This article was downloaded by: [New York University]

On: 18 February 2015, At: 18:54

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Transactions of the Royal Society of South Africa

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/ttrs20>

COLOUR AND CHEMICAL CONSTITUTION

James Moir

Published online: 08 Apr 2010.

To cite this article: James Moir (1921) COLOUR AND CHEMICAL CONSTITUTION, Transactions of the Royal Society of South Africa, 9:3, 205-216, DOI: [10.1080/00359192109520213](https://doi.org/10.1080/00359192109520213)

To link to this article: <http://dx.doi.org/10.1080/00359192109520213>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

COLOUR AND CHEMICAL CONSTITUTION.

PART XII.—THE CALCULATION OF COLOUR FROM THE TAUTOMERIC THEORY.

BY JAMES MOIR.

The scheme suggested in Part X of this work for calculating the colours of the triphenylcarbinol dyes, while no doubt of considerable practical importance, has two great drawbacks from the point of view of chemical theory, viz. : (1) that the parent-substance, fuchsene, of wave-length 593, may be wholly imaginary, and (2) that no light is thrown on coloured substances of smaller complexity or of different chemical families.

In the search for a general and fundamental theory of colour I have examined all that have been put forward in the last forty years, an excellent summary of which appears in E. R. Watson's *Colour in Relation to Chemical Constitution* (Longmans, 1918). It is evident first of all that no one theory fits all cases, from diazomethane to indigo for example. The most promising from a quantitative point of view (*i. e.* leading to the possibility of calculating colour with some exactitude), appeared to be the Watson-and-Meek modification of Hewitt's suggestion that depth of colour depends on length of continuous tautomeric change or alternation of single and double bonds in the molecule (*l. c.*, pp. 87-91).

I have therefore analysed my observations of the wave-lengths (absorption-centres) of all the common dyes to see whether numerical values in wave-length could be assigned to each possible kind of tautomerism, which could then be added up to give a result approximating to that observed in the dye. This I found to be the case, and the main part of this paper will be found to consist of calculations of colour, with the observed figure appended for comparison. It will be seen that the theory embraces many other classes of coloured substances than the "aniline dyes."

The additive property of colour has been sufficiently demonstrated in the earlier sections of this work; it now remains to give it a physical basis. The reader has first to remember that frequency of vibration is the inverse of periodic time, and that wave-length is inverse to frequency. It follows that wave-length is directly proportional to periodic time. The simplest assumption therefore is that the observed wave-length (absorbed by a highly-dilute coloured solution) is physically caused by an electron travelling through a sinuous orbit, which is completed (on the average) in a periodic time during which light would travel through that distance (*e. g.* 602 μ u

for Michler's hydrol in water). The additive property means that the sinuous orbit is made up of roughly semicircular portions through which the electron passes in turn from one end of the chain to the other, *e. g.* :

Fig. 1.—Michler's hydrol.*

so that the total periodic time is the sum of the separate periodic times taken in each loop. Also at this stage I may mention that there is not much difference between the values of the different tautomerisms, so that 5 loops give a wave-length in the middle of the spectrum (λ 500 in unloaded molecules); 4 loops give about λ 400, viz. yellow substances; 3 loops give about λ 300 (colourless substances with photographable absorption bands); whilst substances with less than 3 tautomeric loops, unless very heavily loaded with side-groups, are in general colourless, even to the photographic plate.

It is to be noted that such a sinuous orbit would not be expected to have an exact and constant periodic time, but only an average one. This explains why absorption-bands are diffuse and not narrow lines as in the case of sodium vapour, where the periodic time is constant. The diffuseness of the bands means a diffuse periodic time, *i. e.* a periodic time affected by perturbations, to use the astronomical analogy.

It is probable that the path of the electron is not as shown in the diagram, Fig. 1, namely passing *through* carbon atoms, but that the path goes in between the successive atoms of the tautomeric chain, making in the above case ten sinuosities instead of five (eleven if the particle goes *round* the final atom to continue the orbit in the reverse direction—Fig. 2).

Fig. 2.—Path of electron.

