CCXXXVII.—*Colour and Molecular Geometry. Part V. A Search for a Crucial Test of Colour Theories.*

By JAMES MOIR.

ANY theory of colour must, to be really successful, cover the whole field of absorbing substances—and this not merely qualitatively but quantitatively. It is not sufficient, for example, to establish a scheme in which most "coloured" (*i.e.*, absorbing) substances can be formulated with a little manipulation as "quinonoid" or as possessing alternate double and single linkages, inasmuch as there are plenty of exceptions to these schemes, namely, cases in which the amount of manipulation of the formula required to make it quinonoid is beyond belief (for example, *m*-aminophenol) or even beyond possibility (for example, the coloured solution of dihydroanthracene in concentrated sulphuric acid). It is also not sufficient to establish a scheme in which the various absorption bands of a substance examined in different media are related to one another in the same way as harmonics of a fundamental tone are, inasmuch as the connexion between the value of the fundamental and the chemical constitution has still to be discovered, also the reason why unexpected harmonics such as the 19th appear. A 19th harmonic is only credible if accompanied by the 7th, 13th, and 25th, or similar series; in other words, prime numbers as harmonics require a special explanation.

The author's theory, whilst admittedly a makeshift, is the only one capable of giving predictions of colour from constitution. Its use, however, is very greatly restricted by our lack of knowledge of the actual dimensions of many common molecules. Even the true configuration of benzene is still in doubt,* although the relation between anthracene and naphthalene is considered to be beyond doubt.

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* Many writers appear to think that Körner's model is the same as Bragg's —which is not the case. The angle between adjacent carbon atoms in the skew-hexagon is 109° in Bragg's model and 90° in Körner's; consequently the representation of the position of the hydrogen atoms in Körner's model is quite erroneous.

The author therefore presents in this paper an experimental study of some of the oxygen derivatives of anthracene (together with a few of the corresponding derivatives of naphthalene) with the view of providing data for a crucial test of his own and other colour theories, a test founded on the fact that there is hardly any dispute as to the size and spatial configuration of the anthracene and naphthalene molecules.

Tables I and IA contain the author's observations of the positions of the bands of these oxygen derivatives, made in dilute aqueous sodium hydroxide solution, in presence of sodium sulphite to prevent aërial oxidation.

TABLE I.

Absorption of Hydroxy-derivatives of Anthracene in Excess of Alkali.

	Central λ (in $\mu\mu$) of chief band.	Fainter bands.
1-Hydroxy-9 : 10-dihydroanthracene *	312	Nil.
1-Hydroxyanthracene (α-anthrol)	364	347, 410 broad
2-Hydroxyanthracene (β-anthrol)	335	Nil.
9-Hydroxyanthracene (anthranol)	378	,,
1 : 9-Dihydroxyanthracene (α-hydroxyanthranol)	490	460
2 : 9-Dihydroxyanthracene (β-hydroxyanthranol A)	476	447
3 : 9(or 2 : 10)-Dihydroxyanthracene (β-hydroxyanthranol B)	510	480
1 : 5-Dihydroxyanthracene (rufol)	371	354, 420 broad
2 : 6-Dihydroxyanthracene (flavol)	345	312, 378 broad
2 : 7-Dihydroxyanthracene	390	Nil.
9 : 10-Dihydroxyanthracene (anthraquinol)	495 broad	,,
1 : 5 : 9-Trihydroxyanthracene (anthrarufin-anthranol)	427	370
1 : 2 : 10-Trihydroxyanthracene (deoxyalizarin)	480	Nil.
2 : 6 : 9-Trihydroxyanthracene (anthraflavin-anthranol)	416	490, 515
2 : 7 : 9-Trihydroxyanthracene (*iso*anthraflavin-anthranol)	492	466
2 : 9 : 10-Trihydroxyanthracene (β-hydroxyanthraquinol)	575	685
2 : 6 : 9 : 10-Tetrahydroxyanthracene (hydroanthraflavin)	486	454
1-Hydroxyanthraquinone	480	500
2-Hydroxyanthraquinone	470	495
1 : 2-Dihydroxyanthraquinone (alizarin)	613	568, 523
1 : 4-Dihydroxyanthraquinone (quinizarin)	595	552, 516
1 : 5-Dihydroxyanthraquinone (anthrarufin)	470	500
2 : 6-Dihydroxyanthraquinone (anthraflavin)	430	400, 485
2 : 7-Dihydroxyanthraquinone (*iso*anthraflavin)	475	390, 500

* The author finds that 1-hydroxy-9 : 10-dihydroanthracene (contrary to the statements of Liebermann, *Annalen*, 1882, **212**, 15, and Pleus, *Ber.*, 1902, **35**, 2928) is a phenolic substance closely resembling the cresols and has no colour in alkali. The author's specimen was made by sodium reduction of α-anthrol and agreed in appearance and melting point with the data in the literature.

