper shews that good resolution was obtained by him and the wave-lengths of maxima agree closely with other data, but the intensities of absorption appear throughout to be much too high. Not only are the extinction coefficients rather more than 10 times too high, but the persistence of individual bands is greatly exaggerated. The influence of these errors lies in the fact that Kimura's data on the hydro-naphthalenes, which are the only results based on quantitative methods which we have been able to trace, exhibit similar defects.

We have repeated the study of the absorption spectrum of naphthalene in hexane and alcohol. It is not perhaps easy to determine extinction coefficients with high accuracy at the actual maxima of narrow bands such as those of naphthalene, but we found no difficulty in obtaining substantially the same results as Henri and Steiner and De Laszlo. The absorption of naphthalene in hexane and alcohol is entirely the same: the order of resolution is the same in both solvents and the maxima appear in the same positions. In our work the band of high intensity in the further ultra violet was resolved in two sub-maxima at 221.0 $m\mu$ and 217.5 $m\mu$; although it has been observed with other compounds the quantification of vibrational energy in this region of the spectrum is not usual.

The data of De Laszlo, ours and those of Kimura are compared in the following Table:

De Laszlo data in hexane		Our data in hexane		Kimura's data in alcohol	
λ max	log e	λ max	log e	λ max	log e
320.6 $m\mu$	1.21	320.5 $m\mu$	1.3	338.4 $m\mu$	0.5
314.5 —	1.94	314.8 —	1.95	321.9 —	2.6
310.8 —	2.30	311.0 —	2.54	316.0 —	3.0
306.6 —	2.16	306.8 —	2.4	312.6 —	3.95
303.8 —	2.09	304.5 —	2.4	307.1 —	3.5
300.9 —	2.30	302.0 —	2.54	305.9 —	3.5
299.2 —	2.36	299.8 —		303.1 —	3.8
297.3 —	2.50	297.5 —	2.6	301.9 —	3.05
293.0 —	2.56			299.2 —	3.8
288.0 —	3.68	286.5 —	3.74	288.8 —	4.95
285.2 —	3.68	283.5 —	3.74	285.6 —	4.05
283.0 —	3.68			282.5 —	4.8
275.8 —	3.81	275.5 —	3.90		
272.2 —	3.81	272.2 —	3.90		
265.0 —	3.68	266.5 —	3.78	268.4 —	4.5
261.8 —	3.68	256.5 —	3.70		
256.2 —	3.60	221.0 —	5.18	256.7 —	3.95
220.2 —	4.98	217.5 —	5.18		

Our extinction curve is given in fig. 9

ALKYL-NAPHTHALENES

The absorption spectra of a number of di — and tri — substituted alkyl-naphthalenes kindly supplied by Prof. I. M. Heilbron and Dr. D. G. Wilkinson have been examined and the data are reproduced in Table II and figs. 10, 11, 12, 13, 14, 15, and 16.

Δ^1 — DIHYDRONAPHTHALENE

Kimura examined Δ^1 — dihydronaphthalene prepared from ac-tetraydro — β — naphtol by dehydration with potassium

TABLE II

Absorption maxima of naphthalene derivatives in hexane solutions

Unsubstituted		1—Methyl		2—Methyl		2:6—Di-methyl		2:7—Di-methyl		1—Methyl-5—ethyl		1—Methyl-6—ethyl		1—Methyl-7—ethyl		1:3:5—Tri-methyl		1:3:8—Tri-methyl		2:3:5—Tri-methyl		1:6-Dimethyl 4—iso propyl (cadalene)		Quinoline		Iso quinoline	
λ max	log e	λ max	log e	λ max	log e	λ max	log e	λ max	log e	λ max	log e	λ max	log e	λ max	log e	λ max	log e	λ max	log e	λ max	log e	λ max	log e	λ max	log e	λ max	log e
320.5 mμ	1.3	322.2 mμ	1.62	325.8 mμ	1.65	322.8 mμ	3.16	321.5 mμ	2.32	321.2 mμ	2.46	322.0 mμ	2.15	321.5 mμ	2.93	324.4 mμ	2.88	325.8 mμ	3.18	323.2 mμ	2.48	325.3 mμ	3.3			317.5 mμ	3.55
		318.7	2.13	319.0	2.54	316.2	2.73	317.5	2.43	317.0	2.70			317.2	2.54	319.2	2.83	320.1	2.91	318.6	2.70	317.4	2.99			312.5	3.42
314.8	*1.95*	314.0	2.39	314.0	2.31					314.9	2.93			315.0	2.62			315.8	2.96							309.2	3.37
311.0	2.54			310.8	2.43	310.0	2.93	312.4	2.41	*312.0*	*2.86*					*310.0*	*2.99*	311.0	3.10	313.0	2.71	310.2	3.36	310.8 mμ	3.8		
306.8	2.4	307.0	2.4					307.2	2.63	*305.0*	*3.3*	307.0	3.24	307.0	2.97			*306.0*	*3.15*	307.8	2.88	*306.0*	*3.55*	305.8	3.5	304.6	3.30
304.5	2.4			304.0	2.56	303.1	2.64	303.1	2.65													*300.0*	*3.75*				
302.0	2.54	302.8	2.6							298.8	3.83					299.2	3.78							299.1	3.55	298.5	3.50
299.8		299.0	2.7							291.0	3.73	291.0	3.73	291.8	3.77	295.1	3.84	298.0	3.65			295.4	3.84	292.6	3.55	290.0	3.38
297.5	2.6			297.8	2.56	296.3	2.94			287.0	3.98					290.5	3.90	295.0	3.70	296.0	3.76			286.8	3.55		
		293.2	3.54	294.0	2.68			BROAD UN-				280.8	3.86	281.8	3.90	288.9	3.97									284.3	3.38
286.5	3.74	289.0	3.56	287.0	3.48			275.0	3.60	276.0	3.86					*287.0*	*3.90*	285.0	3.83	283.8	3.89	284.0	3.90	275.3	3.65	262.0	3.55
283.5	3.74	281.0	3.71					RESOLVED				273.5	3.81	274.0	3.86	277.2	3.86	277.5	3.79	279.8	3.90	279.8	3.90			227.2	*3.9*
275.5	3.90			275.1	3.73	BROAD UN-				*267.5*	*3.70*									273.6	3.86	275.0	3.75			215.5	4.70
272.2	3.90	270.5	3.69			272.5	3.68			*258.5*	*3.47*									264.8	3.73						
266.5	3.78			266.0	3.68	RESOLVED				228.4	5.25	228.0	5.04	228.7	5.01	231.3	5.30	231.5	5.12	229.8	5.06	232.0	4.96				
256.5	3.70									222.0	5.04	223.0	4.94	225.0	5.00	226.1	5.16	225.0	5.05	225.3	5.06	228.0	4.92				
221.0	5.18	220.5	4.98	220.8	4.98																						
217.5	5.18																										

NOTE: Numbers underlined represent inflexions.

Fig. 9 — Extinction curve of naphthalene
in alcohol.

Fig. 10 — Extinction curve of 1 - methyl —
5 - ethyl naphthalene in hexane.

Fig. 11 — Extinction curve of 1 - methyl —
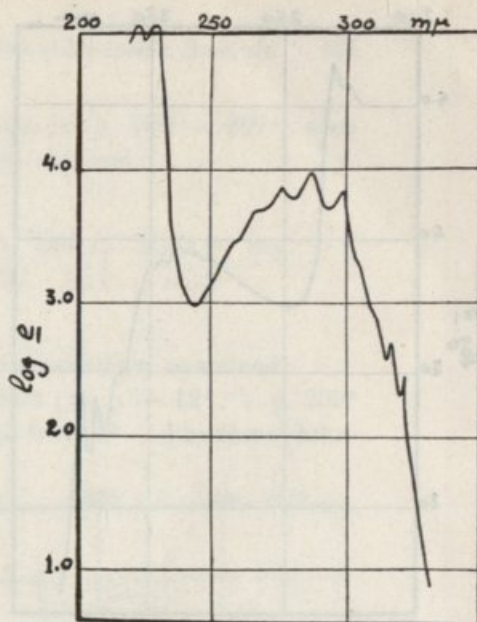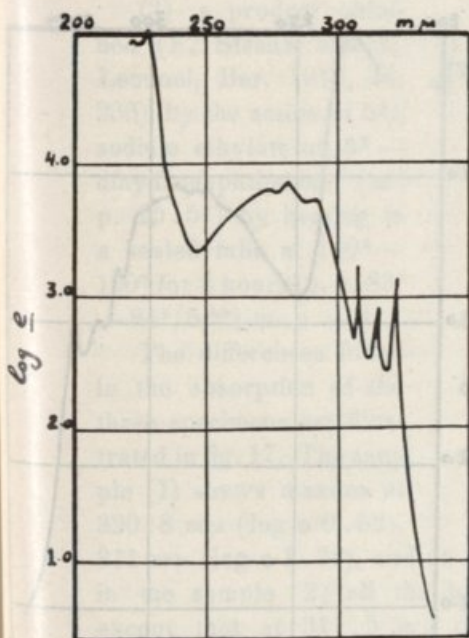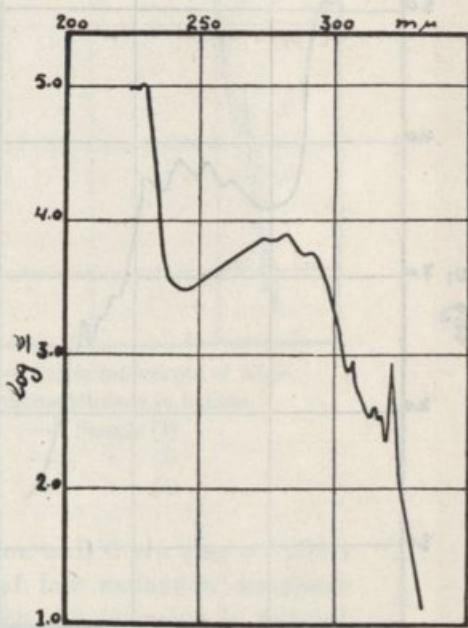6 - ethyl naphthalene in hexane.

Fig. 12 — Extinction curve of 1 - methyl —
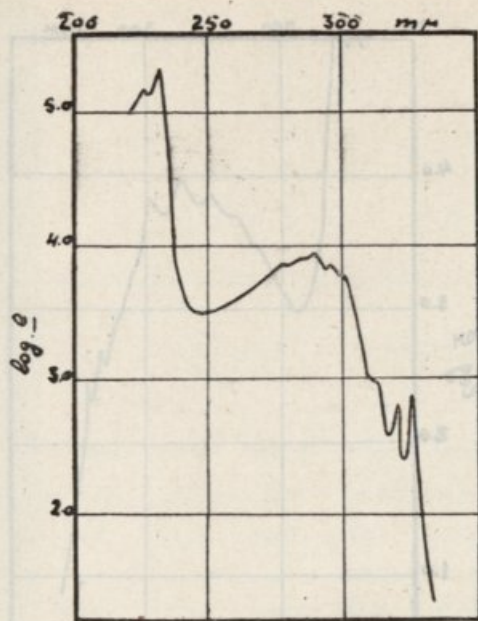7 - ethyl naphthalene in hexane.

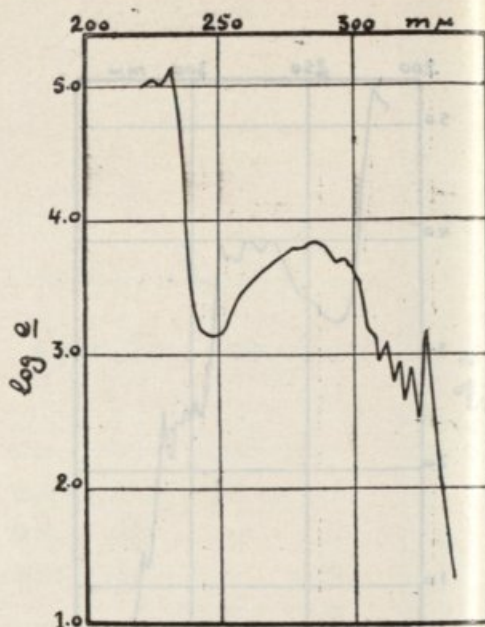F.ɢ. 13 — Extinction curve
of 1 . 3 . 5 . - trimethyl naphthalene in hexane.

Fig. 14 — Extinction curve
of 1 - 3 - 8 - trimethyl naphthalene.
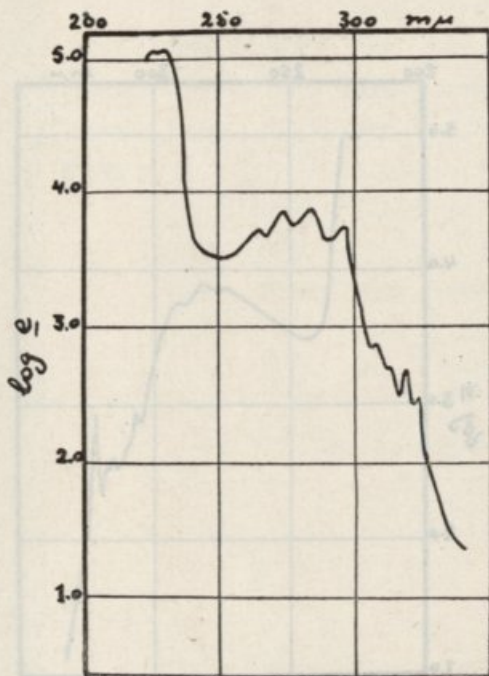
Fɪɢ. 15 — Extinction curve
of 2 - 3 - 5 - trimethyl naphthalene.
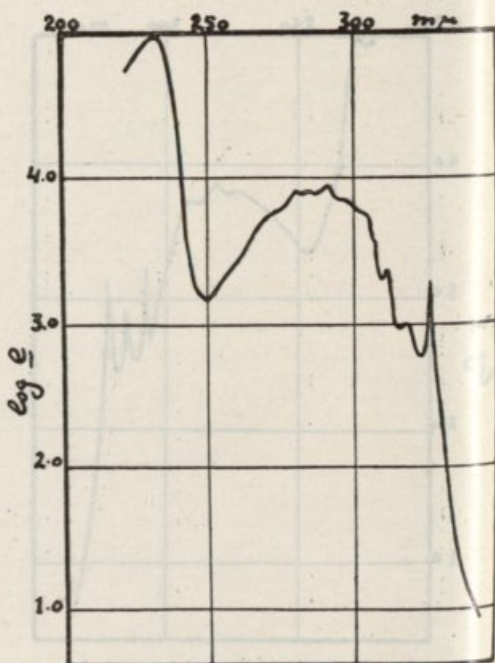
Fɪɢ. 16 — Extinction curve of cadalene.

hydroxide and purified by distillation (b. p. 206° — 207°) over metallic sodium. Five maxima were obtained:

$$\text{λ}_{max} \quad 322.0 \quad 317.0 \quad 312.5 \quad 297.3 \quad 277.5 \quad m\mu$$
$$\log e \quad 0.27 \quad 0.65 \quad 1.33 \quad 3.9 \quad 4.9$$

In the present work three specimens have been examined:

(1) a redistilled purchased product (m. p. — 12°; b. p. 209° — 210°) which was shewn to be free from Δ^2 — dihydronaphthalene by the fact that the derivative prepared with mercuric acetate was entirely insoluble in benzene.

