15. On 5-amino-4-ketodihydroquinazolines and 5-amino-2-methyl-4-ketodihydroquinazolines. M. T. Bogert and V. J. Chambers, *Ibid.*, **28**, 207.

16. On the condensation of succinylosuccinic esters with amidines. M. T. Bogert and A. W. Dox, *Ibid.*, **28**, 398.

17. On a 3-aminoquinazoline and the corresponding 3,3'-diquinazolyl, from 6-nitro acetanthranil and hydrazine hydrate. M. T. Bogert and H. A. Seil, *Ibid.*, **28**, 884.

18. Synthesis of 6-nitro-2-methyl-4-ketodihydroquinazolines from 5-nitro acetanthranil and primary amines. M. T. Bogert and E. P. Cook, *Ibid.*, **28**, 1449.

1907 19. The synthesis of quinazoline carboxylic acids from 4-aminoisophthalic acid and from aminoterephthalic acid.' M. T. Bogert, J. D. Wiggin and J. E. Sinclair, *Ibid.*, **29**, 82.

20. A strange case of poisoning. M. T. Bogert, *Ibid.*, **29**, 239.

21. On 2,3-dialkyl-4-quinazolones and the products obtained by alkylating 2-alkyl-4-quinazolones (2-alkyl-4-hydroxyquinazolines). M. T. Bogert and H. A. Seil, *Ibid.*, **29**, 517.

22. The synthesis of 1,3,6,8-naphthotetrazines from paradiaminoterephthalic acid and from certain of its derivatives. M. T. Bogert and J. M. Nelson, *Ibid.*, **29**, 729.

1908 23. On certain 7-nitro-2-methyl-4-quinazolones from 4-nitroacetanthranil. M. T. Bogert and W. Klaber, *Ibid.*, **30**, 807.

1909 24. 3-Amino-*o*-phthalic acid and certain of its derivatives. M. T. Bogert and F. L. Jouard, *Ibid.*, **31**, 483.

25. On certain quinazoline oxygen ethers of the type —N:C(OR)— and the isomeric —NR.CO— compounds. M. T. Bogert and C. E. May, *Ibid.*, **31**, 507.

26. On some amino and nitroamino derivatives of benzoic, metatoluic and metaphthalic acids. M. T. Bogert and A. H. Kropff, *Ibid.*, **31**, 841.

27. On 2-methyl-3-amino-4-quinazolone and certain of its derivatives. M. T. Bogert and R. A. Gortner, *Ibid.*, **31**, 943.

28. On 6-methyl-7-aminoquinazolones, 7-nitroquinazolone-6-carboxylic acids, and 1,3,7,9-naphthotetrazines. M. T. Bogert and A. H. Kropff, *Ibid.*, **31**, 1071.

1910 29. On oxalyl anthranilic compounds and quinazolines derived therefrom. M. T. Bogert and R. A. Gortner, *Ibid.*, **32**, 119.

HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY,
March 28, 1910.

THE CAUSE OF COLOR IN ORGANIC COMPOUNDS.[1]

BY RICHARD SYDNEY CURTISS.

Received April 16, 1910.

During an investigation in the mesoxalic ester series, I have been led to a study of the causes which underlie the phenomenon of color in some of these very simple aliphatic compounds.[2] In doing so I have found the subject fascinating, and it has seemed to me that it might be of interest to a general audience, in which I assume the great majority are not organic chemists. I shall try to present some of the simpler facts and theories on which our ideas of color cause rest.

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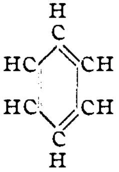
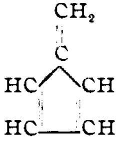
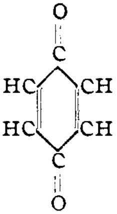
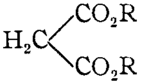
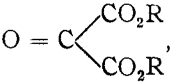
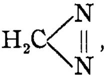
[1] Address of the Chairman of the Division of Organic Chemistry of the American Chemical Society delivered in general session of the Society at Harvard University, December 29, 1909.

