

XLII.—*The Colour of Polyhydroxyanthraquinone Dyes.*

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It has been suggested by us (T., 1915, **107**, 1567 *et seq.*) that the vibration causing the colour of dyes is a change, or tendency to change, from one quinonoid form to another, involving alternation of double and single bonds along a conjugate chain. It was shown that where such dyes were chosen with similar structure but with conjugate chains of different lengths the wave-lengths of the maxima of absorption were in the ratio of the lengths of the chains of double and single bonds. In that investigation the chains of double and single bonds differed only in length. The present work was undertaken with the object of ascertaining why the multiplication of auxochromes in a dye molecule deepens the colour. This is an empirical rule which is true for many groups of dyes, and in the anthraquinone group in particular the multiplication of auxochromes has led to the production of some very valuable dyes.

From the point of view of the theory already mentioned, the results now obtained may be considered as throwing light on the effect of varying the nature of the conjugate chains whilst keeping their lengths unaltered. We may consider that the chains have been varied in two ways, namely, (1) by changing the end-groups, for example, by observing the behaviour of alizarin, etc., in alcohol, in potassium hydroxide, and on different mordants; (2) by varying the number and positions of the attached auxochromes throughout the chains, for example, by considering the absorption of alizarin, quinizarin, etc., under the same conditions, say, all in alcohol or all in potassium hydroxide solution, etc.

No. (1) has led to the discovery of a very definite relationship between the absorption spectra of the dyes themselves in neutral solvents and the absorption spectra of their salts, and a hypothesis has been suggested to explain this relationship. No. (2) has not led as yet to any simple relationship between the absorption spectra of the dyes and the number and positions of the contained auxochromes, but it has yielded experimental evidence which is not in complete concordance with various hypotheses suggested by other investigators.

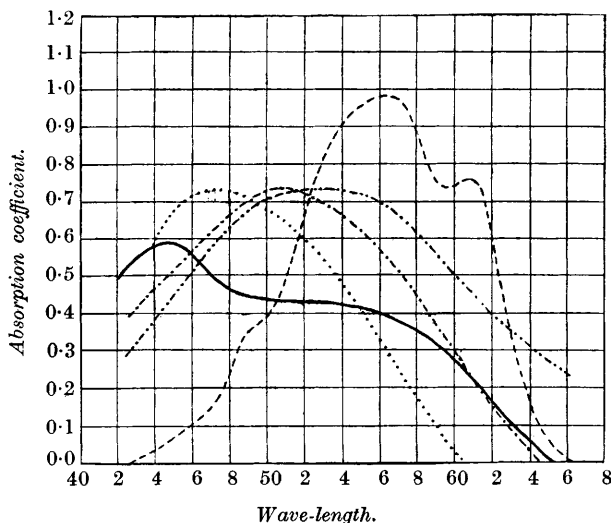
EXPERIMENTAL.

In this investigation the absorption spectra were observed for the visible spectrum only, and the instrument used was a Nutting

spectrophotometer in conjunction with a large model wave-length spectrometer both by Adam Hilger, London. The substances chosen for examination were:

- (1) Alizarin, 1:2-dihydroxyanthraquinone.
- (2) Quinizarin, 1:4-dihydroxyanthraquinone.
- (3) Purpurin, 1:2:4-trihydroxyanthraquinone.
- (4) Anthragallol, 1:2:3-trihydroxyanthraquinone.
- (5) Alizarin-Bordeaux, 1:2:5:8-tetrahydroxyanthraquinone.
- (6) Alizarin-cyanine, 1:2:4:5:8-pentahydroxyanthraquinone.
- (7) Anthracene-blue, W.R., 1:2:4:5:6:8-hexahydroxyanthraquinone.
- (8) Rufigallol, 1:2:3:5:6:7-hexahydroxyanthraquinone.

FIG. 1.



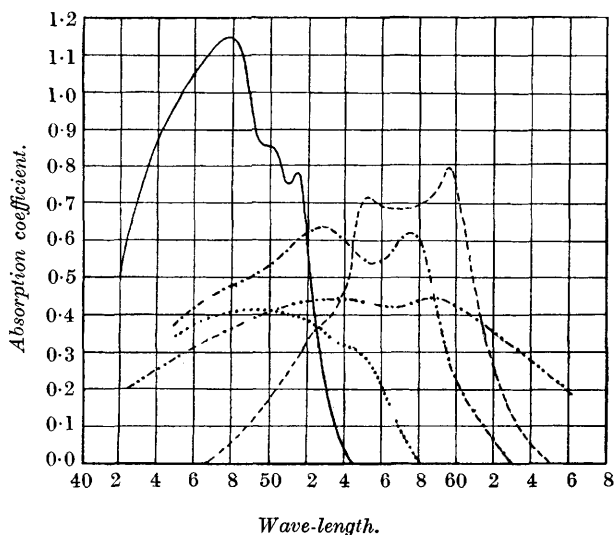
Alizarin or 1:2-dihydroxyanthraquinone.