(2) a second purchased product after repeated fractional distillation under reduced pressure (m. p. — 12°; b. p. 81° — — 83°/6 — 7^{mm}).

(3) a product obtained (F. Straus and L. Lemmel, Ber. 1913, *46*, 236), by the action of 5% sodium ethylate on Δ^2 — dihydronaphthalene (m. p. 25.5°) by heating in a sealed tube at 140° — 150° for 8 hours (b. p. 83° — 84°/5^{min}; m. p. — 4°).

The differences found in the absorption of the three specimens are illustrated in fig. 17. The sample (1) shews maxima at 320.8 $m\mu$ (log e 0.32),

Fig. 17 — Extinction curves of Δ^1 — dihydronaphthalene in hexane.
—— Sample (1)
.... » (2)
.... » (3)

311 $m\mu$ (log e 1.38), and an inflexion at 306 $m\mu$ (log e 1.34); in the sample (2) all the bands of low extinction disappear except that at 311.5 $m\mu$ of which the intensity is reduced to log e 0.8 and loses its persistence; in sample (3) the

maxima of low extinction although of lower intensity and persistence than in sample (1) appear again: 320.7 $m\mu$ (log e 0.15), inflexion 314.5 $m\mu$ (log e 0.72), 311.5 $m\mu$ (log e 1.26).

(2) is evidently the best sample of which the extinction curve is given in fig. 18. The impurity of samples (1) and (3) appears to be naphthalene as this compound exhibits sharp maxima at 320.5, 314.8, and 311.0 $m\mu$.
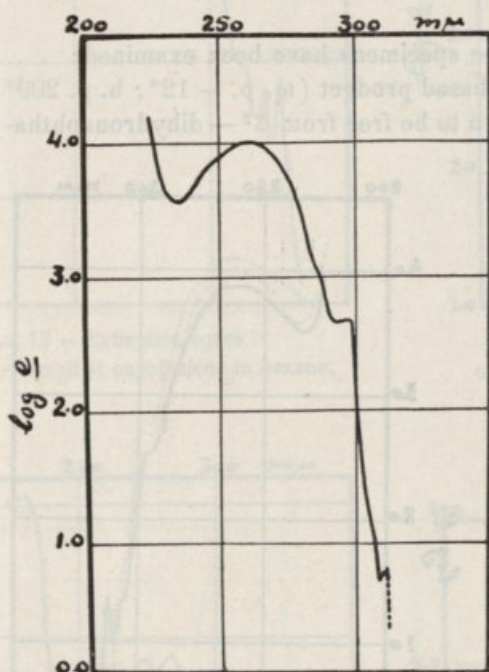
The absorption of Δ^1 — dihydronaphthalene exhibits a well defined maximum at 262 $m\mu$ (log e 4.01) which in hexane solution represents the peak of a broad unresolved band. The curve shews a feeble inflexion near 273 $m\mu$ and there is also a narrow band between 290 and 300 $m\mu$ (λ_{max} 296 $m\mu$, log e 2.68). The *very* weak band at 311.5 $m\mu$ may have been due to the

Fig. 18 — Definitive extinction curve of Δ^1 — dihydronaphthalene in hexane.

presence of a trace of impurity, since its intensity varied in the three samples and was almost negligible in the best product.

The intensities of absorption recorded by Kimura are again too high, but by applying a correction similar to that required for naphthalene the intensity of absorption at 277.5 $m\mu$ may be reduced to about log e 4. This procedure does not however suffice to bring our results and those of Kimura into agreement. In order to test the possibility that Kimura's data are vitiated by contamination of his pro uct with naphthalene, we may take his own data:

Naphthalene		Δ^1 — dihydronaphthalene	
λ max	e max	λ max	e max
$321.9\ m\mu$	357	$322.0\ m\mu$	1.86
316 0 —	891	317.0 —	4.47
312.6 —	71.61	312.5 —	21.38

From the first two values of e_{max}, it is possible to infer the presence of 0.5% naphthalene in the Δ^1 — dihydronaphthalene. It is scarcely possible to doubt the presence of appreciable quantities of naphthalene in view of the good agreement of the wave lengths of the maxima. Had Kimura's preparation consisted of 99.5% of Δ^1 — dihydronaphthalene, he should have been able to record the $262\ m\mu$ band. The appearance of an unresolved band with its maximum at $277.5\ m\mu$ indicates that superimposed on the absorption of Δ^1 — dihydronaphthalene is that of naphthalene present in appreciable amount and displacing the observed maximum.

Δ^2 — DIHYDRONAPHTHALENE.

In the earlier literature there appears to have been some confusion between Δ^1 and Δ^2 — dihydronaphthalene. Thus Baly and Tuck (loc. cit.) examined a dihydro-derivative and found qualitatively the same bands as in naphthalene, the intensities being about 1/10 of those recorded for the parent substance except at $270\ m\mu$. In any case the published data allow the presence of appreciable quantities of naphthalene to be inferred.

The Δ^2 — dihydronaphthalene used in the present work was prepared as follows: Naphthalene was reduced by means of sodium and ethyl alcohol (Bamberger and Lodter, Ann. 1895, *288*, 75) and Δ^2 — dihydronaphthalene obtained by steam distillation yielding crystals (m. p. 15°; b. p. 212°). The crude product dissolved in ether was shaken during 24 hours with a saturated aqueous solution of mercuric acetate (Strauss and Lemmel, Ber. 1913, *46*, 236) and an addition compound prepared and recrystallised. From this, all Δ^1 — dihydronaphthalene was eliminated easily by extraction in a soxhlet apparatus with benzene, the Δ^2 — dihydronaphthalene addition compound alone being soluble. The purified material (m. p. 120°) was treated

with 30% hydrochloric acid and the Δ^2 — dihydronaphthalene regenerated (m. p. 25 — 26°). The final product was obtained by redistillation and yielded perfectly colourless crystals m. p. 25° (Strauss and Lemmel give m. p. 24.5° — 25°).

The absorption curve of this material in hexane consisted of a series of narrow bands of very low extinction coefficient (1.5 — 10) between 331 and 297 $m\mu$ with ill-defined bands at 293, 287 and 262 $m\mu$ and well-defined bands at 274 and 267 $m\mu$, e_{max} 850 and 800 respectively.
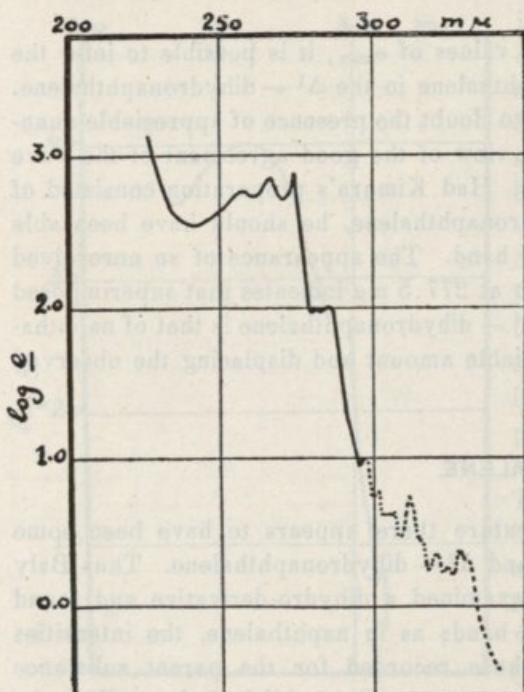
The data are reproduced in Table III and fig. 19.

The complete absence of naphthalene from this material is very difficult to guarantee, although the preparation studied satisfies the usual criteria of purity.

Fig. 19 — Extinction curve of Δ^2 — dihydronaphthalene in hexane.

The group of bands at 274, 267 and 262 $m\mu$ agree with a benzenoid substance containing an additional ethenoid linkage not conjugate to the benzene ring. Such a double bond would not be expected to affect the absorption appreciably, and Δ^2 — dihydronaphthalene and 1.2.3.4 — tetra-hydronaphthalene should on this basis be practically indistinguishable as regards ultra-violet absorption. How then are the narrow bands of low intensity to be accounted for?

The following possibilities must be considered: —

(a) that the bands are due to naphthalene.

TABLE III

λ max mμ		e max	log e	1/λ cm⁻¹	Δ cm⁻¹ values
a 331.0	inflexion	1.5	0.18	30210	
b 328.5	persistent	2.65	0.42	30440	e−m=1670 c−a=1540 d−a=970
c 324.5	v. small	1.65	0.22	30810	
d 320.7	small	2.1	0.32	31180	m−l=1660 i−e=1470 e−c=940
e 315.0	inflexion	2.85	0.45	31750	
f 311.0	persistent	5.7	0.76	32150	l−i=1620 g−d=1450 f−d=970
g 306.5	v. small	4.2	0.62	32630	
h 303.7	v. small	4.2	0.62	32930	f−b=1710 k−g=1500 g−e=880
i 301.0	small	5.7	0.76	33220	
j 297.0	sharp	7.65	0.88	33670	h−d=1750 j−f=1520 k−i=910
k 293.0	inflexion	ca 30	1.48	34130	
l 287.0	not sharp	100	2.0	34840	n−m=950
m 274.0	v. persistent	850	2.93	36500	1500
n 267.0	persistent	800	2.90	37450	means 1690 950
o 262.0	inflexion	500	2.7	38170	

Raman frequencies (Bonino)

Δ² — Dihydronaphthalene	3041, 2873, 2825, *1663*, 1592, 1433, 1287, 1163, 1047, *739*, 499, 468, 244
Naphthalene	3046, *1573*, 1412, *1377*, 1245, 1142, *1023*, 936, 610, 505
Tetralin	3049, 2922, 2862, 1602, 1583, 1456, 1433, 1374, 1283, 1204, 1160, 1038, 938, 848, 815, 759, 724, 585, 567, 432
Decalin	2922, 2856, 1448, 1360, 1260, 1165, 1046, 1017, 990, 851, 804, 753, 593, 554, 490, 402
Benzene	3185, 3162, 3060, 3047, 2947, 2928, 2784, 2617, 2597, 2460, 1506, 1178, *991*, 849, 605
Indene*	3053, 2913, 1607, 1546, 1453, 1355, 1288, 1204, 1057, 1015, 938, 829, 726, 591, 533, 407

* Data by T. C. Calloway

(*b*) that the bands are due to a small quantity of an addition compound between naphthalene and Δ^2 — dihydronaphthalene (Bamberger and Lodter, loc. cit., describe a material of m. p. $43^\circ - 44^\circ$ which may be of this type).

(*c*) that the bands are due to a hydronaphthalene of unknown structure with two double bonds in each ring.

Suggestion — (*a*) suffers from the disadvantages that the 331 $m\mu$ inflexion and the 328.5 $m\mu$ and 324.5 $m\mu$ bands are not shewn by pure naphthalene, neither do the relative intensities of the different bands correspond with those of naphthalene.

To test (*b*) the first four or five bands may for the moment de left out of consideration and attention directed to the following bands:

Δ^2 — dihydronaphthalene.

λ max	311.0	306.5	303.7	301.0	297.0	293.0	287.0 $m\mu$
e max	5.7	4.2	4.2	5.7	7.6	30	100

Naphthalene

λ max	311.0	306.8	304.5	302.0	297.5	293.0	287.0 $m\mu$
e max	345	257	257	345	400	450	6900

Proceeding on the assumption that the above good agreement in wave-lengths of maxima indicates contamination with naphthalene, the percentage of impurity may be calculated as 1.65%, 1.63%, 1.63%, 1.65%, 1.91%, 1.46%.

Thus the possibility of the presence of 1.6% of naphthalene cannot be ruled out in spite of the very careful purification since the stability of Δ^2 — dihydronaphthalene may be less than has been hitherto assumed.

Now the extinction coefficient of pure naphthalene at 275.5 $m\mu$ is of order 7000. 1.6% of naphthalene corresponds with 110 whilst the observed e value for our Δ^2 — dihydronaphthalene at 274 $m\mu$ is 850. The intensity of absorption of the dihydroderivative is therefore high enough largely to mask the effect of 1.6% of naphthalene. The is therefore reasanable evidence for regarding the bands e — l as possibly due to contamination with naphthalene. This hypothesis does not however account for bands a — d and the possibility of a naphthalene — Δ^2 — dihy-

dronaphthalene addition compound now merits further consideration.

A preparation of Δ^2 — dihydronaphthalene containing unchanged naphthalene and of m. p. $40° — 45°$ was therefore prepared and examined, and the bands a — d were found to be entirely lacking. This material, from its absorption spectrum seems to be a $1:1$ molecular compound, and there is no trace of the 328 $m\mu$ band.

