anthraquinone, phenylacetic acid and *p*-nitrobenzoic acid.

2. The validity of ultraviolet spectrophotometry as a method of measuring ionization has been demonstrated for a carboxylic acid and a phenol, and for an oxygen and a nitrogen base.

3. Mathematical methods have been devised for taking into account the effect of changing solvent in measuring the strength of very weak bases.

4. Criteria have been established for the choice of indicators to be used in changing media.

5. The strengths of the following very weak bases have been measured: acetophenone, benzoic acid and phenylacetic acid.

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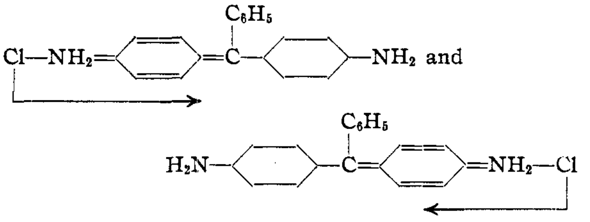
[CONTRIBUTION FROM EDWARD DAVIES CHEMICAL LABORATORIES, UNIVERSITY COLLEGE OF WALES]

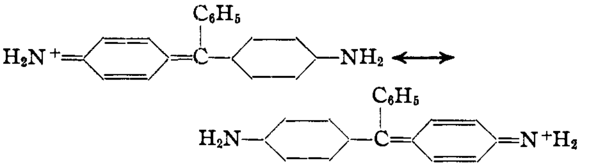
Auxochromes and Resonance

BY C. R. BURY

Baeyer[1] suggested that the color of the triphenylmethane dyes was due to the oscillation of an atom in the molecule. Döbner's violet (the hydrochloride of *p*,*p*-diaminotriphenylcarbinol) was considered to be in a state of oscillation between the two forms



Now that the distinction between electrovalent and covalent bonds is known, it is clear that the oscillation is purely structural

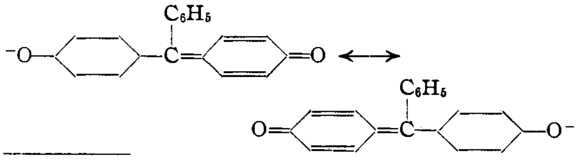


since change from one form to the other involves movement of electrons only, but no movement of atoms. Further, such an oscillation is to be expected: it is merely an example of resonance. Baeyer's hypothesis can be restated in terms of modern theory as follows. The intense absorption of light that characterizes dyes is due to an intimate association of a chromophore and of resonance in the molecule.

There is much indirect evidence that this hypothesis is true, not only for the triphenylmethane dyes, but also for most of the best investigated types of dyes. In particular, it gives some explanation of the function of an auxochrome. Willstätter and Piccard[2] called attention to the fact that certain simple compounds containing the quinonoid group were colorless, or very feebly colored: the development of color in these compounds depends on the introduction of certain substituent groups—auxochromes. In the light of the hypothesis put forward, the function of the auxochrome is to introduce the possibility of resonance. (Auxochromes also facilitate the attachment of the dye to the fabric, but this aspect is not considered further here.)

The hypothesis enables one to understand what groups can act as chromophores and what positions they must occupy. Thus, fuchsonimine $HN{=}C_6H_4{=}C{-}(C_6H_5)_2$ is colorless, though it contains the same chromophore as Döbner's violet. Introduction of an amino group in the *p*-position results in the development of color and the possibility of resonance. Other substituent groups are ineffective in producing color, though they may alter the shade of color of a dye that already contains an amino group. The amino group may be alkylated ($-NR_2$), but conversion to a trialkyl substituted group ($-N^+R_3$) renders resonance impossible and is found in practice to render it ineffective. The destruction of the color of methyl violet and similar dyes by excess concentrated acid can be attributed to the same change.

The color of the hydroxytriphenylmethane dyes is associated with a similar resonance, *e. g.*, the anion of benzaurin.