TABLE IA.

Absorption of some Corresponding Naphthalene Derivatives in Excess of Alkali.

	Central λ (in μμ) of chief band.	Fainter bands.
1-Hydroxynaphthalene	330	Nil.
2-Hydroxynaphthalene	349	,,
1 : 5-Dihydroxynaphthalene	350	,,
2 : 6-Dihydroxynaphthalene	340	356
2 : 7-Dihydroxynaphthalene	338	393
5-Hydroxy-1 : 4-naphthaquinone (juglone)	510	570
5 : 6-Dihydroxy-1 : 4-naphthaquinone (naphthazarin)	619	571

TABLE II.

Sulphonates in Aqueous Alkali.

Name.	Position of bands.
Anthraquinone-1-sulphonate	340 and 385
Anthraquinol-1-sulphonate	493 and 515
Anthranol-1-sulphonate	385 and 363
Anthracene-1-sulphonate	383, 364, 345, 326, and 308
Anthraquinone-1 : 5-disulphonate	333 and 420
Anthraquinol-1 : 5-disulphonate	491, 533, and 590
Anthranol-1 : 5-disulphonate	432, 460, and 490
Anthracene-1 : 5-disulphonate	389, 370, 350, and 305

The first point to be noted from the observations is the very interesting one that both of the anthrols and both of the symmetrical anthradiols are *visibly* coloured in moderately concentrated ($N/500$) solution, whereas the corresponding derivatives of naphthalene, all of which have absorption bands situated below λ 390 (the usually accepted lower limit of human vision), are not coloured in alkaline solution unless the solutions are very concentrated (over $N/10$). The α-compounds are more highly coloured than the β-compounds.

The second point is that the behaviour of the 1 : 5-dihydroxy-compounds is almost the same as that of the 1-hydroxy-compounds and that the 2 : 6-dihydroxy-compounds resemble the 2-hydroxy-compounds in behaviour. This symmetry clearly points to an influence of the centre (or the central plane) of the molecule on the height of colour.

The third point is the high colour (λ above 470) produced when one hydroxyl group is present in the 9-position. All the anthranols and anthraquinols show this, and, as is well known, all the hydroxyanthraquinones can be formulated in an alternative form with an OH-group in position 9. Usually the anthranol has a similar colour to that of the anthraquinone. This high colour is not easy to explain on any theory of colour.

The fourth point is that the highest colours of all occur in 2 : 9 : 10-, 1 : 2 : 9 : 10-, and 1 : 4 : 9 : 10-compounds (the 1 : 9 : 10-compound, α-hydroxyanthraquinol, could not be obtained). This is evidently due to superposition of effects due to the 9 : 10 arrangement—in itself capable of giving a red colour—on effects due to the co-operation of hydroxyl and the anthracene skeleton—in itself capable of giving a yellow colour, as shown above.

The last point is that the phenomena are almost exactly duplicated in the naphthalene series, so that the third ring in anthracene is of little significance. Thus juglone resembles erythrohydroxyanthraquinone, naphthazarin resembles alizarin, and all the mono- and di-hydroxynaphthalenes examined resemble the corresponding derivatives of anthracene. Nevertheless, anthraquinol (red in alkali) does not closely resemble 1 : 4-dihydroxynaphthalene in colour, although the alkaline solution of the latter compound is yellow (in presence of reducing agents to avoid oxidation), in contradistinction to that of ordinary quinol. 9 : 10-Anthraquinol in alkali absorbs from λ 520 to λ 470, 1 : 4-naphthaquinol at about λ 400, and quinol at λ 316.*

Those who have followed the author's attempts to find a theory of colour will remember that six years ago he put forward a factorial scheme whereby 90% of the data for dicyclic coloured substances could be correctly predicted (J., 1921, **119**, 1654), and later he showed that alteration of the angle between the rings is the reason why dicyclic coloured substances linked by carbon have lower colours than the corresponding substances in which nitrogen or oxygen forms the joint between the rings.