It seems therefore that this band must be due to a new substance, probably an isomeric dihydronaphthalene, e. g :
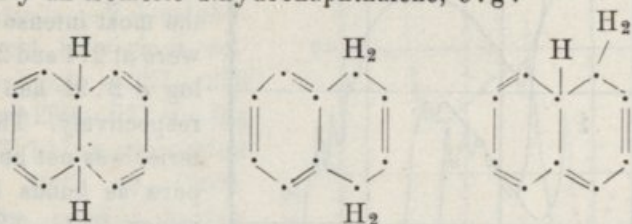
It must however be emphasised that the absorption spectrum of our product is entirely consistent with Δ^2 — dihydronaphthalene as the principal absorbing constituent.

TETRAHYDRONAPHTHALENE

Kimura (loc. cit.) purified commercial tetralin by distilling (b. p. $204° — 206°$) and obtained and absorption curve very like that of naphthalene.

Similar treatment of purchased tetralin gave in our hands a product shewing almost exactly the same bands as those obtained by Kimura, except that the extinction coefficients were throughout about $1/10$ of those recorded by him, but the data unfortunately agree very well with a product containing 10% of naphthalene. Attempts to remove naphthalene as picrate fail when the tetralin contains 10% of naphthalene.

As one of the possible impurities of tetralin is the dihydronaphthalene, 50 cc of tetralin dissolved in ether were treated with the saturated solution of mercuric acetate in water and shaken during 24 hours. Only a small yellow precipitate was obtained, the tetralim being entirely free of dihydronaphtalene. After this treatment, the absorption spectrum of the redistilled tetralin does not present any improvement.

Accordingly the barium salt of tetralin-sulphonic acid was prepared following Willstatter and Seitz (Ber. 1923, *56*, 1392). This was converted into the sodium salt, which was recrystallised, and the tetralin regenerated by adding 66 % sulphuric acid and fractionally distilling with steam superheated to 160° — 180°. In the purest fraction, the most intense bands were at 274 and 267 $m\mu$ log e 2.91 and 2.87 respectively. The material was not however pure as bands in the region 280 — 320 $m\mu$ were present at intensities indicating some 2 % of naphthalene.

Several hundred grammes of barium tetralin-sulphonate were then prepared and fractionally crystallised, the progess of the purification being controlled spectrographically. In order to facilitate control the corresponding barium salts of naphthalene and of benzene-sulphonic acids were prepared and their spectra measured:

Fig. 20 — Extinction curves of
(1) Barium benzene sulphonate
(2) Barium tetralin sulphonate
(3) Barium naphthalene sulphonate in water.

$(C_{10}H_7SO_3)_2$ Ba		$(C_6H_5SO_3)_2$ Ba	
λ max. $m\mu$	e max	λ max. $m\mu$	e max.
317.0	650	269.3	565
312.5	820	265.1	340
306.7	1200	262.7	620
303.2	1600	258.4	430
280.0	6000	256.4	450
		252.1	310

The characteristic bands of the naphthalene sulphonate were observed in the impure tetralin sulphonate, but after many recrystallisations from water, a product entirely free from them was finally obtained: pure barium tetralin sulphonate:

λ max.	277.8	271.1	265.0 $m\mu$
e max.	840	840	700

This result agrees well with the data of Hantzsch on tetralin — 2 — sulphonic acid in various solvents, bands at $227 - 278$ $m\mu$ and $269 - 271$ $m\mu$. log $e = 3$ being recorded (Ber. 1927, *60*, 1933).

The purified barium salt was converted into the sodium salt which was recrystallised and found on examination to be free from selective absorption in the region $290 - 320$ $m\mu$.

Tetralin was regenerated by the action of superheated steam on the acidified sodium salt, and redistilled under reduced pressure. The final pro-

FIG. 21—This figure shews the different stages of purification of tetralin.

•••• Kimura's maxima

Extinction curves of

.... commercial tetralin distilled over sodium,

—— definitive curve

duct exhibited two sharp maxima at 274 and 267 $m\mu$, the e values being c a 760 and 740 and an inflexion at 261 $m\mu$ (e = 600).

In the course of the recrystallisation of the barium sulphonate a rather elusive «impurity» was encountered. Three sharp equally intense bands were repeatedly observed at 321.5, 313.5, and 306.7 $m\mu$ and were unmistakeably different from those of barium naphthalene sulphonate. Unfortunately, the material responsible could not be isolated as on recrystallising fractions exhibiting the bands, the selective absorption disappeared both from the mother liquor and the crystals.

The results may be possibly construed as a hint that isome-

ric tetrahydronaphthalene may exist in equilibrium. The proportion of the anomalous material is however quite small, and it is clear that the principal constituent of commercial tetralin is a substance devoid of the $290 - 320$ $m\mu$ narrow bands pre-
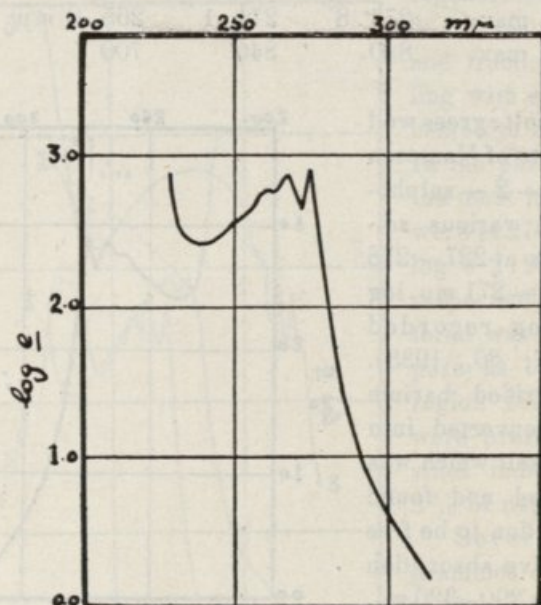
Fig. 22 — Definitive extinction curve of tetralin in hexane.

sent in naphthalene. Its absorption is in fact reasonably close to that of the xylenes.

Baly and Tuck (loc. cit.) describe the absorption spectrum of $1.2.3.4$ — tetrahydronaphthalene. One maximum only appears (ca 256 $m\mu$) in the published curve, the intensity being apparently just as great as that of naphthalene at 272 $m\mu$ (log e 4). It is difficult to understand this observation, especially since the authors examined the so — called α — tetrahydronaphthalene
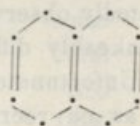
made by the reduction of naphthalene by means of phosphorus and iodine. The published curve for this material agrees closely

with our data for $1.2.3.4$ — tetrahydronaphthalene, contaminated with a little naphthalene.

TETRAHYDRO-NAPHTHOLS

Komatsu, Masumoto and Kumamoto (Mem. Coll. Sci. Kyoto, 1924, 7, 287) have examined ar — tetrahydro — α — naphthol and ar — tetrahydro — β — naphthol. The former shews two maxima at 281 and 269 $m\mu$ and the latter at 286 and 267 $m\mu$, the extinction coefficients being apparently of the order $1000 - 2000$. This

Fig. 23 — Extinction curve of ac — tetrahydro — β — naphthol in alcohol.

may be compared with the more recent data of Conrad-Billroth (Z. physikal Chem. 1933, 20, 222) on $1.2.3$ — and $1.3.4$ — xylenols : —

	λ max. $m\mu$	e max
$1.2.3$ — xylenol	279.0	1690
	273.5	1530
	270.3	1430

1.3.4 — xylenol	280.9	1850
	274.0	1670
	254.5	

We have examined ac·tetrahydronaphthol with the following results:

λ max.	273.0	266.5 $m\mu$
log e	3.15	3.14

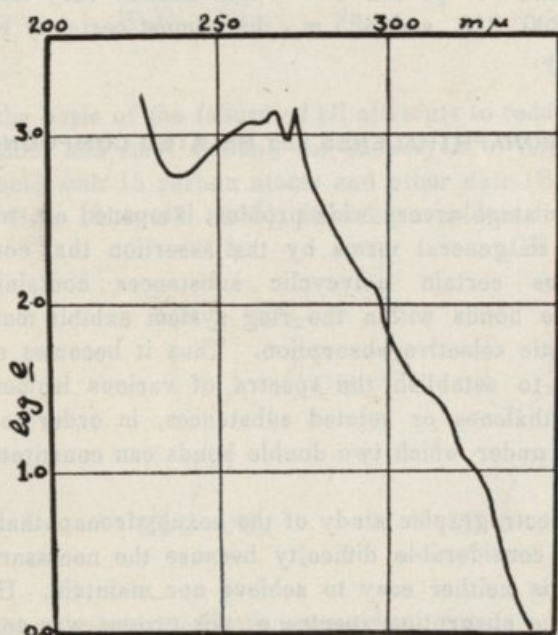The material (b. p. $135°/5^{mm}$) also shewed very feeble inflexions at 296, 315, and 325 $m\mu$ due almost certainly to a trace of impurity.

HEXAHYDRONAPHTHALENES and RELATED COMPOUNDS

At this stage a very wide problem is opened up, which may be stated in general terms by the assertion that contrary to expectations certain polycyclic substances containing only two double bonds within the ring system exhibit marked and characteristic selective absorption. Thus it becomes especially important to establish the spectra of various isomeric hexahydronaphthalenes or related substances, in order to find the conditions under which two double bonds can constitute a chromophore.

The spectrographic study of the hexahydronaphthalenes is a matter of considerable difficulty because the necessary degree of purity is neither easy to achieve nor maintain. Hence the study of the absorption spectra of this groups was commenced with two terpenes, cadinene and isocadinene, both being hexahydroderivatives of cadalene. The presence in the molecules of the methyl and isopropyl groups will not appreciably affect the absorption of the hexahydronaphthalene nucleus as may be concluded from the study of the alkylderivatives of naphthalene. The alkyl groups may in fact to a certain extent protect the hexahydroderivatives from oxidation.

CADINENE

The dehydrogenation of cadinene to cadalene reveals the car
bon skeleton
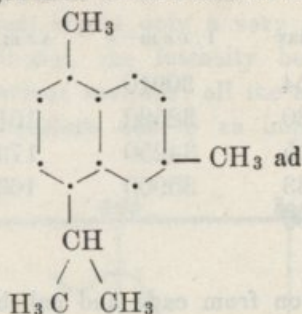
and on the basis of the failure of all attempts to reduce cadinene
with sodium and amyl alcohol, the ozonolysis of this compound
into an acid with 15 carbon atoms and other data (Semmler and
Stenzel, Ber. 1914, *47*, 2555), Ruzicka considers that cadinene
is either
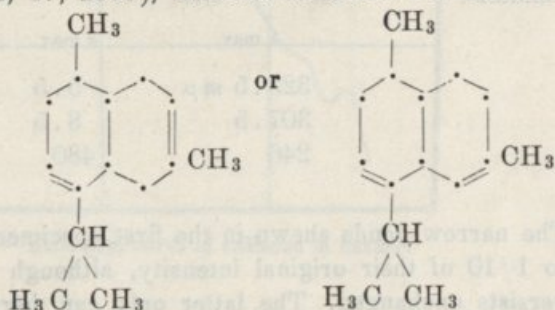
or possibly a mixture of both isomerides.

Cadinene was prepared according to the instructions of Ruzi-
cka and Meyer (Helv. 1921, *4*, 505) from cubeb oil and also
from cade oil. The oils were fractionated under reduced pres-
sure and the fraction $125° - 138°/12^{mm}$ was dissolved in ether
and saturated at $0°$ with dry hydrogen chloride. The cadi-
nene dihydrochloride crystallises in needles from the ether
solution and is purified by recrystallisation from ethyl acetate
(m. p. $117° - 118°$). The dihydrochloride was refluxed with
an alcoholic solution of caustic soda, the alcohol distilled off
and the regenerated cadinene distilled under reduced pressure

b. p. 138°/12^{mm}. This material dissolved in hexane exhibits selective absorption with the following maxima:

λ max.	e max	$1/\lambda$ cm^{-1}	Δc m^{-1}	mean Δc m^{-1}
323.5 $m\mu$	54	30910		
307.5	80	32520	1610	
292.0	115	34250	1730	1663
278.5	133	35900	1630	
246	480			

A second preparation from cade and cubeb oils yielded the dihydrochloride in quantity, so that it could be recrystallised several times from ethyl acetate until the m. p. 117° was absolutely constant. Treatment with alcoholic soda again yielded the hydrocarbon of b. p. 136° — 138°/12^{mm}.

The absorption spectrum in hexane shewed the following maxima:

λ max.	e max.
323.5 $m\mu$	5.5
307.5	8.5
246	480

The narrow bands shewn in the first specimen are thus reduced to 1/10 of their original intensity, although the 246 $\dot{m}\mu$ band persists unchanged. The latter only can therefore survive as a property of cadinene itself. The narrow bands must however be due to a substance capable of yielding a crystalline hydrochloride separable only with great difficulty from cadinene dihydrochloride, or else a certain amount of cadinene is oxidised during the regeneration and redistillation. Successive redistillations of cadinene have shewn an increasing intensity for the narrow bands over the region 323 — 308.5 $m\mu$.

In order to ascertain whether the narrow bands over the region 323.5 — 278.5 $m\mu$ belong to the absorption spectrum of cadinene or whether they are due to a more highly unsaturated impurity, the alcoholic solution of cadinene was treated with metallic sodium. No change in the molecule of cadinene is to be expected as the double bonds are not conjugated.