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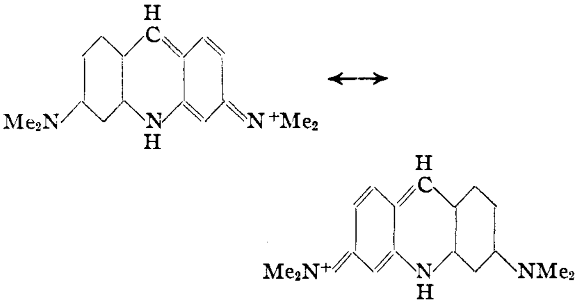
[1] Baeyer, *Ann.*, **354**, 152 (1907).

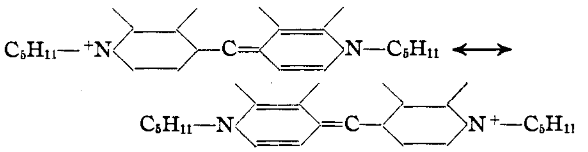
[2] Willstätter and Piccard, *Ber.*, **41**, 1458 (1908).

The hypothesis demands that the color of phenolphthalein in alkaline solution should be due to a dibasic ion, though most textbooks continue to attribute the color to a monobasic ion, which is adequate to explain the color on the usual theory, but is contrary to all experimental evidence.[3]

Resonance similar to that of the triphenylmethane dyes must also occur in the diphenylmethane dyes, the indamines, indophenols and auramines, and again in a group of dyes in which the two benzene nuclei are joined by a second bridge, such as the acridine, pyronine, azine, oxyazine and thiazine dyes. For instance, the colored cation of acridine orange can be represented.

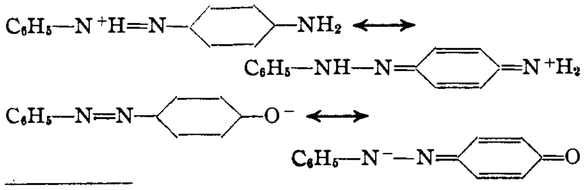


A closely related type of resonance is probable in the cyanines



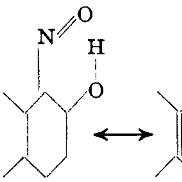
Mills and Ordish[4] have proposed tautomeric formulas, that are identical in principle with the resonance formulas of this paper, for the apocyanines.

Turning to a different type of dye, the azo dyes, it is well known that most molecules that contain the azo group are colored, but their color is feeble compared with that of the azo dyes; compare, for example, the color of methyl orange in alkaline solution with its color in acid. The resonance of this type of dye can be illustrated by formulas of the cation of aminoazobenzene and the anion of hydroxyazobenzene.

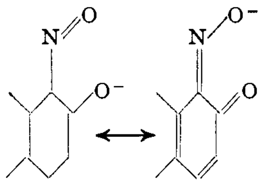


In support of these formulas is the fact that some syntheses and reactions of hydroxyazobenzenes suggest that they are really quinone phenylhydrazones. The change azo compound to hydrazone obviously occurs readily, but must be a slow reaction since it involves movement of a hydrogen atom. Change of the corresponding ions is, however, a purely structural change that involves no movement of atoms; the ions, therefore, may be expected to be in a state of resonance. Again, Hantzsch and Hilscher[5] have shown that the hydrogen ion introduced on formation of a salt of an aminoazobenzene is not attached to the amino group, but is probably in the position required by the above formula. Lastly, the hypothesis gives an explanation of the function of the auxochrome amino and hydroxy groups, and enables one to predict what substituent groups can act as chromophores, and what positions they must occupy. As with the triphenylmethane dyes, conversion of an amino group to a trialkylated group renders it ineffective.

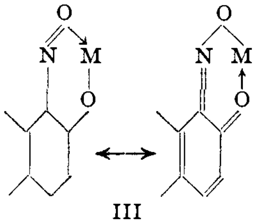
A third important type of dye is the mordant or lake type, of which α-nitroso-β-napthol is a simple example. This type differs from previous examples in that the same resonance can persist in the neutral molecule I, in the ion II, and in the coördinate compound III which is the basis of the lakes.[6]



I



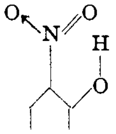
II



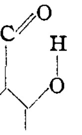
III

Similar groups that can exhibit a similar resonance are IV, V and VI.