— — — — —	<i>Alizarin in alcohol, N/10⁴, 10 mm. thickness.</i>
— — — — —	„ „ KOH, N/10 ⁴ , 10 mm. thickness, 400 mols. KOH.
.....	„ on tin mordanted wool, $\frac{1}{4}$ per cent. dyeing.
— · — · —	„ „ alum „ „ „ „
— · · — · ·	„ „ chrome „ „ „ „

The absorption spectrum of each of these dyes was examined (1) in alcoholic solution, (2) in aqueous potassium hydroxide solution, and on wool mordanted with (3) tin, (4) alum, and (5) chrome respectively. In the Nutting spectrophotometer there are two apertures, one to receive the light the spectrum of which has to be examined, and the other to receive the comparison light from the same source. By placing two fabrics at 45° to the axis of the

instrument and allowing the light from the dyed fabric to enter one aperture and the light from the undyed mordanted fabric to enter the other aperture, the absorption spectrum of the dyed fabric was obtained. For fabrics, a carbon arc lamp was required as source in order to raise the intensity of light to such a degree that measurements could be made easily. The mordant of the undyed comparison fabric used was always the same as the mordant of the dyed fabric being examined. In all cases where the colour

FIG. 2.



Quinizarin or 1:4-dihydroxyanthraquinone.

—————	Quinizarin in alcohol, $N/10^4$, 10 mm. thickness.
-----	„ „ KOH, $N/10^4$, 10 mm. thickness, 400 mols. KOH.
.....	„ „ on tin mordanted wool 1 per cent. dyeing.
— . — . — .	„ „ alum „ „ „ „
—	„ „ chrome „ „ „ „

of a solution was fugitive, sets of time readings were taken, and the observed absorption curves were corrected for fading. To the best of our knowledge, this is the first recorded investigation of the absorption spectra of dyes on the fabric. It is the colour of the dye on the fabric which is of technical value, and, as is well known, many dyes give quite different colours on the fabric from what they exhibit in alcoholic, alkaline, or acid solution, and frequently the same dye gives very different colours on different mordants.

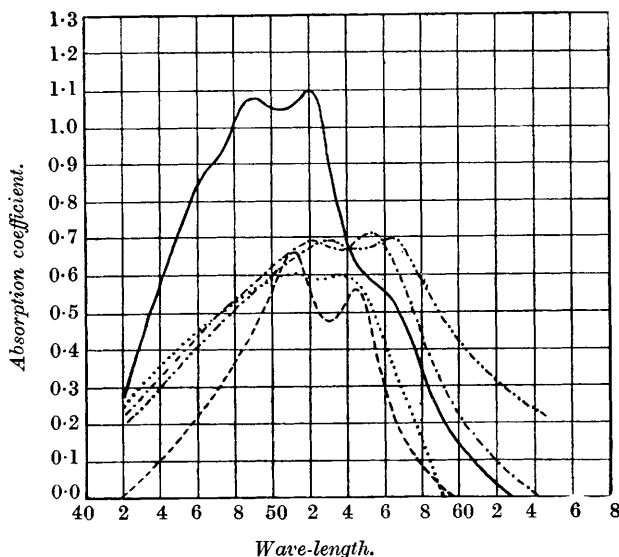
Figs. 1 to 8 give the observed curves. The two points which will be discussed in relation to these curves are:

(1) The change of the absorption spectrum of each dye as the conditions are varied.

(2) The change of the absorption spectra of the group of dyes in relation to the number and position of auxochromes.

The absorption spectra were first examined (E. R. W.) with a Brace spectrophotometer modified by one of us (D. B. M.), and the results obtained seemed to indicate a simple relation between the spectra examined, which also offered a mechanical explanation of the regularities already noticed in ocular observations. Accord-

FIG. 3.



Purpurin or 1:2:4-trihydroxyanthraquinone.

Purpurin in alcohol, N/10⁴, 10 mm. thickness.

„ „ KOH N/10⁴, 10 mm. thickness, 400 mols. KOH.

„ „ on tin mordanted wool $\frac{1}{4}$ per cent. dyeing.

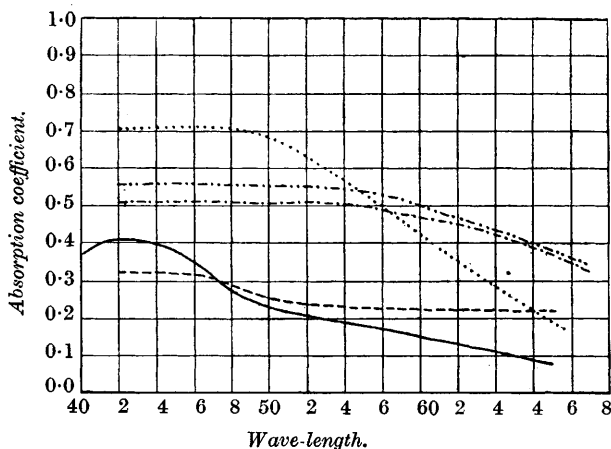
„ „ alum „ „ „ „

„ „ chrome „ „ „ „

ing to this interpretation, the absorption spectra of all the dyes of this group consist of two bands, one at about $\lambda=5000$ and the other at about $\lambda=7000$; the wave-length of these bands is somewhat increased by the multiplication of auxochromes; the relative intensity of the band of longer wave-length is increased when there are two hydroxyl groups in the *o*- or *p*-positions with respect to one another in the nucleus; the relative intensity is still more increased when the *o*- or *p*-grouping occurs in both nuclei, or when