[2] Curtiss and Spencer, THIS JOURNAL, **31**, 1033; Curtiss, *Am. Chem. J.*, **35**, 477.

To discuss a subject in an hour, upon which so many thousands of pages of interesting researches have appeared, would be difficult enough, but my task is the harder since our good secretary has limited us to thirty minutes.

In deference to my non-organic friends, I shall try to eliminate, as far as possible, those incomprehensibly long names and formulas, which, while so simple and luminous to us, are always thorns in the flesh to most young chemists.

By a colored substance we all understand one which has the power of retaining or holding back some of the ether vibrations of certain definite wave length of the white light falling on it, the color being the resultant effect of all waves which pass through the substance to the eye. In other words, the color seen is the complement of the color absorbed.

It might be asked, Why is one compound colored and another not? Why is benzene, , colorless while its isomer, fulvene,[1] , like its oxygen derivative quinone, , is yellow? Or again, why is malonic ester,  $H_2C<\begin{smallmatrix}CO_2R\\CO_2R\end{smallmatrix}$, without color and oxomalonic ester,  $O = C<\begin{smallmatrix}CO_2R\\CO_2R\end{smallmatrix}$, green, formaldehyde, $H_2C = O$, colorless, and diazo methane,  $H_2C<\begin{smallmatrix}N\\\|\\N\end{smallmatrix}$, yellow? These are simple cases of color. They all contain an *unsaturated* group of atoms—the ethylene, the carbonyl, the azo groups.

Graebe and Liebermann,[2] who made the first studies of the relation of color to structure, noticed in 1867 that reduction of these unsaturated groups destroyed the color instantly. In the sixties little was known about the constitution of any of the organic colored substances—though, alizarin, purpurin, fuchsin, indigo and others were being investigated. Quinone was the only one whose constitution was known. It was the study of compounds like quinone and azobenzene containing such groups, and their loss of color on reduction, that led Witt[3] to formulate in 1876 his celebrated "chromophore theory." This states that the color in an

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[1] J. Thiele, *Ber.*, **33**, 667; *Ann.*, **348**, 12.

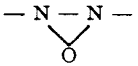
[2] *Ber.*, **1**, 106.

[3] *Ibid.*, **9**, 522–524.

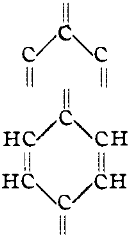
organic compound is caused by the presence of a certain group which he called a *chromophore,* or color-forming group.

Chromophores.

$=C=C=$
$=C=O$
$=C=S$
$-N=O$



$-N=N-$
$-N=C=$
etc.

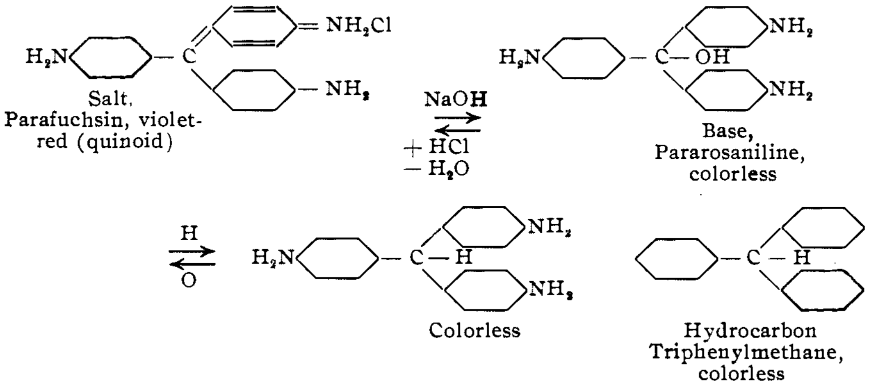


"quinoid form"
Color lost by reduction

Such a colored substance he called a *chromogen.* He also noticed that a colored substance might lack the power of imparting its color to a fabric, and that the presence of an hydroxyl or amine group, both salt-forming groups, usually tended to deepen the color and to cause it to fix to the fiber, that is, to produce a dye. Such groups he called *auxochromes*—and stated that both chromophore and auxochrome groups must be present to produce a *dye.* Witt's color theory has been of great value as a guide in the synthesis of a multitude of colored substances and dyes.