The hydrocarbon was thrown out of solution by dilution with water and the separated cadinene was dried in an exsicator over calcium chloride. The absorption spectrum of cadinene after this treatment shews only a very shallow band over the region $245-250\ m\mu$, the intensity being the same as that shewn by the previous samples: all the narrow bands disappeared and were therefore due to an impurity, which probably
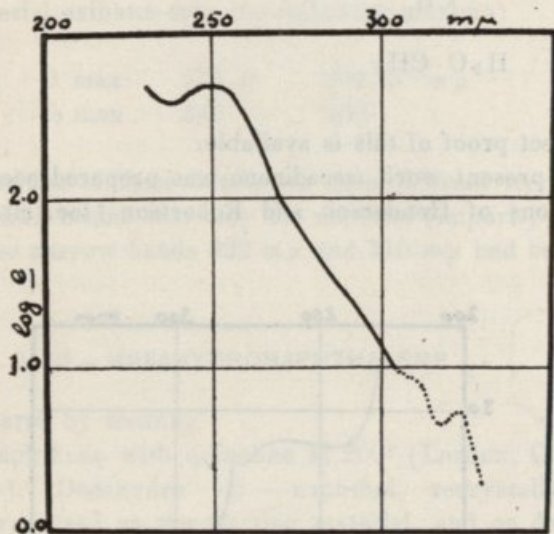
Fig. 24 — Extinction curve of cadinene in hexane.

possessed two or more conjugated double bonds. The definitive extinction curve is given in fig. 24.

isoCADINENE

Cadinene is isomerised when treated with the Bertram-Walbaum mixture, with acetic acid at $230°-235°$ under pressure or with formic acid at $100°$ and transformed in *iso*cadinene (Henderson and Robertson, J. 1924, *125*, 1992: Robertson, Kerr and Henderson, ibid, 1925, *126*, 1946).

*Iso*cadinene, although a hexahydrocadalene, differs from cadinene in that it does not yield a crystalline hydrochloride.

Robertson and Henderson suggest that it is possibly representend by

$$
\begin{array}{c}
CH_3 \\
| \\
\text{(ring structure)} \\
— CH_3 \\
CH \\
/ \backslash \\
H_3C \quad CH_3
\end{array}
$$
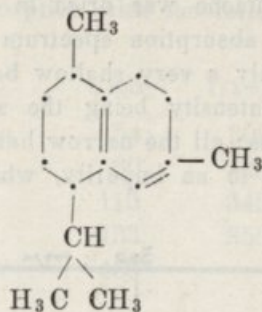
but no direct proof of this is available.

In the present work *iso*cadinene was prepared according to the directions of Henderson and Robertson (loc. cit.). Cadi-
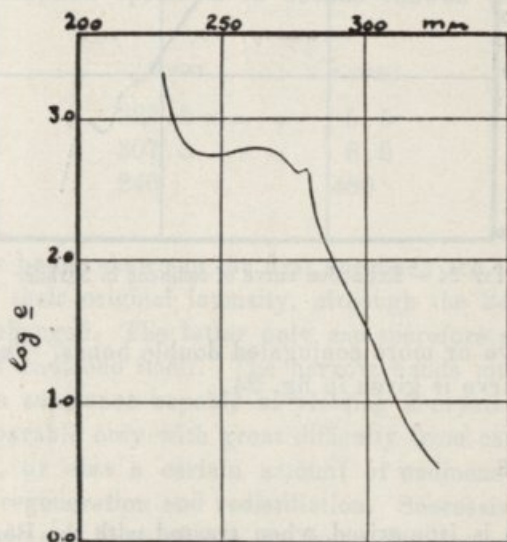
Fig. 25 — Extinction curve of *iso*cadinene in alcohol.

nene (5 g.) and glacial acetic acid (15 g.) were heated together in a sealed tube at $230° — 235°$ for 24 hours. The colourless oil which separated on neutralisation was purified by distillation under diminished pressure, b. p. $102° — 105°/4^{mm}$.

The absorption curve exhibited by this product shews the following maxima:

λ max.   322 , 315 , 279.5 , 262.5 $m\mu$
e max   14 ,   14 ,   443 ,   569

An alcoholic solution of *iso*cadinene was subjected to a very mild reduction with metallic sodium. The absorption of the isolated material exibhits only the following maxima:

λ max   279.5 , 262.5 $m\mu$
e max   440 ,   580

The intensities of these bands are note different from the first results which means that only the material (impurity) responsible for the narrow bands 322 $m\mu$ and 315 $m\mu$ had been hydrogenated.

1.2.3.4.9.10 — HEXAHYDRONAPHTHALENE
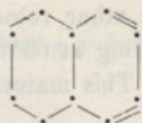
was prepared by treating
dibromonaphthane with quinoline at 200° (Leroux, C. R. 1910, *151*, 384). Decahydro — β — naphthol, recrystallised from hexane, was used as the starting material, and on dehydration yielded 1.2.3.4.5.8.9.10 — octahydronaphthalene.

50 g. of decahydro — β — naphthol were mixed with 100 g. of recently fused and pulverised potassium bi-sulphate in a 250 c c pyrex Claisen distilling flask. The mixture was heated in an oil bath. the temperature being increased slowly until it reached 200° — 220°. The dehydration then took place and the octahydronaphthalene distilled with a little water. The product was dissolved in ether, shaken with aqueous potash, washed with water, dried over anhydrous sodium sulphate and redistilled (b. p. 183° — 184°). The crude octahydronaphthalene was then fractionally redistilled under reduced pressure, the fraction distilling at 71°/7^{mm} or 43.5°/0.5 — 1^{mm} being collected. A chloroform solution of octahydronaphthalene (23 g. in 150 c c.) was cooled to — 20° and a 20 °/0 solution of bromine in chloroform was added drop by drop until a slight excess of bromine was evident by the persistence of a pale yellow colour. The

mixture was shaken with a dilute aqueous solution os sulphurous acid, and afterwards with water, dried with anhydrous sodium sulphate and finally the chloroform distilled off After cooling, a crystalline residue was obtained and dissolved in hot alcohol. Colourless needles and an oily liquid were separated from the alcoholic solution. The colourless needles were recrystallised from alcohol (m. p. 83°) and found to correspond with the material described by Leroux (Ann. de Chim. et de Phys. 1910 . *21* . (8) . 473) as *cis* — 2 . 3 — dibromonaphthane. The red oily liquid was cooled with solid carbon dioxide and ether: colourless crystals were separated and recrystallised from alcohol (m. p. 41°). According to Leroux (loc. cit.) this is a mixture of *cis* and *trans* — 2 . 3 . dibromonaphthane.

16 g. of *cis* . 2 . 3 . dibromonaphthane were mixed with 25 g. of quinoline in a sealed tube and heated at 200° during 20 hours. The residue was extracted with ether, shaken with diluted sulphuric acid and water, dried over anhydrous sodium sulphate, the ether removed and the hydrocarbon redistilled, the fraction boiling at 65°/1 . 2 mm being collected.

This material exhibits the following maxima:

λ max.	319.4	314.5	311.5	309.5	305.0	296.5	288.0
log e	0.53	0.26	0.66	0.71	0.72	1.06	1.91

λ max.	284 0	274.0	267.2	261.0 mµ
log e	2 00	2.38	2.30	2.18

These maxima are undoubtedly due to naphthalene (*ca* 1 . 3 % calculated from the intensity of the 311 . 5 mµ band) and tetralin (*ca* 31 % from the 274 mµ band).

It appears from the above data that the hexahydronaphtalene prepared as described suffers considerable oxidation-reduction yielding the more stable compoudds tetralin, naphthalene and probably decalin.

(Continua)

António Jorge Andrade de Gouveia.

Cálculo Simbólico

(CONTINUAÇÃO)

CAPÍTULO II

OPERADORES DIFERENCIAIS

110. A *derivação* é uma operação *uniforme, aditiva* e *permutável* com os números, como é sabido. Pode, além disso, executar-se uma infinidade de vezes sôbre uma dada função.

111. Representaremos por $\dfrac{d}{dx}$, a derivada duma função de x em ordem a x; por $\dfrac{\partial}{\partial x}$, a derivada parcial em ordem a x duma função de diversas variáveis, x, y, ...

112. Segundo as notações do Cálculo Simbólico, poremos:

$$\frac{d^n}{dx^n} = \left(\frac{d}{dx}\right)^n$$

$$\frac{\partial^{h+k}}{\partial x^h \, \partial y^k} = \left(\frac{\partial}{\partial x}\right)^h \cdot \left(\frac{\partial}{\partial y}\right)^k$$

$$\int f(x)\,dx = \left(\frac{d}{dx}\right)^{-1} f(x)$$

$$\int \left[\int f(x)\,dx \right] dx = \left(\frac{d}{dx}\right)^{-2} f(x)$$

. . . .

113. Chamaremos *operadores diferenciais* àqueles em que entram sinais de derivação.

Por exemplo: $e^{\frac{d}{dx}}$, $\dfrac{\partial}{\partial x} + \dfrac{\partial}{\partial y}$, etc.

114. A derivação é uma operação bem definida, aditiva e permutável com os números, mas os operadores formados com sinais de derivação, podem não gosar destas propriedades.

Por exemplo, o operador $\left(\dfrac{d}{dx}\right)^{-1}$ não é bem definido, porque introduz uma constante arbitrária.

115. Teorema. — *Se* $S(m) = \Sigma A_k m^k$ *fôr um polinómio em* m, *ou uma série convergente, dar-se há a relação simbólica*

$$S\left(\frac{d}{dx}\right) e^{mx} = S(m)\, e^{mx}.$$

Com efeito,

$$\begin{aligned}
S\left(\frac{d}{dx}\right) e^{mx} &= \Sigma A_k \left(\frac{d}{dx}\right)^k e^{mx} \\
&= \Sigma A_k\, m^k\, e^{mx} \\
&= e^{mx} \Sigma A_k\, m^k \\
&= S(m)\, e^{mx}
\end{aligned}$$

c. d. d.

116. Escólio. — Se a série $S(m)$ fôr o desenvolvimento duma função $f(m)$, ainda se verifica a relação

$$f\left(\frac{d}{dx}\right) e^{mx} = f(m) \cdot e^{mx},$$

podendo, porém, suceder que

$$f\left(\frac{d}{dx}\right) e^{mx}$$

seja susceptível duma expressão mais geral do que a que é dada por

$$f(m)\, e^{mx}.$$

117. E o que sucede quando $f(m)$ é uma função racional em m e ainda em muitos outros casos.

118. Exemplo. — A relação

$$\left[1 - \frac{d}{dx} + \left(\frac{d}{dx}\right)^2 - \ldots\right] e^{\alpha x} = e^{\alpha x}(1 - \alpha + \alpha^2 - \ldots),$$

que é verdadeira e tem sentido para $|\alpha| < 1$, pode escrever-se:

$$\frac{1}{1 + \dfrac{d}{dx}} e^{\alpha x} = \frac{1}{1 + \alpha} e^{\alpha x}.$$

Porém, fazendo

$$\frac{1}{1 + \dfrac{d}{dx}} e^{\alpha x} = y,$$

vem:

$$y' + y = e^{\alpha x}$$

e

$$y = e^{-x} \int e^{(1 + \alpha.x} \, dx = \frac{e^{\alpha x}}{1 + \alpha} + c e^{-x}$$

valor êste mais geral do que o dado pelo teorema anterior.

119. Dum modo geral, se a função $f(x)$ se puder desenvolver em série de Maclaurin, $f(m) e^{mx}$ será um dos valores de $f\left(\dfrac{d}{dx}\right) e^{mx}$, mas não o mais geral. Assim como a série de potências não representa, em geral, todos os valores da função $f(x)$, também o produto $f(m) e^{mx}$ não representa todos os valores de $f\left(\dfrac{d}{dx}\right) e^{mx}$.

120. Daqui se conclui que o teorema do n.º 115, aplicado a um operador funcional com sentido próprio, não tem fôrça demonstrativa quanto ao operador funcional, mas tem fôrça demonstrativa quanto à série de potências a que êsse operador dá origem.

121. **Teorema.** — *Se* f (x) *fôr um polinómio inteiro ou uma série de potências positivas e inteiras, teremos*

$$f\left(\frac{d}{dx}\right) e^{mx} \varphi(x) = e^{mx} f\left(\frac{d}{dx} + m\right) \varphi(x)$$

Com efeito: pondo $\dfrac{d}{dx} = \dfrac{d_1}{dx} + \dfrac{d_2}{dx}$, onde $\dfrac{d_1}{dx}$ significa a operação que consiste em derivar o produto $e^{mx} \varphi(x)$ conside-

rando constante o 2.º factor; e $\dfrac{d_2}{dx}$ o operador semelhante, mas em que se considera constante o 1.º factor; teremos, por fôrça do teorema anterior,

$$f\left(\frac{d_1}{dx} + \frac{d_2}{dx}\right) e^{mx} \varphi(x) = e^{mx} f\left(m + \frac{d_2}{dx}\right) \varphi(x).$$

Mas, como $\dfrac{d_2}{dx}$ significa o operador que deriva o produto $e^{mx} \varphi(x)$, considerando constante o 1.º factor, teremos:

$$f\left(m + \frac{d_2}{dx}\right) e^{mx} \varphi(x) = e^{mx} f\left(m + \frac{d_2}{dx}\right) \varphi(x)$$
$$= e^{mx} f\left(m + \frac{d}{dx}\right) \varphi(x).$$

Logo. .

122. A demonstração pode fazer-se também como no teorema anterior.

Com efeito, pondo

$$f\left(\frac{d}{dx}\right) = \sum A_n \left(\frac{d}{dx}\right)^n,$$

vem:

$$f\left(\frac{d}{dx}\right) e^{mx} \varphi(x) = \sum A_n \left(\frac{d}{dx}\right)^n [e^{mx} \varphi(x)]$$
$$= \sum A_n [e^{mx} \varphi(x)]^{(n)}.$$

Mas, pela fórmula de Leibnitz, teremos:

$$[e^{mx} \varphi(x)]^{(n)} = \sum_{h=0}^{n} \binom{n}{h} (e^{mx})^{(h)} \varphi^{(n-h)}(x)$$
$$= \sum_{h=0}^{n} \binom{n}{h} (m^h e^{mx}) \varphi^{(n-h)}(x)$$
$$= e^{mx} \sum_{h=0}^{n} \binom{n}{h} m^h \left(\frac{d}{dx}\right)^{n-h} \varphi(x);$$

ou ainda,

$$[e^{mx} \varphi(x)]^{(n)} = e^{mx} \left(m + \frac{d}{dx}\right)^n \varphi(x).$$

Logo:

$$f\left(\frac{d}{dx}\right) e^{mx} \varphi(x) = \sum A_n e^{mx}\left(m + \frac{d}{dx}\right)^n \varphi(x)$$

$$= e^{mx}\left[\sum A_n \left(m + \frac{d}{dx}\right)^n\right] \varphi(x)$$

$$= e^{mx} f\left(m + \frac{d}{dx}\right) \varphi(x),$$

<div align="right">c. d. d.</div>

123. Teorema. — *Sejam quais forem os operadores ρ e π, bem definidos e aditivos, assim como os seus inversos, será sempre*

$$f(\rho^{-1} \pi \rho) = \rho^{-1} f(\pi) \rho,$$

se f (x) fôr susceptível de ser desenvolvida segundo as potências inteiras (positivas ou negativas) de x.