The result of my calculations is that (1) the tautomerism

has a value of 103 $\mu\mu$ in wave-length, (2) the tautomerism

has a value of 94, and (3) the tautomerism

* For clearness, the hydrogens and the non-tautomeric double bonds are omitted.

has a value of 98. All other parts of a molecule have *small* values: *any* group attached to the inner *end* of a tautomerism and itself incapable of tautomerism has a value of about $7\frac{1}{2}$, viz. 7 for small groups, *e. g.* Me, Et, Cl, and 8 for large groups such as iodine or phenyl. Groups of the above kind, but attached to the *middle* of the tautomerism, have double value, viz. about 15 (14 for methyl, 16 for iodine or phenyl). An anomaly may be noted, namely that groups on the *final* nitrogen of tautomerism 3 have this double value also, the tautomerism

having the value of 126 (viz. $98 + (2 \times 14)$).

Now in a colour containing a phenol-ring, the following dissection of the ring is to be imagined:

The part on the left within the thick lines is the CCO tautomerism loaded with a non-tautomeric group CH in the *middle*; its value is therefore $94 + 15 = 109$. The next tautomerism is CCC loaded with a group CH (rest of benzene-ring), this time at its *end*; its value is thus $103 + 7 = 110$. The CH in the square of the diagram is common to both tautomerisms. The total value of the phenol-ring is thus 219, and this is CCO + CCC + 22. Thus the non-tautomeric portion of the benzene-ring -- CH = CH -- has always a value of 22.

In the same way the value of the aniline or para-aminophenyl-ring is $\text{CCN} + \text{CCC} + 22 = 223$; and the value of the para-dimethylaminophenyl-ring is $126 + 103 + 22 = 251$.

Any halogenated phenol-ring will have the value $219 + 7 = 226$ if the halogen is *ortho* to the hydroxyl, and the value $219 + 15 = 234$ if the halogen is *meta*, the one being a terminal and the other a central loading of the tautomerism (if the substituent is large, viz. iodine, the value is one or two more). Alkyl derivatives have the same values, viz. 7 or 15, if attached to carbon.

Similarly halogenated aniline-rings have the values $223 + 7 = 230$ if *ortho*, and $223 + 15 = 238$ if *meta*, and so on, all the substituents having nearly the same value if non-tautomeric, and everything being additive. Examples will be given later on in the paper. A few concrete cases may now be studied:

(1) *Dioxybenzhydrol (aqueous alkali).*

The formula is

in which only the tautomeric double-bonds are written. This consists of two of the phenol- or para-oxyphenyl-rings, joined by a middle tautomerism:

The calculated wave-length is therefore $2 \times 219 + 103 = 541$. The observed λ was about 539 (own observation).

(2) *Benzaurine in alkali (aqueous).*

This is the phenyl-derivative of the foregoing, with CPh in the middle instead of CH. As this is a middle loading, the value is 14 to 16 according to the size of the group. Taking 16 for phenyl, the calculated value for benzaurine is $541 + 16 = 557$. The observed λ was 553. The other two bands at $\lambda\lambda$ 370 and 290 are, in my opinion, due to shorter tautomerisms of three and two units respectively.

(3) *Diaminobenzhydrol (neutral chloride in water).*

The formula is

and consists of two para-aminophenyl-rings united by the tautomerism CCC. The calculated wave-length is therefore $2 \times 223 + 103 = 549$. I have observed in a crude product λ 548. Watson (*l. c.*, p. 88) gives λ 564 in alcohol. It is to be noted that in alcoholic solution such dyes are not ionised, *i. e.* are loaded with chlorine on the nitrogen, and therefore give a higher wave-length than in water.

(4) *Doebner's violet in water.*

This is the C-phenyl-derivative of the foregoing, related to No. 3 as No. 2 is to No. 1. The calculated wave-length is therefore 16 more than 549, or 565. The observed λ was 562. Meyer and Fischer (*Berichte*, 1913) give λ 570 in alcohol, with two lower bands at $\lambda\lambda$ 400 and 300 due to shorter tautomerisms.

(5) *Michler's hydrol in water.*

The formula is as in Fig. 1. The calculated colour is $2 \times (\text{Me}_2\text{NCC}) + \text{CCC}$ or $2 \times 251 + 103 = 605$. Observed in water λ 602, in alcohol λ 610.