One feature that Graebe and Liebermann, in 1868, considered of fundamental importance for color production was the presence in aromatic chromogens of a quinone group or a quinone-like union of atoms, called also "quinoid form," and it is remarkable that this idea, based as it was at that time on wholly insufficient data, has been, and is even to-day in a modified form, one of the most valuable concepts in our theories of the cause of color.

In 1878–9 the cousins Emil and Otto Fischer,[1] in a series of masterly researches, established the relation of the important dyes, fuchsin and related compounds, to the parent hydrocarbon triphenylmethane and ascribed to parafuchsin a paraquinone structure, though they gave it the peroxide form. The chart shows the simple relation and color changes of this important class of dyes.



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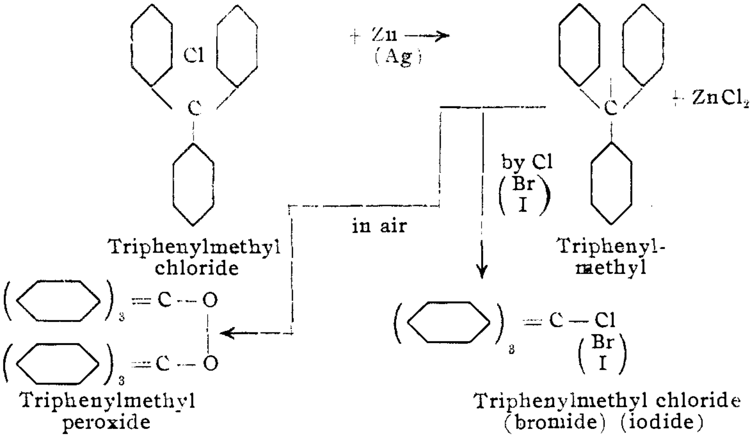
[1] *Ber.*, **12**, 2344.

Such a molecular rearrangement as is shown in this salt formation, accompanied by an intensification of color, we shall note as a very important fact in the study of the causes of color.

The structure of these important dyes being thus settled as quinoid compounds, the color question of triphenylmethane derivatives remained quiescent for twenty years.

In 1900, Professor Gomberg[1] discovered triphenylmethyl, a colorless, crystalline product of the action of zinc on triphenylmethyl chloride in dry benzene, air being excluded during the reaction.



Triphenylmethyl chloride

Triphenylmethyl

Triphenylmethyl peroxide

Triphenylmethyl chloride (bromide) (iodide)

Its behavior is very remarkable. It unites with oxygen of the air to form a peroxide. Chlorine produces triphenylmethyl chloride. Its chloride forms with metallic chlorides colored addition products; with acids it gives colored salts. It even adds neutral substances like benzene and ether. Its great reactivity and apparently unsaturated character led Gomberg to believe that at last the object was attained for which Frankland had sought in vain in the early days of organic chemistry, the preparation of a free methyl radical. In the meantime the trivalency of carbon received an apparent set back when it was discovered that Gomberg's triphenylmethyl had a molecular weight corresponding to hexaphenylethane, $(C_6H_5)_3C{-}C(C_6H_5)_3$. The reactivity and unsaturated nature of this new substance cannot, however, be explained by this formula.

As a result of studies on this substance by Ullmann and Borsum,[2] Heintschel,[3] Chichibabin,[4] Schmidlin, Jacobson,[5] Gomberg,[6] Gomberg and Cone[7] and others, a formula was proposed by Jacobson, which well explains its properties, *when in solution.* This formula (below) shows it as a derivative of quinol. In quinol the CH_3 group easily dissociates, or wanders, to another part of the molecule.

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[1] THIS JOURNAL, **22**, 757; *Ber.*, **33**, 3150.

[2] *Ber.*, **35**, 2877.