Further consideration shows that this scheme must sometimes break down when there is more than one joint, and this merely because the two joints cannot approach one another closely when one of them is carbon with its comparatively severe bend of 109°. Consequently, the calculated values for dihydroxyxanthhydrol and dihydroxyacridine are slightly incorrect (—3%), whereas those for dihydroxyanthracene, dihydroxyacridone, and dihydroxyxanthone are seriously incorrect (—12 to —25%). This means that the factor 0·65 used for calculating linkage by carbon can only be used once, so that if there is linkage by a second atom (in the ortho-position to the first linkage, of course) it occurs in such a way as to keep the molecule as flat as possible. Bragg's model for anthracene is an example, for, if my 1921 theory had been entirely correct, the anthracene model resulting would have been "buckled" in the

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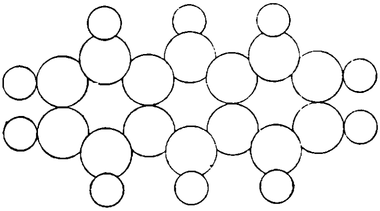
* If these effects are merely due to "loading" of quinol with one or with two benzene rings respectively, they are much the largest loading effects known.

middle, this being the only way in which both the central carbon atoms could make the normal (109°) angle with both rings.

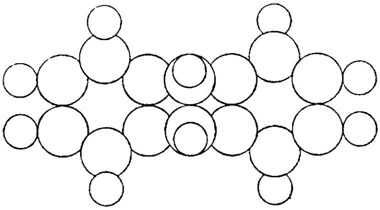
Figs. 1 and 2 represent two possible ways in which Bragg's measurements may be satisfied without any "buckling." Fig. 1, being without a cross bond, really represents dihydroanthracene, but is Bragg's own original diagram, with the β-hydrogen atoms put in the same plane as the β-carbon atoms. Fig. 2 shows the cross bond of anthracene as part of a Dewar–Ingold benzene model (triangular prism). Both models measure 11·18 Å. by 6·00 Å. The dimension 11·18 Å. of anthracene is made up of two ordinary benzene rings each of width 2·57 Å., one central ring of width 2·50 Å., two halves of a carbon atom, equal to 1·54 Å., and two hydrogen atoms, equal to 2·00 Å. The other dimension (vertical) is made up of $2{\cdot}57 \div (\sqrt{3}/2)$ (from the properties of a hexagon), plus two halves of a carbon atom, plus the projection of two hydrogen atoms lying at 109° to the plane of the paper containing the β-carbon atoms. Similarly, if the middle ring be removed, the diagram agrees exactly with that of naphthalene [$(2 \times 2{\cdot}57) + (2 \times 0{\cdot}77) + 2{\cdot}0 = 8{\cdot}68$ for the length, whilst the breadth remains at 6·00 as in anthracene], these dimensions being exactly those given by Bragg. Inferentially also, the dimensions of the benzene molecule become, in this scheme, 6·11 Å. × 6·00 Å., a much closer approach to a true hexagon than one would expect at first sight from a molecule possessing a carbon skeleton of the skew-hexagon nature prescribed by Bragg.

FIG. 1.



Anthracene (Bragg).
Dihydroanthracene (Moir).

FIG. 2.

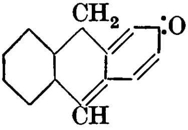


Anthracene (Moir).

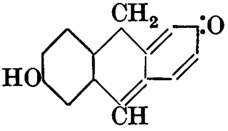
Application of the Model to the Author's Colour Theory.

The extreme form of the author's theory, according to which the distance between the centres of the oxgyen atoms of the auxochromes decides the colour, is at once seen to be incorrect, because if this form of the theory were true, the substance flavol (2 : 6-dihydroxyanthracene), in which the centres of the oxygen atoms are as far apart as possible (10·6 Å. on the model), would possess an absorption band at λ 850. Similarly, 2 : 6-dihydroxynaphthalene, which has, on the model, a distance of 8·1 Å. between its oxygen centres, would have a band at λ 650. Observation shows that the position of the chief band of both these substances is practically the same (λλ 345 and 340 respectively), both being pale yellow in alkaline solution. Light is now thrown on this obscurity by the fact that β-anthrol and β-naphthol have similar absorptions when examined in alkali solution (λλ 335 and 349 respectively). This shows that the colour vibration (colour orbit on the author's theory) is not from auxochrome to auxochrome, but is from *one* (that is to say, from either) auxochrome to a centre of force near the centre of the molecule.

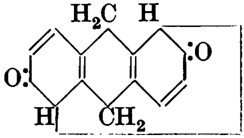
This idea can be correlated with the quinonoid theory as follows : β-Anthrol can be written as a quinonoid compound (I), and similarly flavol can be written as (II) but cannot be written so as to make the oxygens of *both* auxochromes quinonoid. I assume that such a formulation as (III) is patently absurd.