(6) *Malachite-green in water.*

This is the C-phenyl-derivative of Michler's hydrol (Watson, *l. c.*, p. 90); hence its calculated wave-length is $16 + 605 = 621$. Observed λ 619 in water.

(7) *Sodium phenate and (8) aniline.*

This is an example of a simple triple tautomerism in which the whole benzene-ring takes part:

For the former substance, calculation gives $\text{CCO} + 2\text{CCC} = 94 + 206 = 300$; for the latter we have $\text{CCN} + 2\text{CCC} = 98 + 206 = 304$. The observed values are both about λ 290 (Tuck, J.C.S., 1909). It is to be noted that free phenol and aniline hydrochloride give entirely different spectra, which cannot be calculated.

(9) *Sodium paraoxybenzaldehyde*.

This is

in which, as before, the non-tautomeric double bond is not shown. This consists of the tautomerisms $\text{CCO} + \text{CCC} + \text{CCO}$ loaded with the ring residue $-\text{CH}-\text{CH}-$. The calculated figure is therefore $94 + 103 + 94 + 22 = 313$. The observed figure (? in alcohol) is about λ 330 (Baly, J.C.S., 1907). The substance is colourless.

(10) *Sodium salicylaldehyde*.

This is yellow because the tautomerism goes right round the ring:

It consists of $\text{CCO} + \text{CCC} + \text{CCC} + \text{CCO}$, and the calculated figure is: $2 \times 94 + 2 \times 103 = 394$. Baly observed λ 388 (*l. c.*).

At this stage we will now consider the three symmetrical aniline dyes, aurine, parafuchsine and crystal-violet, which have always been a puzzle to the colour chemist because their colours are lower than those of the corresponding unsymmetrical compounds, benzaurine, Doebner's violet and malachite-green. I find that the explanation is that the tautomerism

has a lower value than the simple tautomerism CCC , the existence of two simultaneously available paths apparently making the orbit smaller and the periodic-time less. The value is about 96. It is also to be noted that the whole tautomeric chain in these dyes is no longer than before, viz. 5 tautomerisms, not 8, because the orbit can only go through two of the benzene-rings at a time, never through all three in succession. Consequently aurine is a loaded dioxybenzhydrol, parafuchsine is a loaded diaminobenzhydrol, and crystal-violet is a loaded Michler-hydrol. The general formula being $\text{C}^+(\text{C}_6\text{H}_4\text{X})_3$, my supposition is that the colour is due to *two* groups $\text{C}_6\text{H}_4\text{X}$ united by the tautomerism

of value 96, whereas in the unsymmetrical series $\text{PhC}^+(\text{C}_6\text{H}_4\text{X})_2$ the two groups $\text{C}_6\text{H}_4\text{X}$ are united by the tautomerism $\text{C} - \text{CPh} = \text{C}$ of value $103 + 16 = 119$. We will now calculate these dyes.

(11) *Aurine-sodium in water.* $\text{C}^+(\text{C}_6\text{H}_4\text{O}/)_3$.

According to the above theory we have *two* active rings $\text{C}_6\text{H}_4\text{O}/$ of value 219 each, plus

of value 96. This gives $438 + 96 = 534$. This agrees exactly with observation.

(12) *Pararosaniline in water.* $\text{C}^+(\text{C}_6\text{H}_4\text{NH}_2)_3$.

Here we have two active rings $\text{C}_6\text{H}_4\text{NH}_2$ of value 223 each, plus the same tautomerism; hence the calculated value is $2 \times 223 + 96 = 542$. Observation gives λ 543.

(13) *Crystal-violet (N-hexamethylpararosaniline).* $\text{C}^+(\text{C}_6\text{H}_4\text{NMe}_2)_3$.

Here we have two active rings $\text{C}_6\text{H}_4\text{NMe}_2$ of value 251 each, plus the same tautomerism; hence the calculated value is $502 + 96 = 598$. Observation gives λ 596.