[3] *Ibid.*, 36, 320, 579.

[4] *Ibid.*, **37**, 4709.

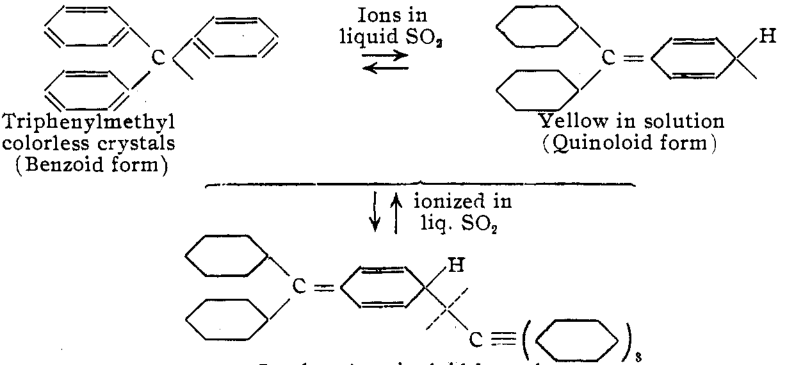
[5] *Ibid.*, **38**, 196.

[6] *Ibid.*, **33**, 3150; THIS JOURNAL, **22**, 757; *Ber.*, **34**, 2726; **35**, 1822, 2018, 2397, 3914; **36**, 376, 3927; **37**, 1626.

[7] *Ibid.*, **37**, 2033, 3538.

When Gomberg's colorless crystalline substance dissolves in liquid sulphur dioxide a yellow color appears (as in all its solvents). This solution, as Walden[1] and also Gomberg and Cone[2] found, conducts electricity as that of an electrolyte. Gomberg[3] believes at the present time that this remarkable substance is, in the colorless crystalline form, triphenylmethyl, containing the methane carbon in the trivalent state, and the three benzene groups in the usual benzoid form.

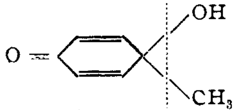
When it dissolves, a tautomeric change occurs, one of the phenyl groups undergoes a molecular rearrangement to a yellow quinoloid form, while all three forms exist in equilibrium, in solution. Only the colorless crystalline form separates out when the yellow solutions are evaporated. These changes of triphenylmethyl are here shown.



Triphenylmethyl
colorless crystals
(Benzoid form)

Yellow in solution
(Quinoloid form)

Jacobson's quinoloid formula
for triphenylmethyl



Quinol

After Gomberg's brilliant discovery in 1900 there followed in rapid succession the announcements by Professor Norris and Mr. Sanders,[4] and later Kehrmann and Wenzel[5] that the colorless triphenylmethyl hydroxide and chloride dissolve in mineral acids giving colored solutions. Norris and Sanders also discovered the first colored double salt of triphenylmethyl, that of aluminium chloride. These were discoveries of fundamental interest for the development of the theories of color. Later Gomberg and Cone[6] discovered a neutral sulphate as a red crystalline compound and many other colored salts of this type. Other colored salts were made by Baeyer[7] and his co-workers. Salts of these types are shown below.

[1] *Z. physik. Chem.*, 43, 443.

[2] *Ber.*, 37, 2045.

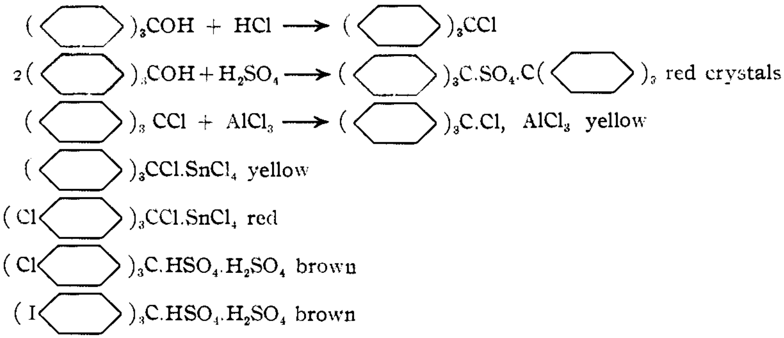
[3] *Ibid.*, 40, 1880–1888.