(I.)

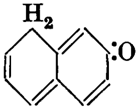


(II.)



(III.)

The cause of the band round about λ 340 in these four compounds (β-naphthol, 2 : 6-dihydroxynaphthalene, β-anthrol, and flavol) thus only concerns one ring. On my theory, λ 340 corresponds to a positive-centre distance of 4·36 Å. if both centres are oxygen atoms,* and about 4·2 Å. if one is a carbon atom. The latter distance on the model agrees with an orbit in which the electron grazes the oxygen atom of the auxochrome and at the other end of the ellipse passes through the double bond outside the para-carbon atom, the positive centres being the auxochrome oxygen and the para-carbon atom. Thus my theory leads to the same result as is reached by the quinonoid theory. The quinonoid formulæ for β-naphthol and 2 : 6-dihydroxynaphthalene involved are (IV) and (V), although they have also been formulated as ortho-quinonoid.

(IV.)


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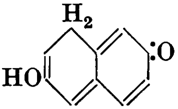

(V.)

The α-compounds may now be considered. α-Naphthol and 1 : 5-dihydroxynaphthalene have much the same absorption as the

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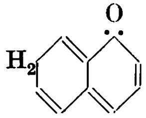
* For these calculations involving oxygen atoms alone, I find that the expression $\lambda = 82d - 20$ is sufficiently accurate.

β-compounds just discussed, *viz.*, an average value of 340 for λ. The corresponding distance is again 4·2 Å. and the corresponding quinonoid formulæ are :

(VI.)



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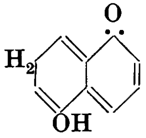
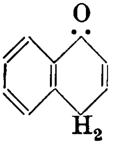


(VII.)

Nevertheless, no distance can be found on the model in agreement with these suppositions. Agreement can, however, be obtained if the more customary quinonoid form be assumed, in which

(VIII.)



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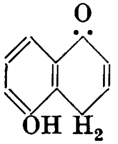


(IX.)

case the distance between oxygen and para-carbon agrees with what is required : the case thus becomes, in this instance, that of phenol with a " load."

The α-compounds of anthracene have a higher colour than those of naphthalene, due to bands at λλ 368 and 415 (on the average).

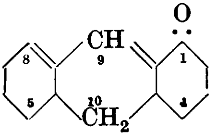
Alkaline solutions of 1-anthrol and of rufol (1 : 5-dihydroxy-anthracene) are yellow even in great dilution.

When, however, it comes to finding an explanation of this, it appears that Bragg's work is unfortunately less decisive as to the relative positions of α-groups than of β-groups.

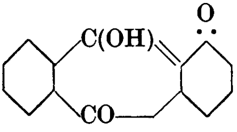
It is usually assumed, nevertheless (as on p. 1813), that α-groups lie in line with the benzene valencies, *i.e.*, inclined to the general plane of the model at the angle of 55° ($\sin^{-1}\sqrt{\frac{2}{3}}$) prescribed by the geometry of the skew-hexagon benzene model. An attempt to depict this *in plano* is shown in Figs. 1 and 2.

I find that an orbit round the α-oxygen and para-carbon atoms does not suit the colour, although the analogous supposition does suit in the case of the β-compounds. Neither does an orbit round the 1-α-oxygen and the 10-*meso*-carbon atom.

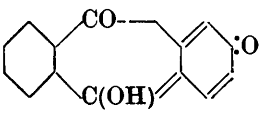
The only orbit which agrees is one which involves the double linkage lying between carbon atom 8 and its neighbour which links it to 9 in the quinonoid formula (X) for 1-anthrol.



(X.)



(XI.)



(XII.)

The centre of this unnumbered linking-carbon atom is at approximately the correct distance from the centre of the 1-oxygen atom to account on my theory for the observed band at λ 415 and the yellow colour.

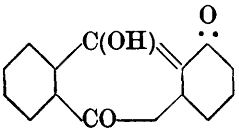
The Hydroxyanthraquinone Dyes.

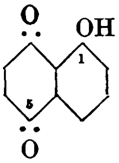
In explaining the colour of these dyes the author accepts the customary theory that the oxygen atoms attached at positions 9 and 10 compete with the hydroxylic oxygen atoms for a tautomerising hydrogen atom, as in the usual formulæ (XI and XII).