It is known that in the case of Nos. 12 and 13 the addition of acid changes the colour, fuchsine becoming purple and crystal-violet green. The true explanation of this now lies to hand, viz. that the symmetry is destroyed, leaving two of the groups as $\text{C}_6\text{H}_4\text{NH}_2$ whilst the third becomes the ion $\text{C}_6\text{H}_4\text{NH}_3^+$. The dyes become then derivatives of the *unsymmetrical* class mentioned just above $\text{PhC}(\text{C}_6\text{H}_4\text{X})_2$. Thus purple (acid) fuchsine is a substituted Doebner's violet, and green (acid) crystal-violet is a substituted malachite-green. The ion $\text{C}_6\text{N}_4\text{NH}_3^+$ and the ion $\text{C}_6\text{H}_4\text{NHMe}_2^+$ are non-tautomeric and appear both to have the value 27; if this number be substituted for the value 16 used for plain phenyl in calculating Doebner's violet and malachite-green, the calculated results are 549 (diaminobenzhydrol) + 27 (or 576), and 605 (Michler-hydrol) + 27 (or 632), which are precisely the observed figures in acid pararosaniline and acid crystal-violet.

(14) *Paraoxy-derivative of malachite-green.*

This interesting substance is another *crux* of the colour chemist, being blue when neutral and purple-pink when alkaline.

On my theory the alkaline phase should have nearly the same colour as the substance

and the neutral phase should have nearly the same colour as

(Michler-hydrol). The observed wave-lengths are $\lambda\lambda$ 578 and 608 respectively. Oxydimethylaminobenzhydrol has not yet been observed, but its calculated wave-length is $219 + 103 + 251$, or 573. Its phenyl derivative (dimethylaminofuchson of Part X) has been observed, giving λ 586, whence oxydimethylaminobenzhydrol itself should have $\lambda = 586$ minus 16 or 570. Taking the unknown, therefore, to have wave-length 571, and remembering that Michler-hydrol has λ 603, we see that the two colours of paraoxymalachite-green (bis-dimethylamino-fuchson) are both about 6 units higher than those of the simple benzhydrol compounds, this being the allowance for the non-tautomeric group or load, $\text{C}_6\text{H}_4\text{NMe}_2$ or $\text{C}_6\text{H}_4\text{OH}$ respectively. The theory, therefore, not only accounts for two colours in this substance, but enables them to be calculated.

(15) *Michler's ketone* (salt in water).

The formula is

The substance is yellow, and there are only three tautomerisms, as shown in the formula. The tautomerising ring $\text{C}_6\text{H}_4\text{NMe}_2$ has been shown to have the value 251; adding the tautomerism CCO of value 94 and 16 for the benzene-ring load (non-tautomeric) we get 361 as the calculated wave-length. The observed figure is about λ 364 (λ 368 in alcohol, Watson, p. 88). The small difference is due to the load on the benzene-ring outside the tautomerism. In previous paragraphs (substances 13 and 14) it is shown that substitution in the benzene-ring outside the tautomerism causes small but variable changes in the value (16) assigned to plain phenyl. These small differences are at present anomalous but do not much affect the validity of the theory. In this particular case, too, one may note that the tautomerism

may be of lower value than the simple tautomerism CCO on the analogy of the tautomerism

in which case the calculated value would be about seven units lower.

An explanation is still required for the marked yellow colour of the dye auramine, which is derived from Michler's ketone by replacement of O by

NH, and therefore should have λ about 365, whereas it is really about 420. Two other partial anomalies are fuchsimonium chloride and its dimethyl-derivative, which have *very broad* absorption bands at $\lambda\lambda$ 430 and 460 respectively in alcohol. The formula

corresponds to the tautomerism

combined with the $\text{C}_6\text{H}_4\text{NH}_2$ ring and two phenyl loads. This would be $96 + 223 + 32 = 351$; similarly the dimethyl derivative would work out at 379, both of which calculations are about 80 units too low. Now colour and broad bands similar to these are obtainable from malachite-green and crystal-violet by adding an excess of acid, the observed wave-lengths being about λ 438 and λ 417 respectively. It is evident that these five cases cannot be explained on an exact quantitative basis, and I suggest that in all of them the tautomerism penetrates into one of the benzene-rings in a highly perturbed orbit, thus accounting for both the breadth of the band and its abnormally high position; the orbit would thus be of the following type in which the irregular orbit varies in value between 80 and 100.