three hydroxyl groups occur in the 1:2:4-position in one nucleus. The 1:2:3-grouping of the three hydroxyl groups in one nucleus causes an almost equal development of the two bands, the result being a brown colour. Further, the relative development of the two bands depends on the condition under which the dye is examined, the band of shorter wave-length being prominent in alcoholic solution, and that of longer wave-length being developed more and more in the salts according to the basicity of the metal with which the dye is combined. This seemed to indicate two different tautomeric forms or modes of vibration, that producing

FIG. 4.



Anthragallol or 1:2:3-trihydroxyanthraquinone.

Anthragallol in alcohol, $N/10^4$, 10 mm. thickness.

„ KOH, $N/10^4$, 10 mm. thickness, 400 mols. KOH.

„ on tin mordanted wool $\frac{1}{4}$ per cent. dyeing.

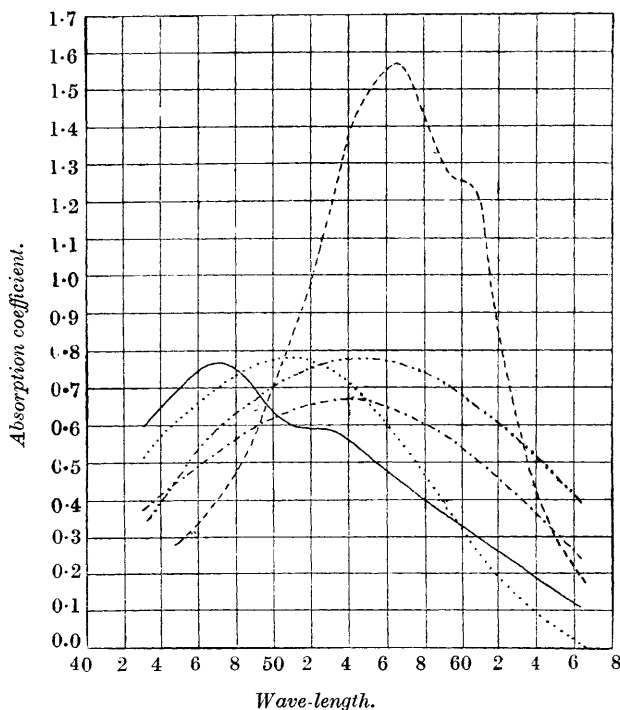
„ „ alum „ „ „ „

„ „ chrome „ „ „ „

the band of longer wave-length being in greater proportion when the *o*- or *p*-grouping of the hydroxyl groups occurred and when the dye was in combination with a basic oxide. This interpretation is similar to that already advanced for the phthalein and benzein dyes (Medhi and Watson, T., 1915, 107, 1581). The present work shows, however, that these observations made the bands very much too broad and also removed all the detail from them. Theoretical curves formed in the manner suggested by compounding two bands of different relative intensities differ from the experimental curves here recorded to a much greater extent than can be explained by any possible experimental error.

In this connexion it may be remarked that the same considerations seem to us sufficient to render untenable the similar hypothesis which Hantzsch (*Ber.*, 1910, **43**, 82) has put forward to explain the various colours which violuric acid and its derivatives and isooxazalone exhibit when in combination with different metals

FIG. 5.



Alizarin-Bordeaux or 1 : 2 : 5 : 8-tetrahydroxyanthraquinone.

—————	Alizarin-Bordeaux in alcohol, N/10 ⁴ , 10 mm. thickness.
-----	" " " KOH, N/10 ⁴ , 10 mm thickness, 400 mols.
.....	Alizarin-Bordeaux on tin mordanted wool, $\frac{1}{4}$ per cent. dyeing.
- . - . - .	" " " alum " " " "
- - - - -	" " " chrome " " " "

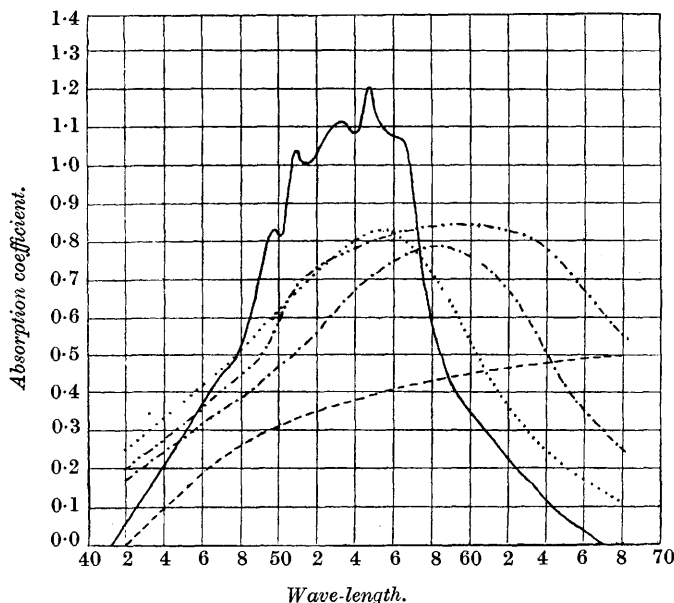
and in different solvents. Its position has been summarised as follows: "The change in colour [as the positive nature of the metallic radicle increases] is attributed to a chemical change, namely, to the passage from the oximino-ketone form to the nitroso-enolic form:



All solutions of the salts consist of a mixture of the two forms in dynamic equilibrium, the proportion of each depending on the positive character of the metallic or substituted ammonium radicle present and also on the nature of the solvent."