Com efeito, se fôr

$$f(x) = \sum_{n=-\infty}^{\infty} A_n x^n,$$

bastará demonstrar o teorema para $A_n x^n$ e $A_{-n} x^{-n}$. Ora

$$(\rho^{-1} \pi \rho)^n = (\rho^{-1} \pi \rho)(\rho^{-1} \pi \rho)\ldots(\rho^{-1} \pi \rho)$$
$$= \rho^{-1} \pi . \pi \ldots . \pi . \rho$$
$$= \rho^{-1} \pi^n \rho.$$

Por outro lado (n.º 64):

$$(\rho^{-1} \pi \rho)^{-1} = \rho^{-1} \pi^{-1} (\rho^{-1})^{-1} = \rho^{-1} \pi^{-1} \rho$$

se ρ^{-1} fôr bem definido. Logo:

$$(\rho^{-1} \pi \rho)^{-n} = (\rho^{-1} \pi^{-1} \rho)^n = \rho^{-1} \pi^{-n} \rho.$$

Consequentemente:

$$f(\rho^{-1} \pi \rho) = \sum_{-\infty}^{\infty} A_n [\rho^{-1} \pi \rho]^n = \sum_{-\infty}^{\infty} A_n \rho^{-1} \pi^n \rho;$$

ou seja:

$$f\left(\rho^{-1}\,\pi\,\rho\right) = \rho^{-1}\left[\sum_{-\infty}^{\infty} A_n\,\pi^n\right]\rho$$
$$= \rho^{-1}\,f(\pi)\,\rho,$$

se ρ e π, forem aditivos.

124. Nota. — O teorema só tem fôrça demonstrativa no caso dos inversos de ρ e π serem bem definidos.

125. Se a função $f(x)$ fôr regular na origem, bastará que ρ^{-1} seja bem definido para o teorema ter fôrça demonstrativa.

126. Como

$$\frac{d}{dx}\left(e^{\varphi(x)}\,y\right) = e^{\varphi(x)}\,\varphi'(x)\cdot y + e^{\varphi(x)}\,y'$$
$$= e^{\varphi(x)}\left(\varphi'(x) + \frac{d}{dx}\right)y,$$

segue-se que

$$\left(\frac{d}{dx} + \varphi'(x)\right)y = e^{-\varphi(x)}\cdot\frac{d}{dx}\cdot e^{\varphi(x)}\,y$$

Aplicando a esta relação a doutrina do número anterior, deduz-se o seguinte:

127. Teorema. — *Quando a função* f (x) *se puder desenvolver segundo as potencias inteiras (positivas ou negativas) de* x, *teremos simbolicamente:*

$$f\left[\frac{d}{dx} + \varphi'(x)\right] = e^{-\varphi(x)}\,f\left(\frac{d}{dx}\right)e^{\varphi(x)}.$$

128. NOTA: Se $f(x)$ fôr um polinómio inteiro ou uma série de potências, o teorema tem fôrça demonstrativa, visto que o operador $e^{\varphi(x)}$ bem como o seu inverso, são bem definidos.

129. A êste teorema pode dar-se a forma

$$f\left(\frac{d}{dx}\right)e^{\varphi(x)}\,F(x) = e^{\varphi(x)}\,f\left[\frac{d}{dx} + \varphi'(x)\right]F(x)$$

pondo em evidência o operando $F(x)$.

130. Fazendo $\varphi(x) = mx$, obtem-se o teorema do n.º 121.

131. Como os operadores x e $\dfrac{d}{dx}$, não são permutáveis, o operador $\left(x + \dfrac{d}{dx}\right)^n$ não pode desenvolver-se pela fórmula do binómio de Newton e, consequentemente, $f\left(x + \dfrac{d}{dx}\right)$ não pode desenvolver-se pela fórmula de Taylor. Vamos ver, porém, que no caso de $f(x)$ ser um polinómio inteiro ou uma série de potências, se verifica um desenvolvimento de $f\left(x + \dfrac{d}{dx}\right)$, segundo as potências de $\dfrac{d}{dx}$, semelhante ao de Taylor e tão fácil de obter como êle. É o que nos mostra o seguinte

132. Teorema. — *Se* f (x) *fôr um polinómio inteiro em* x, *ou uma série de potências inteiras e positivas, temos:*

$$f\left(x + \frac{d}{dx}\right) y = \left\{ F(x) + F'(x)\frac{d}{dx} + \frac{1}{\lfloor 2} F''(x)\frac{d^2}{dx^2} + \dots \right\} y,$$

sendo

$$F(x) = e^{\frac{1}{2}\left(\frac{d}{dx}\right)^2} f(x). \tag{1}$$

Com efeito: seja

$$f(x) = \sum A_n x^n.$$

Como,

$$\left(x + \frac{d}{dx}\right) A_n \left(x + \frac{d}{dx}\right)^n = A_n \left(x + \frac{d}{dx}\right)^n \cdot \left(x + \frac{d}{dx}\right),$$

segue-se que

$$\left(x + \frac{d}{dx}\right) f\left(x + \frac{d}{dx}\right) = f\left(x + \frac{d}{dx}\right) \cdot \left(x + \frac{d}{dx}\right).$$

Suponhamos agora que existe um desenvolvimento de

$$f\left(x + \frac{d}{dx}\right)$$

de forma

$$f\left(x + \frac{d}{dx}\right) = F_0(x) + F_1(x)\frac{d}{dx} + F_2(x)\left(\frac{d}{dx}\right)^2 + \cdots$$

sendo $F_0(x)$, $F_1(x)$, ... funções a determinar.

É claro que

$$\left(x + \frac{d}{dx}\right)f\left(x + \frac{d}{dx}\right) = \sum\left(x + \frac{d}{dx}\right)F_h(x)\left(\frac{d}{dx}\right)^h$$

$$= \sum x\,F_h(x)\left(\frac{d}{dx}\right)^h + \sum\frac{d}{dx}\,F_h(x)\left(\frac{d}{dx}\right)^h$$

$$= \sum x\,F_h(x)\left(\frac{d}{dx}\right)^h + \sum\left[F'_h(x)\left(\frac{d}{dx}\right)^h + F_h(x)\left(\frac{d}{dx}\right)^{h+1}\right]$$

ou seja,

$$\left(x + \frac{d}{dx}\right)f\left(x + \frac{d}{dx}\right) = \sum[x\,F_h(x) + F'_h(x) + F_{h-1}(x)]\left(\frac{d}{dx}\right)^h.$$

Por outro lado,

$$f\left(x + \frac{d}{dx}\right)\left(x + \frac{d}{dx}\right) = \sum F_h(x)\left(\frac{d}{dx}\right)^h\left(x + \frac{d}{dx}\right)$$

$$= \sum F_h(x)\left(\frac{d}{dx}\right)^h x + \sum F_h(x)\left(\frac{d}{dx}\right)^{h+1}$$

$$= \sum F_h(x)\left[x\left(\frac{d}{dx}\right)^h + h\left(\frac{d}{dx}\right)^{h-1}\right] + \sum F_h(x)\left(\frac{d}{dx}\right)^{h+1}$$

$$= \sum x\,F_h(x)\left(\frac{d}{dx}\right)^h + \sum h\,F_h(x)\left(\frac{d}{dx}\right)^{h-1} + \sum F_h(x)\left(\frac{d}{dx}\right)^{h+1}$$

$$= \sum[x\,F_h(x) + (h+1)\,F_{h+1}(x) + F_{h-1}(x)]\left(\frac{d}{dx}\right)^h.$$

Igualando os coeficientes de $\left(\dfrac{d}{dx}\right)^h$ dêstes dois desenvolvimentos, virá:

$$F'_h(x) = (h+1)\,F_{h+1}(x).$$

Conseqüentemente,

$$F_h{}'(x) = \frac{1}{\underline{|h}} F_0{}'^{h)}(x),$$

relação esta que justifica o desenvolvimento suposto no enunciado do teorema.

Falta agora determinar $F_0(x)$.

133. Para tanto, façamos $y = 1$ e teremos:

$$F_0(x) = f\left(x + \frac{d}{dx}\right).1$$

$$= \sum A_n \left(x + \frac{d}{dx}\right)^n.1$$

Mas,

$$\left(x + \frac{d}{dx}\right)^n = e^{\frac{1}{2}\left(\frac{d}{dx}\right)^2} x^n. \tag{1}$$

Com efeito, a igualdade é verdadeira para $n = 1$; e, suposta verdadeira para $n = k$, também o será para $n = k + 1$. Na verdade, pondo, para abreviar, d por $\frac{d}{dx}$, teremos:

$$e^{\frac{d^2}{2}} x^{k+1} = \sum \frac{1}{\underline{|n}} \frac{1}{2^n} d^{2n} x^{k+1}$$

$$= \sum \frac{1}{\underline{|n}} \frac{1}{2^n} \left[x\, d^{2n} x^k + 2\,n.\, d^{2n-1} x^k\right]$$

$$= x\, e^{\frac{d^2}{2}} x^k + \sum \frac{1}{\underline{|n-1}} \cdot \frac{1}{2^{n-1}} d^{2(n-1)}.d.x^k$$

$$= x\, e^{\frac{d^2}{2}} x^k + d \sum \frac{1}{\underline{|n-1}} \cdot \frac{1}{2^{n-1}} d^{2(n-1)} x^k$$

$$= (x + d)\, e^{\frac{d^2}{2}} x^k = (x + d)^{k+1}.$$

Além disso,

$$F_0(x) = \sum A_n e^{\frac{1}{2}\left(\frac{d}{dx}\right)^2} x^n = e^{\frac{1}{2}\left(\frac{d}{dx}\right)^2} \sum A_n x^n = e^{\frac{1}{2}\left(\frac{d}{dx}\right)^2} f(x)$$

o que acaba de demonstrar o teorema.

134. Do mesmo modo se demonstra que

$$f\left(ax + b\frac{d}{dx}\right) = F(x) + \frac{b}{a} . F'(x)\frac{d}{dx} + \frac{b^2}{a^2 \lfloor 2} F''(x)\left(\frac{d}{dx}\right)^2 + \ldots$$

sendo

$$F(x) = f\left(ax + b\frac{d}{dx}\right). 1 \qquad (2)$$

135. O cálculo de $F(x)$, quando é dado $f\left(ax + b\frac{d}{dx}\right)$, terá de fazer-se directamente por meio de (2). Dado $F(x)$, determina-se $f\left(ax + b\frac{d}{dx}\right)$ pelo método dos coeficientes indeterminados.

136. Se π e ρ forem dois operadores tais que

$$f(\pi) . \rho . y = \rho . f(\pi + \Delta\pi) . y \qquad (1),$$

sendo $\Delta\pi$ um acréscimo constante do argumento de $f(\pi)$, teremos também

$$f(\pi)\rho^2 y = \rho f(\pi + \Delta\pi) . \rho y$$
$$= \rho^2 . f(\pi + 2\Delta\pi) . y;$$

e, dum modo geral,

$$f(\pi)\rho^n y = \rho^n f(\pi + n\Delta\pi) . y \qquad (2)$$

137. Note-se que, *se ρ e π satisfizerem à condição* (1), *também* hρ *e π satisfarão, qualquer que seja o número* h.
Com efeito,

$$f(\pi)(h\rho)y = hf(\pi)\rho y = h\rho f(\pi + \Delta\pi)y$$
$$= (h\rho) f(\pi + \Delta\pi)y,$$

c. d. d.