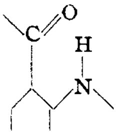
IV



V



VI



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(3) Green and Perkin, *J. Chem. Soc.*, **85**, 398 (1904); Green and King, *Ber.*, **40**, 3724 (1907); Meyer and Spengler, *ibid.*, **38**, 1318 (1905); Kober and Marshall, This Journal, **33**, 59 (1911).

(4) Mills and Ordish, *J. Chem. Soc.*, 81 (1928).

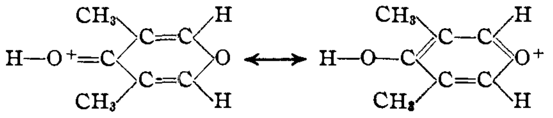
(5) Hantzsch and Hilscher, *Ber.*, **41**, 1171 (1908).

(6) Morgan and Smith, *J. Chem. Soc.*, **119**, 704 (1921).

The physical properties of such *o*-disubstituted benzene derivatives are abnormal[7] compared with those of the corresponding *m*- and *p*-derivatives in such a way as to indicate that the *o*-substituents unite to form a second ring, a behavior that can only be explained by resonance.[8] Again, *o*-quinone monoximes are indistinguishable from *o*-nitrosophenols. With similar *p*-substituted compounds, resonance is restricted to the ion. Thus *p*-nitrophenol gives an intensely colored ion in alkaline solution, but is colorless in acid and in the solid state, whereas *o*-nitrophenol is colored in all conditions. The nitro dyes contain group IV, and the two most important types of mordant dyes, the hydroxyanthraquinones and the flavones, contain group V.

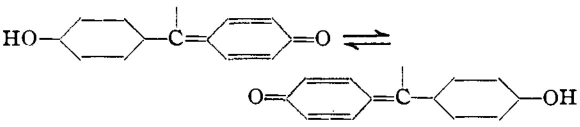
Some of the vat dyes contain similar groups and may be expected to exhibit similar resonance. Thus, alizarin yellow (gallacetophenone), which is probably the simplest vat dye, contains group V, and the side chain derivatives of anthraquinone that are vat dyes, and indanthrene, contain group VI.

An interesting benzenoid–quinonoid type of resonance can occur in the dimethylpyronium ion.



This type of resonance was detected in dimethylpyrone by Sutton[9] from dipole measurements. The same grouping occurs in the flavones.

It is probable that more than one type of resonance is at work in the more complex dyes: thus two types of resonance have been postulated for the flavones. It is improbable, however, that resonance is extremely complex or the simple treatment applied above would be valueless. This implies that only resonance between states of nearly equal energy, or "complete" resonance, is effective in determining the structure that a molecule must have in order that it may be a dye.



There must, however, be more possibilities of resonance in the solid state than there are in solution. Thus, the change involves movement of a hydrogen atom, and therefore cannot produce resonance. A similar change that does not involve movement of a hydrogen atom can, however, take place between suitably placed molecules in the solid state. This may account for the fact that rosolic acid is intensely colored in the solid state though it is colorless in neutral solution, but is given merely as an example of a phenomenon that must be expected frequently with dyes in the solid or in the colloidal state. Quinhydrone, the crystal structure of which has been elucidated by Foz and Palacios,[10] provides an example of exchange of hydrogen atoms between neighboring molecules in the solid state that involves no movement in space. The intense color of this compound may be attributed to the conjunction of resonance and of the chromophore in quinone.

The simple modes of resonance discussed above are sufficient to explain the phenomenon of auxochromes in the majority of the most thoroughly investigated dyes. Other probable modes can be devised for most other dyes the structure and reactions of which are known with any certainty; only the indigo dyes present any difficulty.

ABERYSTWYTH, WALES

RECEIVED AUGUST 8, 1935

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[7] Sidgwick and Callow, *J. Chem. Soc.*, **125**, 527 (1924).

[8] Sidgwick, *Ann. Reports*, **31**, 37 (1934).

[9] Sutton, *Trans. Faraday Soc.*, **30**, 789 (1934).

[10] Foz and Palacios, *Anal. soc. españ. fís. quím.*, **30**, 421 (1932).