Take as an example the absorption curves of diphenylvioluric acid and its salts (*Ber.*, 1910, **43**, 666). According to the hypothesis, the curves for the salts should be obtained by compounding the following two absorption curves in different proportions,

FIG. 6.



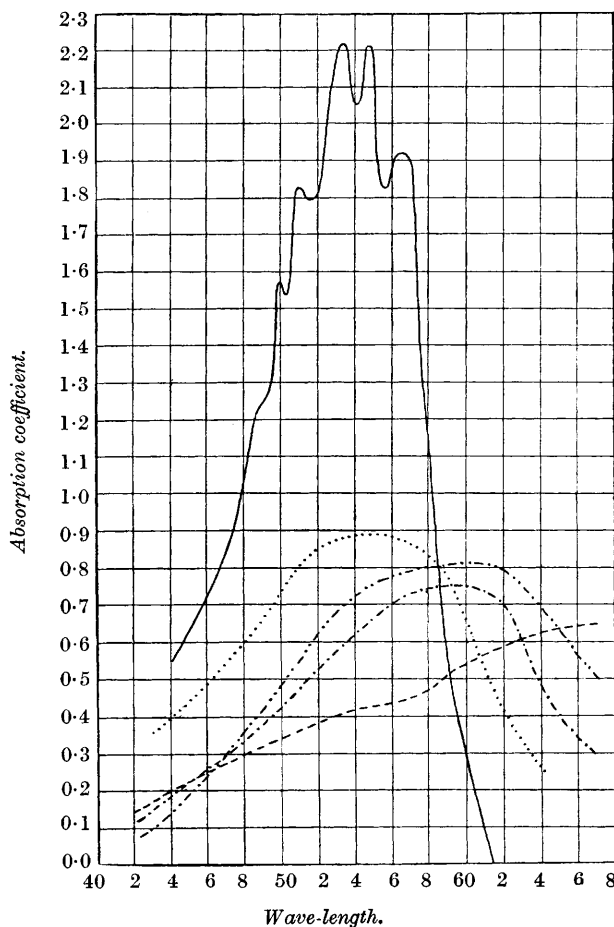
Alizarin-cyanine or 1:2:4:5:8-pentahydroxyanthraquinone.

—————	<i>Alizarin-cyanine in alcohol, N/10⁴, 10 mm. thickness.</i>
- - - - -	" " " KOH, N/10 ⁴ , 10 mm. thickness, 400 mols.
.....	<i>Alizarin-cyanine on tin mordanted wool, $\frac{1}{4}$ per cent. dyeing.</i>
- . - . -	" " " alum " " " "
- - - - -	" " " chrome " " " "

namely, the absorption curve for the pure oximino-ketonic form which may be taken to have its maximum at frequency 1500, and the curve for the pure nitroso-enolic form which has its maximum at 3800. The curve for the caesium salt in acetone solution has its maximum at 1700, that for the lithium salt in acetone has its maximum at 1950, and that for the lithium salt in ethyl acetate has its maximum at 3250. It is possible to compound bands at

frequencies 1500 and 3800 in such different proportions as to give resultant bands with maxima at the required frequencies, 1700.

FIG. 7.



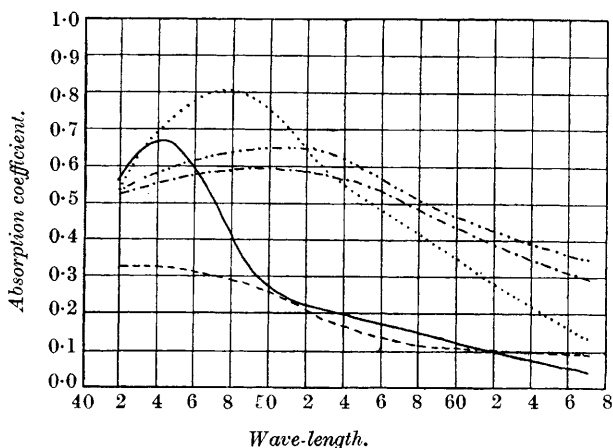
Anthracene-blue or 1 : 2 : 4 : 5 : 6 : 8-hexahydroxyanthraquinone.

- Anthracene-blue in alcohol, $N/10^4$, 10 mm. thickness.
 - - - " " KOH, $N/10^4$, 10 mm. thickness, 400 mols.
 Anthracene-blue on tin mordanted wool $\frac{1}{2}$ per cent. dyeing.
 - " " " alum " " "
 - - . . . " " " chrome " " " "

1950, and 3250, but the fundamental bands at 1500 and 3800 must be at least more than $2(3800 - 1500)$ in breadth, and if such broad

fundamental bands are taken the resultant bands are much broader than those given by direct observation.