138. Mudando π em $\pi - n\Delta\pi$, virá também,

$$\rho^n f(\pi)y = f(\pi - n\Delta\pi)\rho^n y \qquad (3)$$

139. Se $f(x)$ fôr um polinómio inteiro ou uma série de potências,

$$f(x) = \sum A_n x^n,$$

é evidente que

$$(\pi + \rho) f(\pi + \rho) = f(\pi + \rho) \cdot (\pi + \rho), \qquad (4)$$

visto que

$$(\pi + \rho) A_n (\pi + \rho)^n = A_n (\pi + \rho)^n \cdot (\pi + \rho).$$

140. Posto isto, vamos demonstrar o seguinte

Teorema. — *Se* $f(x)$, π *e* ρ, *satisfizerem às condições dos n.°^{s} 136 e 139, será*

$$f(\pi+\rho) = f(\pi) + \frac{\Delta f(\pi)}{\Delta \pi} \rho + \frac{1}{\underline{2}} \cdot \frac{\Delta^2 f(\pi)}{\Delta \pi^2} \rho^2 + \frac{1}{\underline{3}} \frac{\Delta^3 f(\pi)}{\Delta (\pi^3)} \rho^3 + \dots \quad (5)$$

sendo

$$\frac{\Delta f(\pi)}{\Delta \pi} = \frac{f(\pi) - f(\pi - \Delta \pi)}{\Delta \pi}$$

141. O método de demonstração é o mesmo do n.° 132. Suponhamos, pois, que o 1.° membro de (5) é susceptível do desenvolvimento seguinte:

$$f(\pi + \rho) = f_o(\pi) + f_1(\pi) \rho + f_2(\pi) \rho^2 + \dots,$$

sendo $f_o(\pi)$, $f_1(\pi)$, etc. funções a determinar. Sendo, por hipótese,

$$f(\pi + \rho) = \sum A_n (\pi + \rho)^n,$$

virá

$$(\pi + \rho) f(\pi + \rho) = (\pi + \rho) \sum f_n(\pi) \rho^n$$
$$= \sum (\pi + \rho) f_n(\pi) \rho^n$$
$$= \sum \pi f_n(\pi) \rho^n + \sum \rho f_n(\pi) \rho^n$$
$$= \sum \pi f_n(\pi) \rho^n + \sum f_n(\pi - \Delta \pi) \rho^{n+1}$$
$$= \sum \left[\pi f_n(\pi) + f_{n-1}(\pi - \Delta \pi) \right] \rho^n \qquad (6)$$

142. Por outro lado, temos também

$$f(\pi + \rho) \cdot (\pi + \rho) = \sum f_n(\pi) \rho^n (\pi + \rho)$$
$$= \sum f_n(\pi) \rho^n \pi + \sum f_n(\pi) \rho^{n+1}$$
$$= \sum f_n(\pi) \cdot (\pi - n \Delta \pi) \rho^n + \sum f_n(\pi) \rho^{n+1}$$
$$= \sum (\pi - n \Delta \pi) f_n(\pi) \rho^n + \sum f_n(\pi) \rho^{n+1}$$
$$= \sum \left[(\pi - n \Delta \pi) f_n(\pi) + f_{n-1}(\pi) \right] \rho^n \qquad (7)$$

143. Como os desenvolvimentos (6) e (7) são iguais, teremos que

$$n \Delta \pi \cdot f_n(\pi) = f_{n-1}(\pi) - f_{n-1}(\pi - \Delta \pi).$$

Logo:

$$f_n(\pi) = \frac{1}{n} \cdot \frac{\Delta f_{n-1}(\pi)}{\Delta \pi}.$$

Consequentemente:

$$f_1(\pi) = \frac{\Delta f_0(\pi)}{\Delta \pi}$$

$$f_2(\pi) = \frac{1}{2} \cdot \frac{\Delta f_1(\pi)}{\Delta \pi} = \frac{1}{2} \cdot \frac{\Delta^2 f_0(\pi)}{\Delta \pi^2}$$

$$\cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots$$

$$f_n(\pi) = \frac{1}{\underline{n}} \cdot \frac{\Delta^n f_0(\pi)}{\Delta \pi^n},$$

o que demonstra uma parte do teorema. Falta calcular $f_0(\pi)$. Atendendo à doutrina do n.º 137, teremos também

$$f(\pi + h\rho) = f_0(\pi) + f_1(\pi) h\rho + f_2(\pi) h^2 \rho^2 + \dots,$$

qualquer que seja h. Fazendo tender h para zero, vem imediatamente

$$f_0(\pi) = f(\pi),$$

o que acaba de demonstrar o teorema.

144. Os operadores $\rho = e^{mx}$ e $\pi = \dfrac{d}{dx}$, satisfazem à condição (1), pois que (n.º 121)

$$f\left(\frac{d}{dx}\right) e^{mx} y = e^{mx} f\left(\frac{d}{dx} + m\right) y,$$

sendo $\Delta \pi = m$. Há uma infinidade de operadores satisfazendo a esta condição.

145. Teorema da reciprocidade. — *Se as funções* $\varphi(t)$ *e* $\psi(t)$ *fôrem susceptíveis de serem desenvolvidas em série de Maclaurin, virá :*

$$\varphi\left(\frac{d}{do}\right) \psi(o) = \psi\left(\frac{d}{do}\right) \varphi(o),$$

entendendo por

$$\varphi\left(\frac{d}{do}\right)\psi(o)$$

o valor de

$$\left[\varphi\left(\frac{d}{dt}\right)\psi(t)\right]_{t=0}$$

e do mesmo modo se entendendo

$$\psi\left(\frac{d}{do}\right)\varphi(o).$$

Com efeito, pondo

$$\varphi(t)=\alpha_0+\alpha_1 t+\alpha_2 t^2+\ldots+\alpha_h t^h+\ldots$$

e

$$\psi(t)=b_0+b_1.t+b_2 t^2+\ldots+b_k t^k+\ldots$$

virá:

$$\left[\varphi\left(\frac{d}{dt}\right)\psi(t)\right]_{t=0}=\alpha_0 b_0+\alpha_1 b_1+2\alpha_2 b_2+\ldots$$

$$\left[\psi\left(\frac{d}{dt}\right)\varphi(t)\right]_{t=0}=b_0\alpha_0+b_1\alpha_1+2 b_2\alpha_2+\ldots$$

Logo...

146. Teorema. — Simbólicamente, a série de Maclaurin pode escrever-se assim:

$$\varphi(t)=e^{t\frac{d}{do}}\varphi(o).$$

E, pelo teorema da reciprocidade:

$$e^{t\frac{d}{do}}\varphi(o)=\varphi\left(\frac{d}{do}\right)e^{t.o}$$

$$=\varphi\left(\frac{d}{do}\right)\left(1+t.o+\frac{t^2}{\lfloor 2}.o^2+\ldots\right)$$

$$=\varphi(o)+t.\varphi\left(\frac{d}{do}\right)o+\frac{t^2}{\lfloor 2}\ \varphi\left(\frac{d}{do}\right)o^2+\ldots$$

Logo:

$$\varphi(t)=\varphi(o)+t.\varphi\left(\frac{d}{do}\right)o+\frac{t^2}{\lfloor 2}.\varphi\left(\frac{d}{do}\right)o^2+\ldots$$

que é a chamada *forma conjugada* da série de Maclaurin.

147. Só estudaremos operadores diferenciais, começando pelos que são definidos por polinómios e passando em seguida para os operadores definidos por séries.

CAPÍTULO III

OPERADORES POLINÓMIOS

148. Entre os operadores diferenciais ocupam lugar primacial, os da forma

$$\sum A\,(x,\,y,\dots)\,\left(\frac{\partial}{\partial x}\right)^{h}\left(\frac{\partial}{\partial y}\right)^{k}\dots,$$

onde $A\,(x\;\;y\dots)$ é um polinómio inteiro das variáveis independentes e o somatório contem um número finito de parcelas.

149. Estes operadores são bem definidos porque tôdas as operações que neles entram o são. E também são *aditivos*, pela mesma razão. Mas em geral não são permutáveis uns com os outros, embora o sejam sempre com os números, como é evidente.

Assim, os operadores x e $\dfrac{d}{dx}$, não são permutáveis, porque

$$\left(x\,\frac{d}{dx}\right)f(x)=x\,f'(x)$$

$$x\left(\frac{d}{dx}\,x\right)f(x)=\frac{d}{dx}\left[x\,f(x)\right]$$

$$=f(x)+x\,f'(x).$$

Mas tanto um como o outro, como as suas combinações $x\dfrac{d}{dx}$ e $\dfrac{d}{dx}\,.\,x$ são permutáveis com qualquer constante.

150. Mas excepcionalmente estes operadores podem ser permutáveis uns com os outros.

Por exemplo: se fôr

$$\rho = \frac{d}{dx} - x \quad \text{e} \quad \rho_1 = \frac{d}{dx} - x - 1,$$

ρ e ρ_1 são permutáveis. Com efeito:

$$\rho \rho_1 y = \rho \; (\rho_1 y) = \rho \; (y' - x y - y)$$
$$= \left(\frac{d}{dx} - x \right) \; (y' - x y - y)$$
$$= y'' - y - x y' - y' - x y' + x^2 y + x y$$
$$= y'' - y' \; (1 + 2 \, x) + y \; (x^2 + x - 1).$$

Por sua vez,

$$\rho_1 \rho y = \rho_1 \; (\rho y) = \rho_1 \; (y' - x y)$$
$$= \left(\frac{d}{dx} - x - 1 \right) (y' - x y)$$
$$= y'' - y - x y' - x y' + x^2 y - y' + x y$$
$$= y'' - y' \; (1 + 2 \, x) + y \; (x^2 + x - 1).$$

Logo:

$$\rho \rho_1 = \rho_1 \rho.$$

151. NOTA: Os operadores não *mordem* uns nos outros. Só produzem os seus efeitos ao serem aplicados ao *operando* que lhes é dado. Assim, por exemplo, se multiplicarmos os operadores $\rho \, \rho_1$, não podemos substituir nas parcelas do produto $\frac{d}{dx} x$ por 1.

Para efectuar estes produtos é preciso deixar as operações apenas indicadas:

$$\rho \rho_1 = \left(\frac{d}{dx} \right)^2 - \frac{d}{dx} x - \frac{d}{dx} - x \frac{d}{dx} + x^2 + x$$

e

$$\rho_1 \rho = \left(\frac{d}{dx} \right)^2 - \frac{d}{dx} x - x \frac{d}{dx} + x^2 - \frac{d}{dx} + x$$

152. Teorema. — É evidente que, qualquer que seja o operador polinómio $P\left(x, y, \ldots, \frac{\partial}{\partial x}, \frac{\partial}{\partial x} \ldots\right)$, teremos sempre:

$$P\left(x, y \ldots, \frac{\partial}{\partial x}, \frac{\partial}{\partial y} \ldots\right). \, O = O$$

Polinómios em $\frac{d}{dx}$

153. Os operadores polinomiais mais simples, são os da forma

$$P\left(\frac{d}{dx}\right) = a_0 + a_1 \frac{d}{dx} + \ldots + a_n \left(\frac{d}{dx}\right)^n,$$

onde as $a \, a$ são constantes.

154. Estes operadores são permutáveis entre si (n.º 46).

155. Conseqüentemente, estes operadores podem adicionar-se algèbricamente e multiplicar-se, ficando os resultados a que se chega por meio destas operações rigorosamente demonstradas.

156. Daqui resulta, como em o n.º 47, que estes operadores se podem decompor em factores binómios, sendo esta uma das suas propriedades mais úteis.

Inversão de $P\left(\frac{d}{dx}\right)$

157. O problema da inversão dum operador da forma $P\left(\frac{d}{dx}\right)$ é idêntico ao da integração duma equação diferencial linear de ordem n, de coeficientes constantes.

Êste problema é completamente resolvido pelo Cálculo Simbólico.

Com efeito, seja dada a equação

$$P\left(\frac{d}{dx}\right) y \equiv A_0 y^{(n)} + A_1 y^{(n-1)} + \ldots + A_n y - X \qquad (1)$$

onde X é uma função conhecida x. Será, por sua vez,

$$P(x) = A_0 (x - a_1)^{\alpha_1} (x - a_2)^{\alpha_2} \ldots (x - a_k)^{\alpha_k},$$

com $\alpha_1 + \alpha_2 + \ldots + \alpha_k = n$. Teremos, pelos n.ᵒˢ 105 e 106, que satisfazem à proposta os valores de y dados por

$$y = \frac{1}{P\left(\dfrac{d}{dx}\right)} X = \left[\sum_{i=1}^{k} \sum_{j=1}^{\alpha_i} \frac{B_i^j}{\left(\dfrac{d}{dx} - a_i\right)^j} \right] X;$$

ou ainda,

$$= \left[\sum_{i=1}^{k} \frac{\varphi_i\left(\dfrac{d}{dx}\right)}{\left(\dfrac{d}{dx} - a_i\right)^{\alpha_i}} \right] X,$$

onde $\varphi_i\left(\dfrac{d}{dx}\right)$ é um polinómio em $\dfrac{d}{dx}$ de grau inferior a α_i. Ou ainda

$$y = \sum_{i=1}^{k} \left(\frac{d}{dx} - a_i\right)^{-\alpha_i} \varphi_i\left(\frac{d}{dx}\right) X,$$

sendo esta sôma estendida a tôdas as raízes. Mas, pelo teorema do n.º 127,

$$\left(\frac{d}{dx} - a_i\right)^{-\alpha_i} \varphi_i\left(\frac{d}{dx}\right) X = e^{a_i x}\left(\frac{d}{dx}\right)^{-\alpha_i} e^{-a_i x} \varphi_i\left(\frac{d}{dx}\right) X$$

$$= e^{a_i x} \int\!\int \ldots \int e^{-a_i x} \varphi_i\left(\frac{d}{dx}\right) X \, dx^{\alpha_i}$$

Conseqüentemente:

$$y = \sum_{i=1}^{k} e^{a_i x} \int\!\int \ldots \int e^{-a_i x} \cdot \varphi_i\left(\frac{d}{dx}\right) \cdot X \cdot dx^{\alpha_i},$$

resultado êste que vem expresso em quadraturas.

Cada raíz a_i dá origem à introdução de α_i constantes arbitrárias e, portanto, o valor de y a que chegamos, repre-

27

senta o integral geral da proposta, como é sabido do Cálculo Integral.

158. Equação homogénea. — No caso da equação linear ser homogénea, isto é, se fôr $X = 0$, teremos imediatamente:

$$y = \sum_{i=1}^{k} e^{a_i x}\left(c_0 + c_1\, x + c_2\, x^2 + \ldots + c_{\alpha_i - 1}\, x^{\alpha_i - 1}\right)$$

onde os $c\, c$ são as constantes de integração. Neste caso, o integral geral da proposta forma-se imediatamente a partir das raízes do polinómio $P(x)$, ou seja, da chamada *equação característica*.

Cada raiz a de grau de multiplicidade α dá um integral particular da forma

$$e^{a x}\, P_{\alpha - 1}(x)$$

onde $P_{\alpha - 1}$ é um polinómio arbitrário de grau $\alpha - 1$.

159. Equação completa. — No caso de ser conhecido um integral particular da equação completa

$$P\left(\frac{d}{dx}\right) y = X,$$

é sabido do Cálculo Integral que basta acrescentar êsse integral ao integral geral da equação sem 2.º membro, para obter o integral geral da equação dada.

Na investigação dêsse integral particular da equação completa, ainda o Cálculo Simbólico presta serviços.

160. Cálculo do integral particular. — Há quatro casos importantes em que é fácil calcular um integral da equação completa, servindo-nos de teoremas do Cálculo Simbólico já demonstrados.