The tautomerism of the β-compounds is the ordinary quinonoid one, but in the α-compounds the chemical bonds cannot be arranged so as to show a tautomerism between 1- and 10-oxygens. This need not, however, deter us from conceiving the colour as being due to the movement of a single electron round these two oxygen atoms considered as positive centres—inasmuch as the case is similar to that of the "meta-quinonoid" coloured substances such as *m*-nitroaniline.

The distances, 6 Å. (α) and 6·5 Å. (β), between the centres of the oxygen atoms in question agree with what is required to explain bands occurring between λ 470 and λ 510. The *quinonoid* formula for erythrohydroxyanthraquinone (XIII) leads to a much smaller distance (2·6 or 2·9 Å. according as the 1- and 9-oxygen atoms are on the same or opposite sides of the general plane of the molecule), a distance corresponding to bands between λ 215 and λ 240 in the low ultra-violet region. Meyer and O. Fischer (*Ber.*, 1913, **46**, 85), in the cases of 1-hydroxyanthraquinone and anthrarufin, observed no bands below λ 265, but the lower limit of their investigation was probably not low enough to reach bands situated at λ 220.

(XIII.)



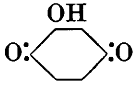


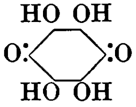
(XIV.)

The cause of the colour of juglone (5-hydroxy-1 : 4-naphthaquinone, *i.e.*, 1-hydroxy-5 : 8-naphthaquinone) (XIV) and of 1-hydroxyanthraquinone is the same, an orbit round the oxygens attached in positions 1 and 5. The third ring in 1-hydroxyanthraquinone has no effect, as is seen also to be the case by comparison of the bands of naphthazarin with those of alizarin.

It is a curious fact, however, and one not easy to explain, that colour of this height (λ 480 or so) can arise in compounds of only *one* ring, such as hydroxybenzoquinone and tetrahydroxybenzoquinone, when examined in alkaline solution. This is nevertheless not strictly analogous, since in juglone the hydroxyl group is

(XV.)





(XVI.)

attached, not directly to the quinone ring, but to a carbon atom attached to that ring. Probably a special explanation, similar to that of the high colour of alizarin (see below), is called for here.

The colour of anthrarufin is explained in the same way as that of 1-hydroxyanthraquinone, and the colour of anthraflavin and of *iso*anthraflavin in the same way as that of 2-hydroxyanthraquinone (see p. 1816).

The high colour of alizarin and naphthazarin constitutes part of a general phenomenon seen also in benzeneazopyrocatechol, 3 : 4-dihydroxybenzophenone, etc., whereby the presence of two hydroxol groups adjacent to one another greatly heightens the colour (Table III).

TABLE III.

Substance.	λ.	Comparison substance.	λ.
Benzeneazopyrocatechol ...	480	Benzeneazophenol	433
Phenolpyrocatechol-phthalein	579	Phenolphthalein	554
Pyrocatecholphthalein	652		
o-Hydroxyfluorescein	523 + 498	Fluorescein	494 + 457
oo′-Dihydroxyfluorescein ...	550 + 527		
3 : 3′ : 4 : 4′-Tetrahydroxy-benzophenone	449 + 406	4 : 4′-Dihydroxybenzo-phenone	323

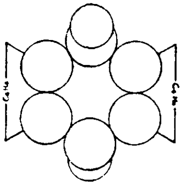
I am of opinion that the explanation is that the electron goes round *both* of the ortho-oxygen atoms as well as the third (distant) oxygen atom (Fig. 5), and thus describes an ovoid orbit which is wider than the normal type of colour ellipse (see J., 1922, **121**, 1810). This connotes a longer path and longer periodic time and higher colour, the eccentricity of the ellipse having been increased. The essential idea in this explanation of the heightening effect of contiguous auxochromes is that the two atoms behave (as in ordinary mechanics) as if their forces were condensed into their "centre of gravity" (the point midway between them), whilst the moving electron has to *touch the outsides* of both of them and so is constrained to move in one plane and thus give an ovoid orbit slightly wider at one end than at the other. In simpler coloured substances, of course, the orbit round two positive centres may be in almost any plane.

The hydroxyanthracenes and the hydroxyanthraquinones having been disposed of, it remains to discuss the colours of the hydroxyanthraquinols and hydroxyanthranols.