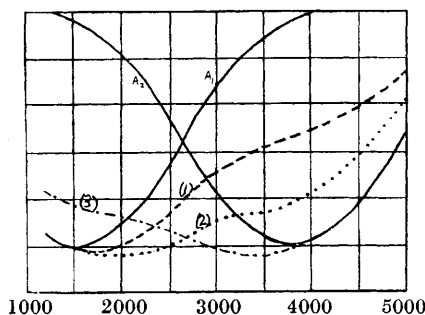
FIG. 8.



Rufigallol or 1:2:3:5:6:7-hexahydroxyanthraquinone.

—————	<i>Rufigallol in alcohol, $N/10^4$, 10 mm. thickness.</i>
-----	" " <i>KOH, $N/10^4$, 10 mm. thickness, 400 mols. KOH.</i>
.....	" " <i>on tin mordanted wool, $\frac{1}{4}$ per cent. dyeing.</i>
- . - . - .	" " <i>alum " " " "</i>
- - - - -	" " <i>chrome " " " "</i>

FIG. 9.

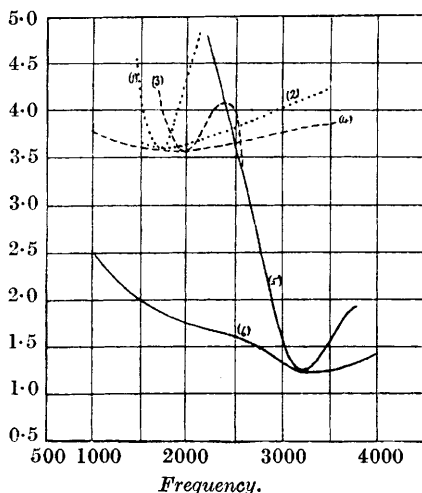


—————	<i>A_1 and A_2 are two fundamental bands at frequencies 1500 and 3800.</i>
(1) ————	<i>Resultant of A_1 and A_2 in the ratio of 10:5.</i>
(2)	" " " " " " 10:8.
(3) - . - . - .	" " " " " " 8:10.

Fig. 9 shows two fundamental bands, A_1 and A_2 , with frequencies at 1500 and 3800 which, taken in the proportions of 10:5, 10:8,

and 8:10 respectively for intensities, yield the curves (1), (2), and (3) with maxima at frequencies 1700, 1950, and 3250 approximately. These curves, (1), (2), and (3), have been proportionately reduced, so that their maxima coincide with those of Hantzsch's experimental curves, and Fig. 10 shows these reduced curves and the experimental curves together. It will be seen that there is not the slightest coincidence between the theoretical curves and the experimental ones. The theoretical curves are much too broad, and yet if the fundamental curves are taken narrower than those given, the compounding of them in any proportion will not shift the maxima

FIG. 10.



(1), (3) (5) are Hantzsch's curves for diphenylvioluric acid (Ber., 1910, 43, 666).

(1) Cs salt in acetone solution.

(3) Li " " ethyl acetate solution.

(5) Li " " ethyl acetate solution.

(2), (4) and (6) are curves compounded from the fundamental bands at 1500 and 3800, so that the maxima of the resultant curves correspond with those of Hantzsch's three curves.

from frequencies 1500 and 3800. The well-marked minima at 2150 and 2400 in Hantzsch's curves (1) and (3) are absent from the theoretical curves. The conclusion is that Hantzsch's hypothesis is not in accordance with his own experimental data.

In the case of the anthraquinone dyes, there is much better agreement than this between the experimental curves and the theoretical curves drawn according to this hypothesis, but yet there is a much greater difference than can be explained by experimental error.

Change of the Absorption Spectra when the Conditions are Varied.

On examination of Figs. 1 to 8 it will be observed that a regular change is produced in the absorption spectrum of a dye in passing from alcoholic solution to the various dyeings on tin, alum, and chrome, and finally to the solution in aqueous potassium hydroxide. In all cases, with the exception of purpurin and perhaps also rufigallol, the maxima of the absorption bands or groups of bands are steadily shifted towards the red end of the spectrum on passing from the free dyestuff to its various salts, and the order of the shift agrees with the order of increase of the positive character of the metallic radicle in combination. The variation of the metallic radicle does not alter the length of the conjugate chain of double and single bonds which may be considered as alternating during tautomeric change, and so we are led to consider the character of the metallic radicle as modifying the period of oscillation of a tautomeric change involving a fixed number of double and single bonds. In alizarin the only conjugate chains of double and single bonds which we can imagine as oscillating during tautomeric change have four, three, and two double bonds respectively. If we regard the long chain as responsible for the band at $\lambda=5690$, the shorter chains should give bands at $\lambda=4270$ and $\lambda=2845$ approximately. The solution in potassium hydroxide does show a band at $\lambda=2700$, and the band exhibited in alcoholic solution perhaps might be identified with that predicted at $\lambda=4270$, but without some addition the theory cannot explain the bands observed in the absorption spectra of the dyeings on tin, alum, and chrome which lie between $\lambda=4270$ and $\lambda=5690$. These bands are too close together to be explained as due to conjugate chains of different lengths, as the ratios of their frequencies can only be expressed by whole numbers much larger than the constitutional formula will allow for the number of alternate double and single bonds in the molecule. In short, the closeness of the bands for any one dye under different conditions leads us to the conclusion that these various bands must be due to oscillating conjugate chains of fixed lengths modified by the metallic radicles with which the dye is combined.