Fuchsonedimethylimonium salt λ 460 in alcohol.

Having now shown the weaker points of the theory, it may be well to show how it explains the colours of the phthaleins or other well-known substances. Since the CO_2H group of the phthaleins is outside the tautomerism it makes scarcely any difference; observation shows that any substituted phenolphthalein has a spectrum which is only one to two units different from that of the corresponding benzaurine. Thus the central

group may be taken to be of value + 18 when phenyl is + 16. Again, it is shown on p. 207 that an ortho-substituent puts the value up by 7 and a meta by 15. Hence the ring

has a value of $219 + 7 = 226$, the ring

has a value of 233, the ring

has a value of $219 + 15 = 234$, the ring

has a value of 241, and so on. In the *p*-amino-rings the values are 4 greater in each case. To calculate ortho-tetrabromophenolphthalein therefore we split it into two rings

plus the tautomerism

which, as shown above, has the value of $103 + 18 = 121$.

Hence the substance should have (in alkali) $\lambda = 466 + 121 = 587$. Observation gives $\lambda 584$. Nearly the same observation is given if chlorine, iodine, or methyl be taken in place of bromine, hence I use X in the formulae.

Consider now thymol-and carvacrolphthaleins. To calculate them they may be split into two

rings, plus the 121 tautomerism. X is methyl and Y isopropyl in the one case, and *vice versa* in the other, but since all non-tautomeric groups have nearly the same value, the two substances have nearly the same colour. Taking the ortho X at 7 and the meta Y at 15 (as if it were meta-X), we have an addition of 22 to each ring; hence both substances should have spectra which are 44 units above that of phenolphthalein. Observed: Phenolphthalein $\lambda 554$, thymolphthalein $\lambda 597$, carvacrolphthalein $\lambda 601$. If we allow the meta-isopropyl group 16 instead of 15, the calculated gain on phenolphthalein will be 46, and $554 + 46 = 600$, which agrees with the observation on carvacrolphthalein. The so-called sulphonophthaleins can also be calculated in the same way, giving the ortho-position in the tautomeric rings the value 7 and the meta-position 15, and allowing 27 for the group

outside the tautomerism, *e.g.* "bromphenol-purple," which has 4 ortho-bromines, should be $(4 \times 7) + 27$ or 55 above dioxycbenzhydrol $= \lambda 596$; observed $\lambda 594$.

All the naphthalene derivatives of the classes already discussed can be brought into the scheme by allowing the value 53 to the grouping

which when added to benzene turns it into naphthalene.

Thus phenol- α -naphtholphthalein is $554 + 53 = \lambda$ 607 and α -naphtholphthalein is $607 + 53 = \lambda$ 662. The tautomeric ring

has thus the value $219 + 53 = 272$ and the para- α -naphthylamine-ring the value 276. The grouping

when non-tautomeric is a combination of the C_4H_4 and the C_2H_2 loads and its value is therefore $53 + 22 = 75$.

Colour of Indigo.

The most probable tautomeric change in this substance is as shown below:

This is CCO + CCC + CCC + CCN + CCN + CCO fully tautomerised, plus the load C_6H_4NH . Allowing 20 as an estimate from analogy for the latter the total is 610. This is evidently quite near the truth, but of course indigo cannot be observed in water solution, for which all the other data are calculated. Sulphindigotic acid in water has λ 614. It is next desirable to discuss the nitro and nitroso-colours, which do not at once fit into the scheme. Unfortunately all the published data deal with substances in alcoholic solution, consequently in the case of alkaline solutions the molecule contains non-ionised sodium or potassium, and in acid solution an acid radicle, thus introducing an unnecessary complication due to varying load on the molecule. The first thing that is noticed is that the spectrum of an alkaline nitro-phenol is frequently about 100 units above that of the parent substance, which certainly on my theory suggests that it has one tautomerism more in the alkaline condition than when free. Examples from Baly's and Tuck's work are *p*-nitrophenol λ 308, K-salt λ 405; *p*-nitroso-phenol λ 311, Na-salt λ 415; *o*-nitrophenol λ 338, K-salt λ 435; *m*-nitrophenol λ 328, K-salt about λ 390, very broad, evidently imperfectly formed.