(*a*) Anthraquinol itself (in alkali) has a much higher colour than anthraquinone, a phenomenon *sui generis*, since it does not occur in the benzene and naphthalene series, in which the quinol has a lower colour than the quinone. It can only be explained on my theory by supposing the central ring flattened and the two (9 and 10) hydroxyl groups attached outside in the same plane. In this way, the oxygen atoms can be sufficiently separated to agree with the theory and the observed colour (see Table I). In anthraquinone, however, the theory requires that the distance between the oxygen atoms shall be only two-thirds of that required for anthraquinol; this agrees with the ordinary buckled-ring structure. Figs. 3 and 4 represent anthraquinone and alkaline anthraquinol according to the theory.

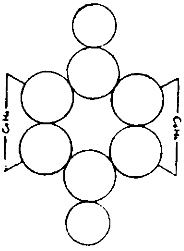
It is difficult to investigate the hydroxyanthraquinols on account of their great liability to oxidation, but they appear to have even higher colours than anthraquinol, requiring for explanation the ovoid orbit round oxygen atoms situated in the 1 : 9 : 10 and 2 : 9 : 10 positions.

FIG. 3.



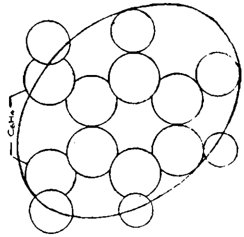
Anthraquinone.

FIG. 4.



Ionised anthraquinol.

FIG. 5.



Colour-orbit in alizarin.

(*b*) The hydroxyanthranols all have much the same colour as anthraquinol, intermediate in "height" between those of the corresponding hydroxyanthracenes and hydroxyanthraquinones. Those of the 1 : 10 and 2 : 10 type have slightly higher colours than those of the 1 : 9 and 2 : 9 type (see Table I). The explanation of their colour on my theory is that the distance between the oxygens is intermediate between that for the hydroxyanthracenes and that for the hydroxyanthraquinones, both of which have been accounted for above.

This shorter distance is accounted for by the fact that the central hydroxyl group of the anthranols is attached in the same way as the *meso*-hydrogen atoms of anthracene. It is thus plain from Fig. 2 that the distance from this hydroxyl to an α- or β-hydroxyl is less than in the case of the hydroxyanthraquinones.

Part II.

Some reference to the views expressed in the Report of the British Association Committee on Spectra and Constitution (1922) is called for from one who still believes that there is a relationship between chemical constitution and the position of absorption bands.

It is, of course, true that the portion of the field of ethereal vibration concerned with colour is less than one five-thousandth of the whole field. The author has, however, shown that the *whole* of the substances chemically related to a single parent substance possessing a band in this minute fraction of the possible field have also a band or bands in this same tiny region (J., 1923, **123**, Tables from p. 2797 to 2803), a fact which if ascribed to coincidence is incredible, but if ascribed to " loading " of the parent substance is eminently reasonable. For example, it appears to be impossible to make any derivative of azobenzene which shall not have a band somewhere between λ 420 and λ 600.

Again, the harmonic results for the anthracene family could be simplified if it is admitted that such of the observations as were made in concentrated sulphuric acid are not directly comparable with those made in alkali. Every such observation should be corrected for the very considerable " loading " effect of the solvent, in the same way as observations in alcohol must be corrected for comparison with observations in water, whereupon the bands coincide.

The case of benzene as studied by McVicker, Marsh, and Stewart is particularly interesting on account of the very definite harmonics arrived at (J., 1923, **123**, 642, 817, 2147). The heads of the Tesla bands were found to be the 33rd, 34th, 35th, 36th, 37th, 38th, and 39th harmonics of a fundamental in the infra-red at $\nu = 987{\cdot}1$ vibrations per cm.* ($\lambda = 10131\ \mu\mu$).

The 36th harmonic ($\nu = 35540$, $\lambda = 281\frac{1}{2}$) is the strongest. There is also a fine structure of subsidiary bands, making probably 84 in all between λ 310 and λ 260, all expressible as submultiples of the fundamental (considered as a double band of $\lambda\lambda$ 10131 and 10162) thus : $\nu = \begin{Bmatrix}987{\cdot}1\\983{\cdot}6\end{Bmatrix}\left(1 \pm \frac{n}{216}\right) \times$ harmonics.

Combining this discovery with the knowledge of the positions of two *observed* infra-red bands of benzene at about $\lambda\lambda$ 1680 and 6750 $\mu\mu$, we find that we must either assume the real fundamental λ of benzene to be twice that given above (20260 $\mu\mu$, $\nu = 493{\cdot}5$), in which case the harmonics go up to No. 78; or else keep to the result given above, with no harmonic higher than 39, and explain the band at 6750 $\mu\mu$ by a special hypothesis.