If we consider these conjugate chains as in a state of tension, the period of oscillation will be shorter the greater the tension, and the tension will be the greater the more firmly the metallic radicle is combined with the dye. When the dye is combined with a strong positive radicle, the degree of dissociation in solution will be greater than when it is combined with a weak positive radicle. In a partly dissociated compound some molecules have still the

metallic radicle attached to the dye molecule. The greater the dissociation the smaller is the number of molecules which have still the attached metallic radicle. We may regard the electric tubes of force from the metallic atom as partly connecting with the dye molecule and partly radiating around. The larger the dissociation, the smaller will be the number of tubes of force joining the metallic radicle to the dye molecule in those molecules which are undissociated, and the smaller will be the tension in the chain, and therefore the longer will be the wave-length of the maximum of the absorption band. Hence by increasing the positive nature of the radicle, the absorption band should be moved towards the red end of the spectrum. This will be found to be the case with all the dyes examined in this paper, the order being (1) alcoholic solution, dyed fabric (2) tin-, (3) alum-, or (4) chrome-mordanted, and (5) solution in aqueous potassium hydroxide. Purpurin is an exception. The conclusion from this portion is that the more electro-positive the nature of the radicle attached to the conjugate chain is the longer will be the wave-length of the maximum of the absorption band.

From examination of the curves in Figs. 1 to 8 some other points may be noted. In several cases, as the radicle is changed the character of the curve remains the same, whilst the band or group of bands moves towards the red end of the spectrum, for example, the pair of bands in quinizarin are retained throughout the varied conditions, and the same also is true with regard to purpurin. In other cases the detail exhibited in the alcoholic solution bands disappears, or tends to disappear, from the absorption spectra on tin, alum, chrome, or potassium hydroxide. The sharp character of the bands also disappears in some cases, the bands becoming shallower and broader as the positive character of the metallic radicle increases, for example, the group of six bands exhibited by alizarin-cyanine in alcohol is changed into one band, which becomes shallower and broader as the positive character of the metallic radicle increases. This is also the case with anthracene-blue W.R. On the other hand, the broad, featureless band of alizarin in alcohol is replaced by two, or even three, bands in potassium hydroxide. There is one point, further, worthy of notice, namely, the intensity of the absorption is of the same order for all the dyes in solution. The same is true for all the dyeings on the fabrics. Owing to the different circumstances, the solutions and the dyeings cannot be compared with each other in this respect.

We may now see how the results obtained agree with Baly's theory (*Phil. Mag.*, 1914, **27**, 632 *et seq.*). According to this theory, each of the maxima observed under these varied conditions

is a definite integral multiple of a fundamental frequency in the infra-red. Take alizarin as an example. The new bands recorded in this paper, considered in addition to those already described by Meyer and Fischer (*Ber.*, 1913, **46**, 74 *et seq.*), would necessitate a reduction of the fundamental frequency and a corresponding increase of the integral multiples, the latter reaching the high figure of at least 57 for the band of highest frequency, thus:

	Cr.	Al.	Sn.	Alcohol.
New bands λ	5275	5070	4730	4470
$1/\lambda$	1920	1980	2130	2230

Introducing these into the series already given (Watson and Meek, T., 1915, **107**, 1575) we get:

Expt.	160—162	180	192—193	198—200	
(Calc.)	162	175.5	189	195.75	
(Calc.)	6.75 × 24	6.75 × 26	6.75 × 28	6.75 × 29	
Expt.	213	223	303	312	372
(Calc.)	209.25	222.75	303.75	310.5	371.25
(Calc.)	6.75 × 31	6.75 × 33	6.75 × 45	6.75 × 46	6.75 × 55
Expt.		376	385		
(Calc.)		378	384.75		
(Calc.)		6.75 × 56	6.75 × 57		

The theory is evidently strained to its utmost, and there is little doubt that the study of other salts, for example, those of calcium, strontium, and barium, would give additional maxima and involve further reduction of the fundamental frequency with corresponding increase of the integral multiples.

The Change in the Absorption Spectra produced by Variation of the Number and Position of the Auxochromes.

At the present stage we cannot offer any explanation which will account completely for the way in which the multiplication of auxochromes alters the absorption spectra under similar conditions. The addition of auxochromes does not give any opportunity for changing the length of the conjugate chains of double and single bonds; nor can the addition of auxochromes be considered as merely "weighting" the chain and causing slower vibrations, for, from this point of view, bromine and ethoxy-derivatives of alizarin might be expected to have absorption bands as far into the red as those of the polyhydroxyanthraquinones. This is not the case.

