CLXXV.—*Observations on Chemical Structure and those Physical Properties on which the Theory of Colour is based.*

By WALTER NOEL HARTLEY, D.Sc., F.R.S.

ARISING out of the foregoing communication on the ureides and murexide, and also several contributions to the Society's Transactions (Trans., 1881, **39**, 153 ; 1882, **41**, 45 ; 1885, **47**, 685 ; 1887, **51**, 153 ; and 1888, **53**, 641) made in previous years, there are numerous

observations which, taken in conjunction with those of other workers (Graebe and Liebermann, *Ber.*, 1867, 1, 104 ; H. E. Armstrong, *Proc.*, 1888, 4, 27 ; 1892, 8, 101, 189, and 194 ; 1893, 9, 52 and 206), tend to elucidate the origin of colour in organic compounds. Coloured compounds and dyes are derived from substances which are invisibly coloured, that is to say, those which exert a powerful selective absorption in the ultra-violet. This absorption property is to be considered as the basis of all colour, and it depends on structural constitution.

It has been explained as being an effect due to the motion of the molecules and to corresponding vibrations resulting within the molecules synchronising with those of the rays absorbed. In connection with chemical constitution, it was pointed out that dyes are derived from endothermic compounds (*Trans.*, 1893, 63, 243).

A particular form of constitution, namely, that of quinone, is advocated as the cause of colour in aromatic compounds by Nietzsche, (*Chemie der organischen Farbstoffe*, Berlin, 1888), H. E. Armstrong, A. G. Green, and more recently by A. Baeyer and Villiger (*Ber.*, 1904, 37, 2848). We have, furthermore (*Ber.*, 1876, 9, 522 ; *Journ. Chem. Soc.*, 1876, 403 ; *Trans.*, 1879, 35, 179 and 356), Otto Witt's theory of chromophores in dyes.

In all these cases structural similarities and differences are made to account for the advent of colour and the conversion of a coloured into a colourless substance.

Certain unsaturated ketones have also been recognised as containing the following chromophoric groups :

(1) $\text{CO}\cdot\text{C}:\text{C}\cdot\text{C}:\text{C}$	(2) $\text{CO}\cdot\text{CO}\cdot\text{C}:\text{C}$
(3) $\text{C}:\text{C}\cdot\text{CO}\cdot\text{C}:\text{C}$	(4) $\text{CO}\cdot\text{C}:\text{C}\cdot\text{CO}$

It was shown by Wallach (*Chem. Centr.*, 1897, i, 373—374 ; also *Abstr.*, 1897, i, 194) that the introduction of an ethylenic linking adjacent to a carbonyl group produces a greater absorptive power for the violet rays in a derivative than that possessed by the parent substance, and hence the substance is green or yellow. If the carbon atoms on *both* sides of the $\text{C}:\text{O}$ group are attached to the rest of the molecule by ethylenic linkings, a still more powerful absorption is exhibited. Kostanecki and Rossbach, and R. Haller and Kostanecki (*Ber.*, 1897, 30, 2947), also Kesselkaul and Kostanecki (*Abstr.*, 1896, i, 606), Friedländer and Löwy (*Abstr.*, 1897, i, 32), have made important observations on this subject.

It has been pointed out that the chromophores (1) and (2) contain the same atomic groupings as *o*-quinones, and that (3) and (4) have the same configuration as *p*-quinones.

The unsaturated ketones $R \cdot C : O \cdot CH : C \cdot R'$ contain the chromophores $C : O$ and $C : C$, as, for instance, benzylideneacetophenone,

The two quinones contain the chromophores of the unsaturated ketones twice in their ring structure, as is indicated by the dividing diagonal lines in each of the above formulæ.

In these instances it is not the ketonic grouping, but the ketonic linked either directly or indirectly with an ethylenic grouping which constitutes the chromophore; if it were otherwise, then diketohexamethylene or a substance such as alloxan would exhibit spectra with absorption bands, but they do not (Hartley and Dobbie, *Trans.*, 1898, 73, 593).

According to Witt, that which contains only a chromophore is a chromogen, but a chromogen may be a substance which absorbs rays either in the visible or ultra-violet, such as, in the former, azobenzene, and in the latter benzene, from which the properties of a dye are developed by a chromophore of an acid or basic character. Among the best examples which illustrate the nature of a chromophore and the production of a dye from a chromogen, with a further alteration in depth of shade depending on the position of the auxochrome, are the six isomeric monohydroxybenzylideneacetophenones (oxychalkones) of Kostanecki and Tambor (*Ber.*, 1899, 32, ii, 1921). In these compounds the two benzene rings are to be regarded as the chromogens; they are linked by a ketoethylenic group, $CO \cdot CH : CH$, the chromophore, and the shade of colour is varied according to the position of the auxochrome (OH) in relation to the ketonic linking. Another example is afforded by the blue dye described by Piloty (*Annalen*, 1904, 333, 36), obtained from dimethyl-*p*-phenylenediamine as the chromogen, with the oximinoketone ring, alloxan, as the chromophore. The ethylenic linkings are contained in the chromogen, the ketonic in the chromophore. A remarkable example is the production of murexide by the union of alloxan and uramil where the ethylenic linking results from the condensation of the two molecules.