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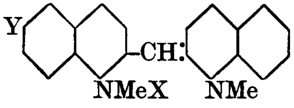
* Stated as 98·71 in their paper, different units being used.

It is fairly clear, however, from the mass of evidence brought forward by Deslandres and referred to later on, that absorption bands possessing a fine structure are caused by the nuclei of the atoms of the molecule and not by the atoms or by the molecule itself.

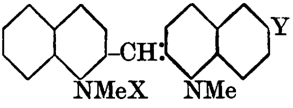
Part III. Stieglitz's Theory.

Stieglitz, on the contrary, believes with me that there is a connexion between colour and chemical structure or constitution. He has put forward a geometrical theory of the same character as mine (Franklin Institute Centenary Address, 17th September, 1924; *Proc. Amer. Chem. Soc.*, 1920, **43**, 36), but differing fundamentally in that an electron orbit is assumed round *one* atom, but disturbed by the proximity of a second positive centre. The orbit, according to Stieglitz, is not an ellipse round the two positive centres, but is a Cassinian oval round *one* of them, apparently exactly as in Morgan's theory of combination, the electrons being never sufficiently disturbed to become governed by two nuclei (see *Chem. and Industry*, 1924, 1071). A diagram is given there which in my opinion explains the whole subject, not only of chemical combination, but also of absorption and colour. The inner Cassinian ovals (3 in number in Morgan's figure) represent some of the Bohr orbits as disturbed (but not seriously altered) by the proximity of a second positive centre; they represent what happens when electrons are affected by radiation when the second positive centre is distant. The outer ellipse, on the other hand, is the orbit suggested by the present author to explain colour and involves a comparative proximity of two ionised positive nuclei, so that the electron is completely displaced from one and can go round both. An intermediate stage is shown by the permanganate, uranyl, uranous, neodymium, erbium, and praseodymium ions, in which rhythmically related bands occur, but no fine structure in the bands. This is just possibly connected with the intermediate lemniscate orbit.

Stieglitz's theory has not yet had its mathematics worked out and therefore cannot be tested quantitatively against my own, but he produces one case which is inconsistent with my theory (and also inconsistent with the theory of tautomerism), *viz.*, the existence of two distinct dimethylmurexides, one of which is alloxandimethyluramilazomethine and the other dimethylalloxanuramilazomethine. Similarly, on Stieglitz's theory there should be two isomeric forms of every unsymmetrical cyanine, for example,



and



In Stieglitz's theory, which is founded on the general principle of $\alpha\gamma$-tautomerism, the carbon atom adjoining but outside a double bond is the one round which the perturbed oval orbit is performed by an electron; and the other positive centre is the farthest-away atom of the doubly bonded pair.

Stieglitz's theory gives a better explanation than mine of such problems as the colour of nitrosobenzene, sodium-benzophenone, and other metal-ketyls, and Wieland's substances with bivalent and quadrivalent nitrogen.

Part IV. Deslandres's Theory.

H. Deslandres propounds a law among infra-red absorptions of simple substances whereby they are all connected together, whatever the observed substance may be. He expresses it (*Compt. rend.*, 18 May, 29 June, 17 Aug., and 28 Sept., 1925) in the form $\nu = d_1q/rs$, in which d_1 is a universal constant or frequency ($1062\frac{1}{2}$ vibrations per cm.), q is the harmonic number of the particular band, r is the number of " octets " in the compound, one being assigned to each hydrogen,* and s is a vulgar fraction (*usually greater than unity*), the value of which is irregular and has not yet been connected with the chemical constitution either of the molecule or of its atoms.

Deslandres's formula can of course be also written: $\lambda = krs/q$, in which q, r, and s are as just defined, but $k = 9412$ $\mu\mu$ when λ is expressed in $\mu\mu$.

Deslandres ascribes the origin of his universal constant to vibration of the α-particle contained in all higher atomic nuclei.

This vibration in the nucleus is supposedly synchronous with the irregular motion of the electron in the ovoid orbit suggested by Morgan (see p. 1820).

I have nevertheless thought it interesting to work out what the values of the vulgar fraction are in the compounds discussed at the beginning of the paper.

In constructing the following table the total variation of the constant has been kept less than $\pm \frac{1}{2}\%$, so as to fix the vulgar fraction. The vulgar fractions resulting are *wholly erratic and disconnected*, and therefore have no real existence.

Benzene gives $\nu = 1066/12 \times 100/9 \times$ (harmonics, *viz.*, 6, 33, 34, 35, 36 . . . 39) for the brighter bands and $\nu = 1062\frac{1}{2}/12 \times 100/9 \times$ (harmonics) for the satellites. Here 12 is the value of r; and the vulgar fraction s is 9/100. Henri's vapour-absorption results (*J. Phys. Radium*, 1922, 181) give the fraction as 12/125.