161. Primeiro caso. — O 2.º membro da equação é um polinómio inteiro:

$$P\left(\frac{d}{dx}\right) y = \pi(x).$$

Neste caso, resolvida a equação em ordem a y, vem:

$$y = \frac{1}{P\left(\dfrac{d}{dx}\right)}\, \pi\,(x).$$

Desenvolvendo $\dfrac{1}{P\left(\dfrac{d}{dx}\right)}$ segundo as potências crescentes de $\dfrac{d}{dx}$,

obtemos uma série em $\dfrac{d}{dx}$ que, aplicada ao polinómio $\pi\,(x)$, dá um desenvolvimento finito que satisfaz à proposta, embora não seja a sua solução mais geral.

Mas como o nosso fim é o cálculo de um integral qualquer, esta parte do problema fica resolvida.

NOTA: O resultado obtido satisfaz à equação completa, porque multiplicando $P\left(\dfrac{d}{dx}\right)$ pelo desenvolvimento em série

de $\dfrac{1}{P\left(\dfrac{d}{dx}\right)}$ obtem-se, depois de feitas as reduções, o valor 1.

Estas reduções são em número infinito, em geral, mas isso importa pouco quando os desenvolvimentos são finitos, como no caso presente (n.º 52).

162. Segundo caso. — Se o 2.º membro da proposta fôr um somatório de exponenciais, isto é, se fôr

$$P\left(\frac{d}{dx}\right) y = \Sigma\, A\, e^{\alpha x}.$$

virá:

$$y = \frac{1}{P\left(\dfrac{d}{dx}\right)}\, \Sigma\, A\, e^{\alpha x}$$

$$= \Sigma\, A\, \frac{1}{P\left(\dfrac{d}{dx}\right)}\, e^{\alpha x}$$

(pelo n.º 116)

$$= \Sigma\, A\, \frac{e^{\alpha x}}{P\,(a)}.$$

163. Assim, por exemplo, a equação

$$y'' - 3\,y' + 2\,y = e^{a\,x}$$

dá

$$\left[\left(\frac{d}{dx}\right)^2 - 3\,\frac{d}{dx} + 2\right] y = e^{a\,x}.$$

e

$$y = \frac{1}{\left(\dfrac{d}{a\,x}\right)^2 - 3\,\dfrac{d}{a\,x} + 2}\; e^{a\,x}$$

$$= \frac{1}{a^2 - 3\,a + 2}\; e^{a\,x}$$

Êste valor de y satisfaz à proposta, como é fácil de ver ; e é bem determinado.

164. Escólio. — No caso de haver exponenciais que tenham por coeficiente de x, no expoente, raízes de $P\,(x)$, a doutrina não é aplicável, porque o resultado viria infinito. Suponhamos, para fixar ideias, que no segundo membro havia a parcela $e^{a_1 x}$ e tínhamos então :

$$P\left(\frac{d}{dx}\right) y \equiv \left(\frac{d}{dx} - a_1\right)^{\sigma_1} \pi\left(\frac{d}{dx}\right) y = e^{a_1 x} + \Sigma\,A\,e^{\alpha x}.$$

Resolvendo em ordem a y, virá :

$$y = \frac{1}{P\left(\dfrac{d}{dx}\right)}\; e^{a_1 x} + \Sigma\,\frac{A}{P\left(\dfrac{d}{dx}\right)}\; e^{\alpha x}.$$

Como, por hipótese, $P\,(a_1) = o$, poremos

$$\frac{1}{P\left(\dfrac{d}{dx}\right)}\; e^{a_1 x} = \frac{1}{\left(\dfrac{d}{dx} - a_1\right)^{\alpha_1}} \cdot \frac{1}{\pi\left(\dfrac{d}{dx}\right)}\; e^{a_1 x}$$

$$= \left(\frac{d}{dx} - a_1\right)^{-\alpha_1} \frac{e^{a_1 x}}{\pi(a_1)}$$

$$= \frac{e^{a_1 x}}{\pi(a_1)} \left(\frac{d}{dx}\right)^{-\alpha_1} 1$$

$$= \frac{e^{a_1 x}}{\pi(a_1)} \left[\frac{x^{\alpha_1}}{|\alpha_1} + A_0 + A_1 x + \ldots + A_{\alpha_1 - 1} . x^{\alpha_1 - 1}\right].$$

O integral particular procurado, correspondente a êste termo, será pois

$$\frac{e^{a_1 x}}{\pi(a_1)} \cdot \frac{x^{\alpha_1}}{|\alpha_1}.$$

165. Seja, por exemplo, calcular um integral particular da equação

$$y'' - 3 y' + 2 y = e^x.$$

Teremos:

$$\left(\frac{d}{dx} - 2\right)\left(\frac{d}{dx} - 1\right) y = e^x;$$

e ainda

$$\left(\frac{d}{dx} - 1\right) y = \frac{1}{\frac{d}{dx} - 2} e^x = \frac{1}{1 - 2} e^x = -e^x.$$

Logo:

$$y = -\left(\frac{d}{dx} - 1\right)^{-1} e^{+x} = -e^x \int e^{-x} e^x \, dx =$$

$$= -e^x \int dx = -x e^x$$

166. Terceiro caso. — Se o 2.º membro da proposta fôr da forma $\Sigma e^{\alpha x} \pi(x)$, onde $\pi(x)$ é um polinómio em x, vir-nos há,

$$y = \frac{1}{P\left(\frac{d}{dx}\right)} \Sigma e^{\alpha x} \pi(x)$$

$$= \Sigma \, \frac{1}{P\left(\dfrac{d}{dx}\right)} \, e^{\alpha x} \, \pi \, (x)$$

$$= \Sigma \, e^{\alpha x} \, \frac{1}{P\left(\alpha + \dfrac{d}{dx}\right)} \, \pi \, (x).$$

Desenvolvendo $\dfrac{1}{P\left(\alpha + \dfrac{d}{dx}\right)}$ segundo as potências crescentes

de $\dfrac{d}{dx}$, obtemos um desenvolvimento em série que, aplicado a $\pi \, (x)$, dá um resultado finito.

167. Quarto caso. — A êste tipo de equações se reduzem as da forma

$$P\left(\frac{d}{dx}\right)y = \Sigma \left[\pi \, (x) . \cos x + \theta \, (x) \, sen \, x\right],$$

onde $\pi \, (x)$ e $\theta \, (x)$ são polinómios inteiros em x. Basta usar das fórmulas de Euler que exprimem os *cossenos* e *senos* em *exponenciais,* para ficarmos reduzidos ao caso anterior.

NOTA: Todos êstes quatro casos considerados estão compreendidos no terceiro, como é evidente. A solução dêste e, portanto, a solução de todos, obtem-se desenvolvendo em série de potências inteiras de $\dfrac{d}{dx}$, a função racional $\dfrac{1}{P\left(\alpha + \dfrac{d}{dx}\right)}$, desenvolvimento êste que existe sempre, e é fácil de calcular. No caso de $P \, (\alpha) = o$, êste desenvolvimento terá potências negativas, mas em número finito. O cálculo do desenvolvimento pode fazer-se sempre por simples devisão.

CAPÍTULO IV

FORMAS SIMBÓLICAS

168. Forma simbólica das equações lineares. — As equações diferenciais lineares são susceptíveis duma transformação utilíssima que permite integrar muitas delas, e relacionar estas equações com a teoria das séries, facto êste de grande importância.

169. Para fazer essa transformação que consiste essencialmente na mudança da variável independente x, definida pela equação

$$x = e^\theta,$$

sendo θ a nova variável independete, vamos demonstrar a seguinte relação simbólica :

$$\left(\frac{d}{dx}\right)^n = e^{-n\theta}(D-n+1)\ldots(D-1)D \qquad (1)$$

onde

$$D = \frac{d}{d\theta}.$$

Com efeito, representando por X o operando a que se aplicam os operadores dados, teremos :

$$\frac{d}{dx}X = \frac{dX}{d\theta} \cdot \frac{d\theta}{dx} = e^{-\theta}\frac{d}{d\theta}X$$

Logo :

$$\frac{d}{dx} = e^{-\theta}D. \qquad (2)$$

Aplicando esta relação à função $\dfrac{dX}{dx}$. vem :

$$\frac{d^2X}{dx^2} = \frac{d}{dx}\left[\frac{d}{dx}X\right] = \frac{d}{dx}\left[e^{-\theta}\frac{d}{dx}X\right]$$

$$= e^{-\theta} D \left[e^{-\theta} \frac{d}{d\theta} X \right]$$

(pelo n.º 22)

$$= e^{-\theta} D e^{-\theta} \frac{d}{d\theta} X$$

(pelo n.º 121)

$$= e^{-2\theta} (D-1) D X.$$

Logo :

$$\left(\frac{d}{dx} \right)^2 = e^{-2\theta} (D-1) D.$$

O método de indução matemática dá imediatamente

$$\left(\frac{d}{dx} \right)^n = e^{-n\theta} (D-n+1) \ldots (D-1) D$$

que é a relação procurada.

170. Esta relação pode ainda escrever-se (n.º 176) assim :

$$\left(\frac{d}{dx} \right)^n = e^{-n\theta} D (D-1) \ldots (D-n+1) \qquad (3)$$

da qual se tira esta outra

$$x^n \left(\frac{d}{dx} \right)^n = D (D-1) \ldots (D-n+1) \qquad (4)$$

que é a que nos leva directamente à forma simbólica procurada.

171. Seja dada a equação linear de ordem n

$$(a+bx+cx^2+\ldots+qx^k) \frac{d^n y}{dx^n} + (a'+b'x+\ldots) \frac{d^{n-1} y}{dx^{n-1}} + \ldots = X. \quad (5)$$

Multipliquemos ambos os membros desta equação por x^n, e virá :

$$(a+bx\ldots) x^n \frac{d^n y}{dx^n} + (a'x + b'x^2 + \ldots) \cdot x^{n-1} \frac{d^{n-1} y}{dx^{n-1}} + \ldots$$
$$= x^n X.$$

Substituindo $x^n \left(\dfrac{d}{dx}\right)^n$, $x^{n-1} \left(\dfrac{d}{dx}\right)^{n-1} \ldots$, pelas suas expressões (5), e x por e^{θ}, virá:

$$(a + b\,c^{\theta} + c\,e^{2\theta} + \ldots)\, D\,(D-1)\ldots(D-n+1)\,y +$$
$$+ (a'e^{\theta} + b'e^{2\theta} + \ldots)\,D\,(D-1)\ldots(D-n+2)\,y + \ldots = e^{n\theta}\,X(e^{\theta})$$

Ordenando o 1.º membro segundo as potências crescentes de e^{θ}, obteremos uma expressão da forma

$$P_0\,(D)\,y + e^{\theta}\,P_1\,(D)\,y + e^{2\theta}\,P_2\,(D)\,y + \ldots = e^{n\theta}\,X(e^{\theta})$$

ou ainda (n.º 121)

$$P_0\,(D)\,y + P_1\,(D-1)\,e^{\theta}\,y + P_2\,(D-2)\,e^{2\theta}\,y + \ldots \equiv e^{n\theta}\,X(e^{\theta})$$

ou, mais simplesmente,

$$P_0\,(D)\,y + P_1\,(D)\,e^{\theta}\,y + P_2\,(D)\,e^{2\theta}\,y + \ldots = T(\theta) \qquad (6)$$

sendo $P_0\,(D)$, $P_1\,(D) \ldots$ polinómios inteiros em D e $T(\theta) = e^{n\theta}\,X(e^{\theta})$.

É esta equação (6) a chamada *forma simbólica* da proposta.

172. Estas equações dizem-se *binómias*, *trinómias*, etc., se o seu 1.º membro se reduz a dois termos, três, etc.

173. É claro que reduzindo a equação diferencial dada à forma

$$\pi_0\,(x)\,x^n\,\frac{d^n y}{dx^n} + \pi_1\,(x)\,x^{n-1}\,\frac{d^{n-1} y}{dx^{n-1}} + \ldots = X,$$

a equação simbólica terá tantos termos no 1.º membro, quantos os expoentes distintos de x que haja em $\pi_0\,(x)$, $\pi_1\,(x) \ldots$ visto que são essas potências de x que dão as potências de e^{θ} na forma simbólica.

174. Os polinómios em D que afectam as variáveis y, $e^{\theta}y$, $e^{2\theta}y, \ldots$, proveem das expressões simbólicas $x^n \left(\dfrac{d}{dx}\right)^n$, x^{n-1}

$\left(\dfrac{d}{dx}\right)^{n-1}, \ldots$ Logo: *o grau máximo dos polinómios em* D, *é* n; *e também é* n *o grau do polinómio* P_0 (D) *(quando êste não é nulo), visto que nesse entra forçosamente um termo de grau* n *irredutível, por ser único em tôda a equação.*

175. Claro que se supõem ter partido duma equação da forma (5), isto é, cujos coeficientes são polinómios inteiros em x.

176. Se a equação diferencial linear fôr de coeficientes constantes, os polinómios $\pi_0\,(x),\,\pi_1\,(x),\,\ldots,$ coeficientes de $x^n\left(\dfrac{d}{dx}\right)^n,$ $x^{n-1}\left(\dfrac{d}{dx}\right)^{n-1}, \ldots$ na equação dada, depois da multiplicação por x^n, serão:

$$\pi_0\,(x) = A_0$$
$$\pi_1\,(x) = A_1\,x$$
$$\pi_2\,(x) = A_2\,x^2$$
$$\cdots\cdots\cdots\cdots\cdots$$
$$\pi_n\,(x) = A_n\,x^n\,;$$

e a equação transformada será:

$$A_0\,D(D-1)\ldots(D-n+1)y + A_1\,e^\theta\,D(D-1)\ldots(D-n+2)y +$$
$$+ \ldots + A_n\,e^{n\theta}y = e^{n\theta}X;$$

ou

$$A_0\,P_0(D)\,y + A_1\,P_1(D)\,e^\theta\,y + A_2\,P_2(D)\,e^{2\theta}\,y + \ldots +$$
$$+ A_n\,P_n(D)\,e^{n\theta}y = T(\theta)$$

sendo

$$P_0\,(D) = D(D-1)\ldots(D-n+1)$$
$$P_1\,(D) = (D-1)(D-2)\ldots(D-n+1)$$
$$P_2\,(D) = (D-2)(D-3)\ldots(D-n+1)$$
$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$
$$P_n\,(D) = 1$$

177. Á equação simbólica (6) ainda se pode dar outra forma, dividindo ambos os membros por $P_0\,(D)$, o que dá

$$y + \frac{P_1(D)}{P_0(D)}\,e^\theta\,y + \frac{P_2(D)}{P_0(D)}\,e^{2\theta}y + \ldots + = \frac{1}{P_0(D)}\,T$$

ou seja

$$y + R_1(D) e^{\theta} y + R_2(D) e^{2\theta} y + \ldots = U \qquad (7)$$

onde

$$U = \frac{1}{P_o(D)} T.$$

A função U calcula-se resolvendo uma equeação diferencial linear de coeficientes constantes.