[4] *Am. Chem. J.*, 25, 54, 117.

[5] *Ber.*, 34, 3815.

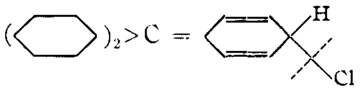
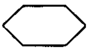
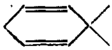
[6] *Ibid.*, 37, 3543, 1626; 35, 1822; 40, 1847, 1872; etc.

[7] *Ibid.*, 38, 569, 1156; 35, 1199.



The old theories of color no longer sufficed. An intense interest was aroused in this whole class of colored derivatives. Baeyer started a very thorough investigation of the entire series of triphenylmethane derivatives, and his work appeared in eleven papers[1] in rapid succession in the *Berichte* and the *Annalen*, from 1902 on.

It is in this field that some of the most interesting color theories, and results, have been worked out.

Why should some of these simple salts of this triphenylmethyl radical be colored and others not? Kehrmann and Wenzel[2] assumed the existence of a colorless, and a colored isomer. The formula ()$_3$C.Cl represents the colorless crystalline chloride, while the structure of the isomeric colored salt (and double salts) containing a quinol chromophore are shown thus:  This last form he considered to be derived from a hydrocarbon, ()$_2$C = , in which a para position carbon is divalent—very reactive—and has *basic properties.* This idea was contained in Professor Norris' work, which had just appeared. Gomberg holds strongly to this view of structure of all such colored salts and has brought out a large amount of experimental evidence to prove the quinol structure as the cause of color in the whole series of colored triphenylmethane derivatives. The idea of basic carbon has since been worked out by Baeyer, in his *carbonium valence theory*[3] and *halochromy.*[4]

Baeyer,[5] however, took exception to the above quinol formula of Kehrmann for these colored salts. He found chlorine not easily removable by silver salts, as is usually the case in a quinol. To explain the color Baeyer[6] assumed, like Kehrmann, Gomberg and others, a colorless non-

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[1] *Ber.*, **35**, 1189, 1754, 3013 (1902); **36**, 2774; **37**, 597, 2848, 3191; **38**, 569, 1156; **40**, 3083; *Ann.*, **354**, 152.

[2] *Ibid.*, **34**, 3818.

[3] *Ber.*, **38**, 572.

[4] *Ibid.*, **35**, 1190, 3014; **38**, 1159.

[5] *Loc. cit.*

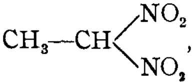
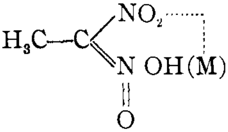
[6] *Ber.*, **38**, 571.

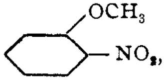
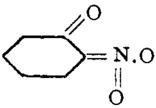
ionizable form, ()$_3$CCl, and in addition an ionizable colored form, ()$_3$C$\sim\sim$Cl. To explain the cause of color in these compounds with identical structure and no chromophore group, Baeyer assumed, in the colored ionizable form, a peculiar difference in the properties of a methane carbon valence. This he indicated by a wavy, ionizing bond and called it the "carbonium valence." Like Kehrmann he considered the methane carbon basic, and to behave in such salt formations as the metal in potassium hydroxide. This property of a colorless carbon compound which contains no chromophore group, forming colored salts, he called *halochromy*. This explanation of color was novel, but not altogether satisfactory.

On the whole we find the chief ideas of the cause of color, as at present held by most chemists, to be, for triphenylmethyl and its two series of colorless and colored salts, first a colorless compound of benzoid structure, second—its molecular rearrangement to a colored form, having a quinone or a quinol structure, this unsaturated quinol ring being the chief cause of the color.

Let us turn to a new field.

The same general causes of color phenomena, namely, the change of a colorless compound into an isomeric colored form by a molecular rearrangement, Hantzsch found to exist in the nitrohydrocarbons, nitroketones,[1] and nitrophenols.