Pyridine gives $\nu = 1066/11 \times 5/3 \times$ (harmonics). Here 11 is the value of r and the vulgar fraction is 3/5.

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* *E.g.*, five, not one, in methane : three in water, four in hydrogen sulphide and five in carbon disulphide.

Anthracene gives two alternative results, *viz.*,
(*a*) $\nu = 1066\tfrac{1}{2}/24 \times 9/8 \times$ (harmonics from 53 to 82), or
(*b*) $\nu = 1060/24 \times 10/3 \times$ (harmonics from 18 to 22); plus
$\nu = 1065{\cdot}3/24 \times 16/5 \times$ (harmonics from 19 to 24).
Naphthalene gives $\nu = 1064/18 \times 14/9 \times$ (harmonics from 34).
Anthraquinone gives $\nu = 1064\tfrac{1}{2}/24 \times 50/11 \times$ (harmonics from 12).
Dihydroanthracene gives $\nu = 1061/26 \times 35/4 \times$ (harmonics from 7).
Anthranol gives $\nu = 1064\tfrac{1}{2}/25 \times 29/14 \times$ (harmonics from 29).
1-*Anthrol* gives $\nu = 1067/25 \times 23/15 \times$ (harmonics from 36).
2-*Anthrol* gives $\nu = 1066/25 \times 35/8 \times$ (harmonics from 14).
Anthraquinol gives $\nu = 1066/26 \times 60/17 \times$ (harmonics from 11).
2-*Hydroxy*-9-*anthranol* gives $\nu = 1067/26 \times 16/5 \times$ (harmonics from 16).
3-*Hydroxy*-9-*anthranol* gives $\nu = 1063/26 \times 3/1 \times$ (harmonics from 16).
Naphthazarin gives $\nu = 1064/20 \times 38/15 \times$ (harmonics from 12).
Alizarin gives $\nu = 1060/26 \times 5/3 \times$ (harmonics from 23).
Quinizarin gives $\nu = 1065/26 \times 4/1 \times$ (harmonics from 10).
Anthrarufin gives $\nu = 1064/26 \times 11/9 \times$ (harmonics from 35).
Rufol gives $\nu = 1062\tfrac{1}{2}/26 \times 11/7 \times$ (harmonics from 36).
Flavol gives $\nu = 1060/26 \times 40/9 \times$ (harmonics from 14).
2 : 7-*Dihydroxyanthracene* gives $\nu = 1065/26 \times 16/11 \times$ (harmonics from 41).
1 : 5-*Dihydroxyanthranol* gives $\nu = 1064\tfrac{1}{2}/27 \times 32/7 \times$ (harmonics from 13).
2-*Hydroxyanthraquinone* gives $\nu = 1065\tfrac{1}{2}/25 \times 25/13 \times$ (harmonics from 24).
2 : 6-*Dihydroxynaphthalene* gives $\nu = 1070/20 \times 5/2 \times$ (harmonics from 21).
1-*Hydroxyanthraquinone* gives $\nu = 1066\tfrac{1}{2}/25 \times 12/5 \times$ (harmonics from 19).

For comparison, Deslandres's results for simple compounds have been recalculated to the same basis, and the vulgar fractions come out quite simple and to some extent interconnected, namely, from $\frac{1}{12}$ to $\frac{1}{2}$.

The inference to be drawn from these considerations is that the absorptions of complex organic substances cannot be correlated with sub-atomic constants in the same way as the absorptions of simple substances.

The absorptions of complex and unsymmetrical substances, whilst no doubt *accompanied* by absorptions due to the valency electrons and the nuclei of the atoms, are therefore essentially molecular. These absorptions arise from the relative positions of the unsaturated atoms in the molecule (N, O, S, along with the group C : C), and will in course of time be fully and quantitatively explained either by Stieglitz's theory or my own.

Deslandres's theory and the harmonic part of the theory given in the British Association Report can be incorporated in mine by supposing that the constant 112 in my equation (connecting λ and molecular distance) is proportional to Deslandres's ratio $10^7 . r/1062\tfrac{1}{2}q$ (r = number of octets, q = harmonic number when the band is not the fundamental). Deslandres's quantity s is then no longer a whole number or vulgar fraction, but is a function of a molecular distance of the form $a^{3/2}f(e)$, as given in Part I of this series (J., 1924, **125**, 1137).

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