The best that we can do at this stage is to formulate certain general rules which are the result of experiment and observation, without being able to give any explanation of these rules.

Georgievics (*Monatsh.*, 1911, **32**, 329 *et seq.*) has formulated certain generalisations on the influence of hydroxyl groups on the

colour of the "lakes" of these dyes. The results have been summarised as follows: "Hydroxyl groups in the α -positions produce red and blue dyes, in the β -positions yellow and brown dyes; however, an α -hydroxyl group may mask the effect of a β -hydroxyl group, and vice versa. . . . The hydroxyanthraquinones, therefore, are divisible into two groups. One group . . . forming yellow and brown lakes has a para-quinonoid structure, for example, anthragallol . . . whilst the other group, which includes alizarin and its derivatives, forming red or blue lakes (except hystazarin, which occupies an intermediate position), has an ortho-quinonoid structure. . . . In individual hydroxyanthraquinones the tendency to the production of one or other of the quinonoid forms may be such that one and the same dye may be ortho-quinonoid in some lakes and para-quinonoid in others."

These generalisations seem open to criticism on the following grounds:

(1) They do not explain why two hydroxyl groups at least are necessary to produce a red or a blue colour. It may be said that the monohydroxy-derivatives are not mordant dyes, and are therefore not included in the generalisations about lakes. We have shown above, however, that there is a simple relationship between the colour of a dye in alkaline solution and on the various mordants, and consequently Georgievics's generalisations should hold also for the colour of the alkaline solutions of the dyes. From his rules we might expect that 1-hydroxyanthraquinone would be a red or a blue colour, but, as a matter of fact, in alkaline solution it has an absorption band at $\lambda = 4960$ and the colour of the solution is yellow. Alizarin (1:2-dihydroxyanthraquinone), according to his rules, should have the blue colour due to the hydroxyl in the α -position partly masked by the yellow of the hydroxyl in the β -position, but, as is well known, alizarin dissolves in potassium hydroxide with a bluish-violet colour.

(2) They do not explain why 1:4-dihydroxyanthraquinone should have a deeper* colour than 1:5- or 1:8-dihydroxyanthraquinone. Quinizarin (1:4-dihydroxyanthraquinone) is blue in

* In this paper, where the term "deeper" is used in connexion with colour the meaning that has to be attached to it is as follows. One colour will be considered deeper than another if its absorption band is nearer the red end of the spectrum than the absorption band of the other. This may seem a little arbitrary at first sight; but when it is remembered that light reflected from dyed fabrics generally gives an absorption band the breadth of which at half its height is about half the length of the visible spectrum, it will be found that displacement of a band of such a breadth from the blue end of the spectrum to the red end will give a series of colours similar to that generally recognised as increasing in "depth" of colour, namely, yellow, orange, red, violet, blue, and green.

potassium hydroxide solution and has a blue-violet barium salt; anthrarufin (1:5-dihydroxyanthraquinone) is reddish-violet in potassium hydroxide and has a carmine-red barium salt; chrysazin (1:8-dihydroxyanthraquinone) is yellow-red in potassium hydroxide and has a red barium salt.

(3) They do not explain why alizarin should have as deep a colour as quinizarin. According to these rules, the β -hydroxyl should have a prejudicial effect.

(4) They do not explain why alizarin should have a much deeper colour than 1:3-dihydroxyanthraquinone.

(5) They do not explain the deep colour of 2:3-dihydroxyanthraquinone, namely, cornflower-blue in potassium hydroxide, red on alum mordant; the calcium salt is violet, and the barium salt blue.

These criticisms suggest a generalisation which seems much more in harmony with the facts than those of Georgievics, namely:

(a) Two hydroxyl groups in one benzene nucleus in the ortho- or para-position with respect to one another are necessary to produce a deep (red, violet, or blue) colour.

(b) The colour is still further deepened if both benzene nuclei contain pairs of hydroxyl groups in the *o*- or *p*-position to one another.

(c) Three hydroxyl groups in the 1:2:4-positions in one benzene nucleus produce a deeper colour than a pair of hydroxyl groups in the *o*- or *p*-position.

(d) Three hydroxyl groups in the 1:2:3-positions in one benzene nucleus produce a brown colour.

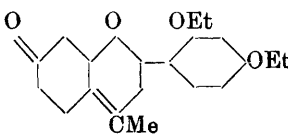
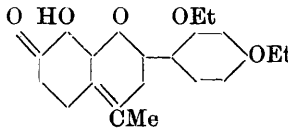
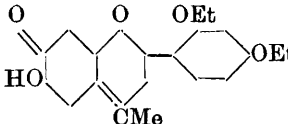
The generalisations bear a marked resemblance to the rules put forward by Kauffmann (Kauffmann and Franck, *Ber.*, 1906, **39**, 2722), and are probably applicable to all groups of dyes, for example, (a) the hydroxy-derivatives of azobenzene dissolve in potassium hydroxide with the following colours:

<i>p</i> -Hydroxyazobenzene.....	Yellow.
<i>o</i> -Hydroxyazobenzene	Yellow.
Benzeneazoresorcinol	Orange.
Benzeneazocatechol	Carmine.
Benzeneazoquinol	Blue.
Benzeneazopyrogallol	Brick-red.