It is probable that the free substances have merely the tautomerism of phenol (λ about 300), viz. CCO + 2CCC, whereas the alkaline forms have the nitroic-acid tautomerism involving a new unit, viz. C — N = O in the nitroso-compounds and

in the nitro-compounds. This would afford an explanation in the case of the ortho-compounds, in which there would be four tautomerisms instead of three, viz. CCO — CCC — CCC — CNO, but in the para-compounds there would still be only three, yet the wave-length is only 30 less. This must remain an anomaly. If the cause of the colour of quinone itself (as well as azobenzene, benzil and other coloured substances incapable of tautomerism in the ordinary sense) were known, no doubt paranitrophenol could be correlated better with quinone than with a tautomeric sodium phenate (quinone having the very high λ 461), seeing that sodium paranitrosophenol is almost certainly a salt of the oxime of quinone.

We come next to the difficult problem of the azo-dyes. Their bands are broad and indefinite, consequently measurements of their centres have no exactitude. The broadness of the bands means a very perturbed vibration or irregular periodic-time of the moving electron in its orbit, which renders the additive law almost inapplicable. In addition, the grouping C — N = N — C is not capable of ordinary tautomerism; hence, for example, in *p-p*-dioxyazobenzene the electron cannot travel from one end to the other as it does in dioxybenzhydrol. Nevertheless a few regularities can be traced. Tuck (J.C.S., 1909) has, for example, pointed out that alkaline oxyazobenzene and neutral aminoazobenzene have nearly the same spectrum, the figures being λ 420 and λ 424 respectively. This can be accounted for on my theory if the vibration in the group PhNNC is assigned the value 201, because the other part of the molecule is clearly tautomeric and has the value 219 for $\text{C}_6\text{H}_4\text{O}^-$ (and 223 for $\text{C}_6\text{H}_4\text{NH}_2$), these giving 420 and 424 on addition to the constant 201.

Again, the colour of *free* oxyazobenzene can be roughly calculated if it be assumed to be quinone-phenylhydrazone (the salt having, on the contrary, the azo-formation). The tautomerism would then be

Assuming by analogy, since the CCN tautomerism is five less than the CCC one, that the CNN tautomerism should have the value 93, we get CCO + CCC + CNN + 22 for half-ring + 16 for phenyl, adding up to 328 for the calculated absorption-band in water (Baly gives λ 332 [plus 455 faint] in alcohol). However, if this theory is the correct one, it follows logically that

free aminoazobenzene is *not* quinone-iminephenylhydrazone, for in that case it would have λ 332 ($328 + 223 - 219$) instead of λ 424.

I have to confess that I have almost abandoned the hope of finding an explanation of the higher azo-dyes. For example, the following substances of widely different constitution have almost exactly the same absorption-band, and I hope that some other worker will attempt an explanation, now that the wave-lengths are available :

whilst the other symmetrical substance

has λ 515.

Substitution of a naphthalene- for a benzene-ring has a larger effect in the azo series than in the di- or tri-phenylcarbinol series. Thus alkaline benzeneazo- α -naphthol has its band about 85 units above that of benzeneazophenol, and the paranitro-derivatives (see Watson, *l. c.*, p. 89, v ; and 91, xiii) have the bands at λ 494 and 576 respectively.

Here, in conclusion, I may mention a most remarkable fact which some other worker may be able to explain, if it is not a mere coincidence, viz. that the bands of (a) phenolphthalein, (b) phenol- α -naphtholphthalein, and (c) (di) α -naphtholphthalein are almost exactly in the ratio 10 : 11 : 12, viz. λ 554, 608 and 662,* and those of (d) nitrobenzeneazophenol and (e) nitrobenzeneazo- α -naphthol are exactly in the ratio 6 : 7, viz. 494 and 576. This certainly appears to be connected with units of tautomeric change also.

* The ratio agrees even better if 18 be subtracted from each for the $\text{C}_6\text{H}_4\text{CO}_2\text{H}$ group, giving benzhydryl derivatives.