By the systematic study of absorption spectra can we alone obtain

the necessary accumulation of facts which may enable us to arrive at a just conclusion as to the origin of colour. That a ring structure is involved and that the mode of linking of the components of the ring, whether it be homocyclic or heterocyclic, is of importance has been proved in the large majority of instances.

Baly and Desch (Trans., 1904, 85, 1029) account for an absorption band in the ultra-violet spectrum of acetylacetone and its aluminium derivative by the occurrence of isodynamic changes in the substance; ethyl acetoacetate shows no band, but its aluminium derivative shows a strong band almost identical with that of acetylacetone. The difference between acetylacetone and ethyl acetoacetate is that there are two ketonic ($C:O$) groups which may become enolic in the former, and only one in the latter. The enolic groupings would thus leave two ethylenic linkings ($C:C$) in the former and but one in the latter. These compounds contain the chromophore of the unsaturated ketones.

The aluminium compounds of acetylacetone and of ethyl acetoacetate both show a similar absorption band, but ethyl acetoacetate itself shows none. This recalls the action of alkalis and alkaline earths, which in many cases develop colour.

The following theory of colour has recently been put forward by Jules Schmiedlin (*Compt. rend.*, 1904, 139, 872). A true colouring matter or dye contains an endothermic group which is the cause of the colour, but the colour is rendered permanent by a particular arrangement of the molecule in which auxochromic and exothermic groups take part.

In other words, a colouring matter is characterised by a molecule containing a strongly exothermic group (the auxochrome), which by means of a particular arrangement at another part of the molecule excites the formation of an endothermic group (the chromophore); this contains ethylenic bonds which admit of a part of the molecule vibrating in response to synchronous luminous vibrations, which act as the motive power. The essential point is the characteristic dualism of the molecule of the colouring matter, which contains two very different groups endowed with very different quantities of energy. Schmiedlin adds a note to the effect that Helmholtz* in developing Sellmayer's theory of anomalous dispersion found it necessary to explain absorption phenomena by the introduction of the following hypothesis. It is necessary to admit, what perhaps does not entirely correspond with reality, that there are heavy central masses in the molecule which remain immovable, and that the mobile part of the molecule tends to maintain a position of equilibrium opposite to these fixed masses and

* H. Helmholtz, "Zur Theorie der anomalen Dispersion," *Ann. der Phys.*, 1875, 154, 582.

opposite to the ether. When there is absorption, the kinetic energy of the undulatory movement is transformed into an irregular internal vibration, that is to say, into heat, by a process resembling friction, and there is reason to admit on that account a force similar to friction between the mobile part and the fixed part of each molecule. Schmiedlin remarks that these purely physical considerations require a dualism of the molecule, and if, starting from another quarter, by chemical and thermochemical experiments it has been thus established that a dualism also characterises the molecule of a colouring matter, it is reasonable to draw the conclusion that the endothermic and exothermic systems established experimentally correspond to the fixed part and the mobile part in the theory of Helmholtz.

This view is certainly in agreement with the facts already observed, and particularly with the observation made by Hantzsch that stable coloured salts are formed from pseudo-acids by the action of alkalis and hydroxides, but not by the heavy metals. Now the former are strongly exothermic, but the latter are only feebly so, and it may be that herein lies the reason for their inability to produce coloured salts.

In some of the ketonic substances, for example, the oxypurins, there are CO groups which are exothermic and others, such as :CH groups which are endothermic; this also agrees with Schmiedlin's view, but colour is developed by the addition of an exothermic base. The view of dynamic isomerism or change of structure from one form to another should, if sound, be applicable with equal facility to an explanation of the occurrence of six bands in the spectrum of benzene, four in that of naphthalene, and four in anthracene. There is little difficulty about that if we accept the view of the constitution of benzene as propounded by Kekulé, with his explanation, not generally accepted by chemists, of the reason why a 1:2-compound has the same properties, or is identical with a 1:6-derivative. This was explained by the change from a single to a double linking between the six carbon atoms in the ring, which change was supposed to be continually in operation. Let us suppose that the alterations in the double and single linkings pass by a vibratory motion regularly from the first to the sixth position in the direction of the hands of a clock, then we may imagine the following successive phases in six different periods, and the mean of these is best represented by the centric formula, because the changes in the linking of the contiguous carbon atoms gives six different alternate modes of linking in all, and these may be likened to a number of alternate compressions and extensions round an elastic ring at six different points, symmetrically arranged, which may be supposed to operate upon the ether. The aggregate effect would be like a resolution of these forces into a change of direction operating internally, as may be understood by the following diagrams, and there would still be perfect symmetry

in the ring. In this way the symbol of Kekulé and that of Armstrong and von Baeyer are brought into harmony.