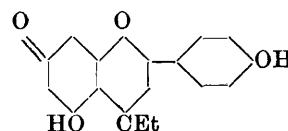
(b) Fluorescein, quinolphthalein, and catecholphthalein dissolve in potassium hydroxide with a yellow colour, hydroxyquinolphthalein gives a cherry-red, gallein a blue, and phloroglucinolphthalein an orange under the same conditions.

(c) In the pyranol series of dyes (prepared partly by Bülow and partly by Watson and Sen) the effect of two hydroxyl groups in

the ortho-position with respect to one another in the benzo-group can be seen from the following comparison:

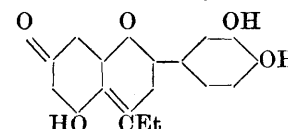
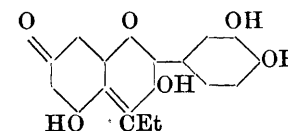
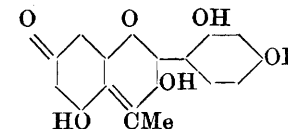
- (1)  Gives redder and yellow dyeings than alizarin brown.
- (2)  Green with sodium alkyl oxide, blue in pyridine. Olive green dyeings on chrome.
- (3)  Dark red with alcoholic potassium hydroxide,

The less favourable effect, so far as depth of colour is concerned, of two hydroxyl groups in the *m*-position with respect to one another in the benzo-group can be seen by comparing the preceding with:

- (4)  Crimson with potassium hydroxide, gives brownish-orange dyeings.

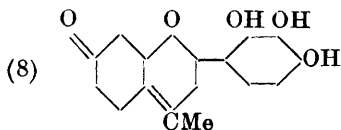
The extra hydroxyl group in the phenyl group cannot counter-balance the unfavourable effect of the meta-grouping in the benzo-nucleus.

The same effect in the phenyl nucleus can be seen by comparing the last-mentioned dye with the following:

- (5)  Violet with potassium hydroxide, mauve dyeings on alum, blue-black dyeings on chrome.
- (6)  Blue with potassium hydroxide, violet dyeings on alum and chrome.
- (7)  Crimson with potassium hydroxide, maroon on chrome.

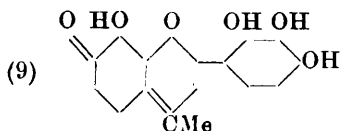
560 THE COLOUR OF POLYHYDROXYANTHRAQUINONE DYES.

The following comparisons show the tendency of three hydroxyl groups in the 1:2:3-position to produce a brown colour. Compare (1) with:



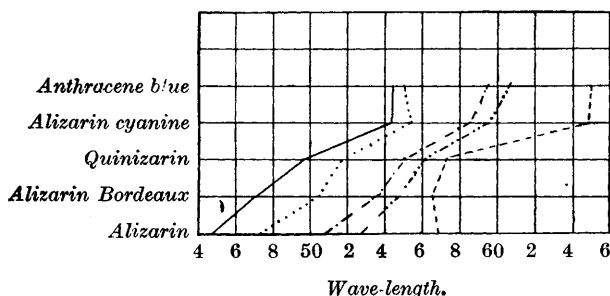
Brownish-red with potassium hydroxide, dyeings are no deeper than those given by (1).

and compare (2) with:



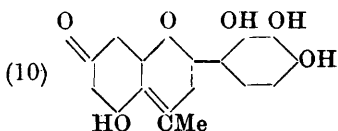
Violet-red with potassium hydroxide, dyeing on chrome is brown similar to that given by anthragallol.

FIG. 11.



.....	<i>In alcoholic solution.</i>
.....	<i>On the fabric mordanted with tin.</i>
.....	" " " " alum.
.....	" " " " chrome.
.....	<i>In aqueous potassium hydroxide solution.</i>

The favourable effect of the *o*-grouping in the benzo-nucleus is eclipsed by the effect of the 1:2:3-grouping in the phenyl group. Compare (5) with:



Dark-red with potassium hydroxide.

In Fig. 11 the wave-length of the centre of the absorption band or group of bands has been plotted for the various dyes under different conditions. The points corresponding with similar conditions have been joined, with the result that a very regular shift of the centre of the absorption band towards the red has been

observed as we pass from alizarin to alizarin-Bordeaux, quinizarin, alizarin-cyanine, and anthracene-blue. This shift is shown equally well in the five different conditions, namely, (1) in alcoholic solution, (2) with potassium hydroxide, (3) on tin, (4) on alumina, and (5) on chrome. Whether any weight should be laid on a result obtained by taking the mean of a group of bands is a matter for further consideration. Purpurin is somewhat anomalous. Increasing the electropositive character of the combined radicle produces much less shift of the band in purpurin than in the other dyes of this series. It is hoped to give later some account of the shift of bands due to addition of hydroxyl groups, on the hypothesis that the tension in an oscillating chain of double and single bands depends also on the modification of the electric field in the molecule by these hydroxyl groups.

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