178. Por exemplo: A equação diferencial

$$\frac{d^2 y}{d x^2} \pm q^2 y = o$$

dá:

$$x^2 \frac{d^2 y}{d x^2} \pm q^2 x^2 y = o$$

e

$$D(D-1) . y \pm q^2 e^{2\theta} y = o.$$

Logo:

$$y \pm \frac{q^2}{D(D-1)} e^{2\theta} y = o$$

que é a forma final.

179. Para passar da forma simbólica (7) para a equação diferencial correspondente (5), desembaraçam-se de dominadores os operadores funcionais $R_1(D)$, $R_2(D)$... e obtemos a equação (6). Passam-se para a esquerda dos operadores funcionais, as potências de e^{θ}, e em seguida reduzem-se os ditos operadores funcionais à forma

$$P_k(D) = A_o + A_1 D + A_2 D(D-1) + \ldots + A_k D(D-1) \ldots (D-k+1)$$

sendo as constantes A_o, A_1,... determinadas pelo método dos coeficientes indeterminados, por exemplo.

Em seguida substituem-se os termos dêste desenvolvimento pelos seus valores dados pela fórmula (4); e e^{θ}, por x.

Obtem-se assim a equação diferencial com sua forma normal.

180. Por exemplo: de

$$y \pm \frac{q^2}{D(D-1)} e^{2\theta} y = o$$

tira-se

$$D(D-1) y \pm q^2 e^{2\theta} y = o$$

o que dá:

$$x^2 \frac{d^2 y}{d x^2} \pm q^2 x^2 y = o \, ;$$

ou seja:

$$\frac{d^2 y}{d x^2} \pm q^2 y = o.$$

181. Escólio. — Para que uma equação simbólica, reduzida à forma (6) do n.º 171, dê origem a uma equação linear de coeficientes constantes, é necessário e suficiente que os polinómios em D que nela entrem tenham a forma indicada no n.º 176.

182. A ordem da equação diferencial correspondente a uma equação simbólica da forma (7) do n.º 177, é dada pelo *maior grau* dos numeradores e denominadores das funções racionais $R_1(D)$, $R_2(D)$... como se conclui imediatamente do processo de passagem desta forma simbólica para a equação diferencial correspondente.

Forma simbólica binómia. — Reduzida a esta forma, a equação simbólica binómia goza de propriedades notáveis que passamos a expor nos teoremas seguintes:

183. Teorema 1.º — *A equação binómia*

$$y + R(D) e^{r\theta} y = X(e^\theta) \tag{8}$$

transforma-se em

$$u + R(D+n) e^{r\theta} u = U \tag{9}$$

por meio das relações

$$y = e^{n\theta} u \, , \quad X = e^{n\theta} U. \tag{10}$$

Com efeito, substituindo na proposta o valor de y, vem

$$e^{n\theta}u + R(D)e^{(r+n)\theta}u = X$$

ou

$$e^{n\theta}u + e^{n\theta}R(D+n)e^{r\theta}u = X$$

e

$$u + R(D+u)e^{r\theta}u = e^{-n\theta}X = U,$$

c. d. d.

184. Se soubermos integrar a equação (9), integrada fica a equação (8).

185. Êste teorema mostra que se pode acrescentar uma constante qualquer ao símbolo D nas equações binómias, mediante uma transformação adequada.

186. Assim, a equação

$$y \dotplus \frac{q^2}{(D+2)(D-3)}e^{2\theta}y = 0$$

transforma-se em

$$u + \frac{q^2}{D(D-5)}e^{2\theta}u = 0$$

por meio da relação

$$y = e^{-2\theta}u.$$

187. Teorema 2.º — *A equação binómia*

$$y + R(D)e^{r\theta}y = X(e^\theta) \tag{8}$$

pode transformar-se em

$$y + R(aD)e^{\frac{r\theta'}{a}}y = X\left(e^{\frac{r\theta'}{a}}\right) \tag{11}$$

por meio da mudança de variável independente dada pela equação de transformação

$$\theta = \frac{\theta'}{a}.$$

Com efeito,

$$\frac{d}{d\theta} = \frac{d}{d\theta'} \cdot \frac{d\theta'}{d\theta} = a\frac{d}{d\theta'}.$$

Logo :

$$y + R\left(a\frac{d}{d\theta'}\right)e^{\frac{r\theta'}{a}}y = X\left(e^{\frac{\theta'}{a}}\right),$$

que é a equação (11), supondo nela $D = \frac{d}{d\theta'}$, como deve ser, visto ser θ' a nova variável independente.

188. Escólio — A combinação dêstes dois teoremas permite-nos substituir $R(D)$ por $R(aD + n)$, quaisquer que sejam a e n.

189. Teorema 3.° — *A equação binómia*

$$y + R(D)e^{r\theta}y = X(e^{\theta}) \qquad (8)$$

transforma-se em

$$u + \frac{1}{R(-D)}e^{r\theta'}u = \frac{1}{R(-D)}X(e^{-\theta'}) \qquad (12)$$

por meio das equações de transformação

$$\theta = -\theta' \quad e \quad y = e^{r\theta'}u$$

Com efeito, a mudança de θ em θ' dá, pelo teorema anterior $(a = -1)$

$$y + R(-D)e^{-r\theta'}y = X(e^{-\theta'}).$$

Substituindo agora y por u vem :

$$e^{r\theta'}u + R(-D)u = X(e^{-\theta'})$$

Dividindo ambos os membros desta equação por $R(-D)$, vem a equação (12).

190. Teorema 4.° — *A equação binómia*

$$y + R(D)e^{r\theta}y = X, \qquad (8)$$

pode transformar-se em

$$u + Q(D)e^{r\theta}y = U \qquad (13)$$

por meio das relações

$$y = \Pi_r \frac{R(D)}{Q(D)} u \quad \text{e} \quad X = \Pi_r \frac{R(D)}{Q(D)} U,$$

onde se tem

$$\Pi_r \frac{R(D)}{Q(D)} = \frac{R(D)}{Q(D)} \cdot \frac{R(D-r)}{Q(D-r)} \cdot \frac{R(D-2^r)}{Q(D-2^r)} \ldots$$

191. A demonstração dêste teorema de Cálculo Simbólico, faz-se do seguinte modo. Suponhamos que substituimos $y = \chi(D) u$, onde $\chi(D)$ é uma função a determinar. Teremos,

$$\chi(D) u + R(D) e^{r\theta} \chi(D) u = X;$$

ou ainda,

$$\chi(D) u + R(D) \chi(D-r) e^{r\theta} u = X;$$

ou ainda,

$$u + \frac{R(D) \chi(D-r)}{\chi(D)} e^{r\theta} u = \frac{1}{\chi(D)} X$$

Fazendo

$$Q(D) = \frac{R(D) \chi(D-r)}{\chi(D)}$$

virá:

$$\chi(D) = \frac{R(D)}{Q(D)} \chi(D-r).$$

Esta relação determinada $\chi(D)$ por meio de recorrência, com a forma de produto infinito:

$$\chi(D) = \frac{R(D)}{Q(D)} \cdot \frac{R(D-r)}{Q(D-r)} \cdot \frac{R(D-2r)}{Q(D-2r)} \ldots$$

ou seja:

$$\chi(D) = \Pi_r \frac{R(D)}{Q(D)}$$

e, consequentemente, fica demonstrado o teorema.

192. Claro que a função $Q(D)$ pode ser qualquer, mas para que a transformação tenha sentido, é preciso que $\Pi_r \dfrac{R(D)}{Q(D)}$ o

tenha, o que sucederá quando êste produto se tornar finito, por aparecerem nos dois termos factores distintos só em número determinado.

193. É fácil de ver que é finito um produto da forma

$$\Pi_r \frac{\chi(D)}{\chi(D+ir)} = \frac{\chi(D)}{\chi(D+ir)} \cdot \frac{\chi(D-r)}{\chi(D+ir-r)} \cdots \frac{\chi(D-ir)}{\chi(D)} \cdots$$
$$= \frac{1}{\chi(D+ir) \cdot \chi(D+ir-r) \cdots \chi(D+r)}$$

onde i é um número inteiro.

194. Do mesmo modo

$$\Pi_r \frac{\chi(D)}{\chi(D-ir)} = \frac{\chi(D)}{\chi(D-ir)} \cdot \frac{\chi(D-r)}{\chi(D-ir-r)} \cdots \frac{\chi(D-ir)}{\chi(D-2ir)} \cdots$$
$$= \chi(D) \cdot \chi(D-r) \cdots \chi(D-ir+r).$$

195. Se fôr $R(D) = \chi(D) \cdot \chi_1(D)$, na equação do n.º 190. ponhamos

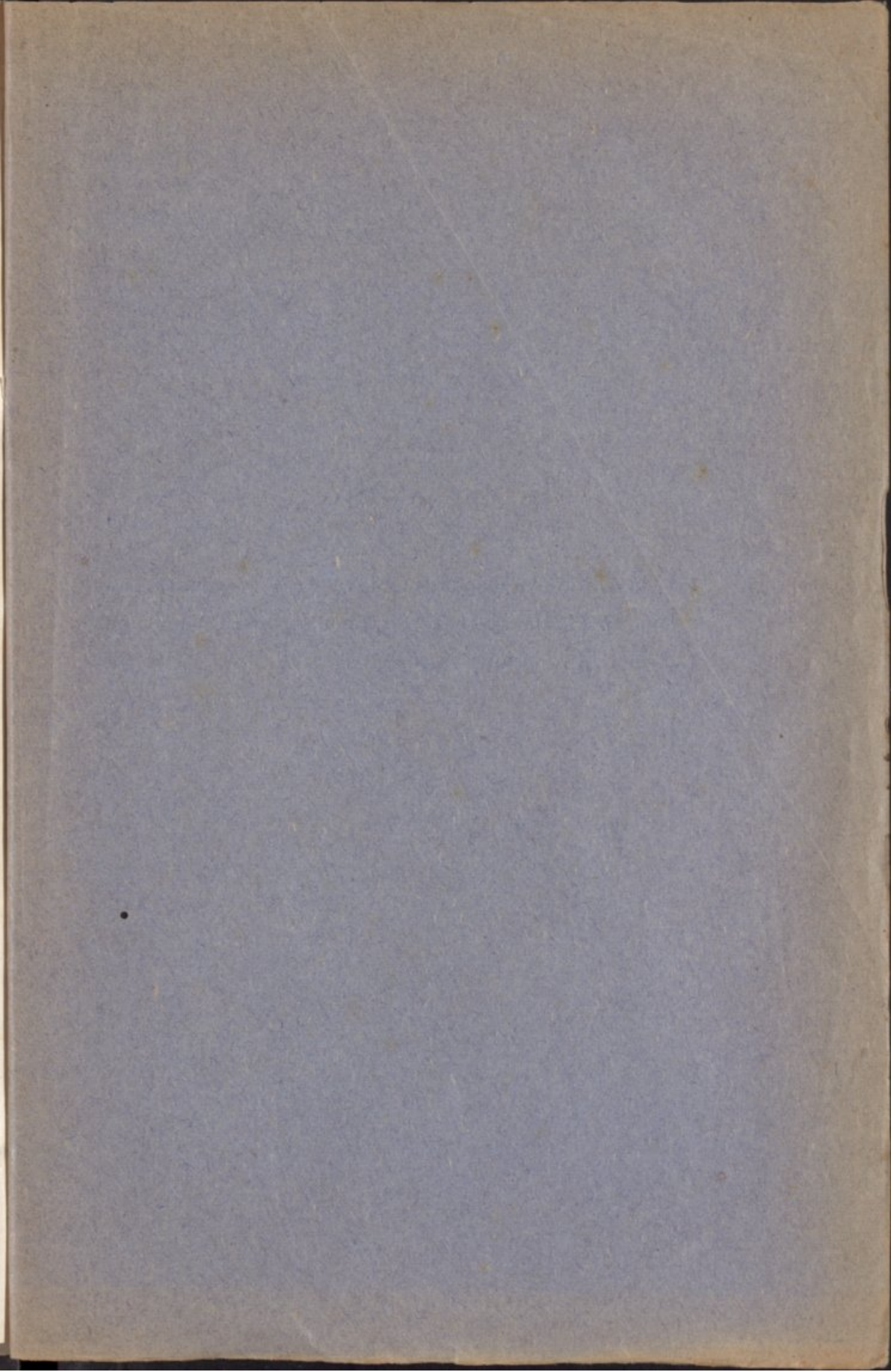$$Q(D) = \chi(D \pm ir) \cdot \chi_1(D)$$

e virá

$$\Pi_r \frac{R(D)}{Q(D)} = \Pi_r \frac{\chi(D)}{\chi(D \pm ir)}$$

que é um produto finito (n.ᵒˢ 193 e 194).

196. Com esta transformação, muda-se o operador $R(D) = \chi(D)\chi_1(D)$, no operador $Q(D) = \chi(D \pm ir)\chi_1(D)$ que pode ser mais conveniente.

(Continua).

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Doutor Pacheco de Amorim.

</div>

AVISO

Tóda a correspondência relativa à redacção deve ser dirigida à Direcção da Faculdade de Ciências, com a indicação de que se refere à REVISTA.