Let us see how this stands in relation to the quinonoid constitution.

If we assume that in quinone the alternation in double linking of the carbon atoms, similar to that which is conceived to be the cause of the bands in benzene, is not suppressed but still continues, then the extraordinarily vigorous absorption, which is a highly characteristic feature of the spectrum of this substance, is easily accounted for, and equally also its energetic oxidising properties.

Thus, we may have the isodynamic forms :

or phases in successive periods of time, of which I and IV, being symmetrical, are identical in every respect, and of which II and III are identical in character and in relation to chemical properties, but specifically different. The phases II and III will occur twice as often as phase I. But the molecule as a whole is not symmetrical, because the carbons in the *para*-position are loaded by the oxygen atoms, and this will not only affect their mode of vibration, but also endow them with the active chemical properties which are characteristic of peroxides. This alteration in the mode of vibration may be taken as accounting for there not being six bands but only two in the spectrum of quinone. It is a feature of the quinone spectrum that one of the bands is much more persistent or powerful than the other, and it is, furthermore, in the position of rays of greater oscillation-frequency, and as there are two distinct phases, I and IV being similar or identical and II and III being similar to each other, but not identical, and different from I and IV, the one band may be considered to belong to the one phase and the other band to the other phase or phases. As the phases

II and III are those which indicate the greatest chemical activity and occur twice as often as phase I, the effect is to cause a preponderance in the chemical properties belonging to these phases.

Then, again, as it has been pointed out, the absorption properties of quinone are those associated with the benzene ring, and different from those of a partially reduced ring, and, as in the phases II and III the linking of the carbon atoms is the same as in the benzene ring, we have that which can account for the absorption spectra of quinone and benzene being similar. This is particularly the case when we consider that the physical property of absorbing the rays of the spectrum is greatly intensified in quinone, and that there are only three phases in quinone, and that two of these occur twice as often as the first, whilst in benzene there are six phases, each occurring regularly and symmetrically in unit of time. That this is so is shown by the oscillation-frequencies of the absorbed rays in benzene being disposed at regular intervals throughout a definite region of the spectrum.

The majority of aromatic derivatives in which only one benzene ring is involved show but one absorption band. We have also the instance of triphenylmethane with one broad band.

In such cases, the symmetry of the ring is destroyed and the intramolecular vibrations are irregular, and from the irregularity of the

motion the bands are fused into one, as if the alternations in the linkings were not successively six but only two, as represented in the formulæ I and II of phenol.

The molecules of naphthalene and anthracene exhibit absorption spectra, when their solutions are examined, which have four bands only. This may be accounted for by the carbon atoms common to the two rings being incapable of alteration, because they are in their mode of

linking as closely connected to each other and to the adjacent carbon

atoms as possible, or, in other words, they have undergone the maximum of condensation. The first phase would then be as above, the second,

and the fifth would be the same as the first ; or we may suppose that, as the changes can affect only four carbon atoms in each of the rings these changes occur in the two rings simultaneously. In anthracene also, these carbon atoms which link the two benzene nuclei have no possibility of

change, neither have the carbon atoms in the benzene nuclei to which they are united, hence there can be only four changes in each ring, and as these may act simultaneously it is possible that this may account for there being only four bands.

If we take into account the relation of the isodynamic forms of nitrosophenol to quinone, we have the following :

The change from β to γ would result in conditions approaching the constitution existing in a.

The isodynamic phases of benzene can be equally applied to heterocyclic rings :

Isodynamic phases of benzene.

Isodynamic phases of pyridine.

Isodynamic phases of pyrazine.

Having shown how the change in the mode of linking of contiguous carbon atoms in a ring structure may account for the bands of absorption, it is incumbent on one to show how the hydro-aromatic derivatives cannot acquire this property.

For instance, there cannot be two such phases in dihydrobenzene,

diketoexamethylene,

or in piperidine,

It is unnecessary to multiply examples.

I think, however, I have now shown that Kekulé's view of the constitution of benzene affords an explanation of the absorption bands in its spectrum. The condensation of the carbon atoms (usually designated double and treble linking) at different points in the molecule must give rise to greater refractive and dispersive powers at those points, as we know, from the researches of Gladstone and of Brühl, they do in the whole molecule, and just as they also increase the actinic absorption. If these condensations and expansions (alternate double and single linkings) in the molecule of benzene are continually in progress, it may be possible to explain how colour may result therefrom when light agitates the molecule.

ROYAL COLLEGE OF SCIENCE,
STEPHEN'S GREEN,
DUBLIN.