Colorless dinitroethane,[2]  $CH_3—CH<^{NO_2}_{NO_2}$, dissolves in sodium hydroxide with a yellow color. This color Hantzsch supposed to be due to a salt of a compound of a tautomeric form,  $H_3C—C<^{NO_2}_{\overset{}{N(=O)}\,OH(M)}$, which contains a chromophore, and in which there is a union of some sort between the nitro groups.

Such colorless substances which yield colored salts he classed among the *pseudo acids*.[3] This view of changing structure as the cause of color is confirmed by Hedley's[4] spectroscopic studies of nitroparaffins and their salts. After years of work on nitrohydrocarbons, Hantzsch was able to prove this theory. In 1906, Hantzsch and Gorke[5] obtained such isomers, not as metal salts, but as esters of nitrophenols. The formulas show this type, one colorless,  and the other intensely red, . Here at last was the confirmation of his theory of pseudo acids, for these crystal-

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[1] *Ber.*, 40, 1523.

[2] *Ibid.*, 32, 578, 610, 626; 39, 3156; 40, 1533.

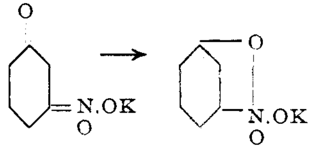
[3] *Ibid.*, 32, 578, 579, 583; 35, 1001.

[4] *Ibid.*, 41, 1195.

[5] *Ibid.*, 39, 1073.

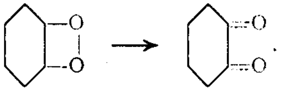
line esters of identical composition and like molecular weight, but differing in color, cannot have the same structure. This discovery was also an important addition to our knowledge of the relation of color to chemical constitution. It also proved[1] the falsity of Oswald's theory[2] that the color of salts of such colorless compounds as phenolphthalein is *primarily* due to the formation of colored ions. Additional proof that such color changes are rather due to a molecular rearrangement has been well given by Hantzsch's[3] work on helianthin and methyl orange, and that of Vorländer[4] Thiele,[5] and Hantzsch and Hilscher[6] on aminoazobenzenes and their two series of colored salts.

Hantzsch and Rosanoff[7] obtained isomeric colored salts of substituted metanitrophenols. One was lemon-yellow and unstable, easily changing into a stable red isomer. The structures have been suggested for these isomeric colored salts, though the question is a complicated one and remains unsettled.



Yellow salt Red salt

The existence of these two forms of metanitrophenol salts suggests the possibility of the existence of metaquinones—as well as two forms of *o*-benzoquinone. The latter were in reality found last year by Willstätter,[8] one labile and colorless, and readily changing to the other stable and colored form.



Colorless labile Yellow stable
orthoquinones.

Hantzsch and his co-workers extended these researches very widely over a period of several years and from a large amount of experimental data drew the following conclusion: All true nitro compounds of the hydrocarbons and derivatives are colorless.[9] The nitro group is *not* a chromophore. Its presence in a molecule only gives color when it interacts with a neighboring group containing a labile hydrogen atom, as the OH or CH group, whereby a tautomeric form is created which contains a chromophore group—yielding colored salts and esters. Kaufmann,[10] however, opposes this theory. Hantzsch makes this of general application in his statement as follows: "Every appearance of, or change of, color of a

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[1] *Ber.*, 39, 1089, 1091.

[2] *Die Wissenschaftliche Grundlagen der analytischen Chemie*, 1894, p. 104.

[3] *Ber.*, 41, 1187, 1193.

[4] *Ibid.*, 36, 1486.

[5] *Ibid.*, 36, 3965.

[6] *Ibid.*, 41, 1171.

[7] *Ibid.*, 39, 1073, 1084; 40, 1535.

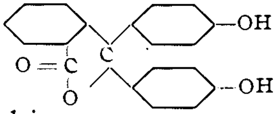
[8] *Ibid.*, 41, 2580.

[9] *Ibid.*, 39, 1084, 1096.

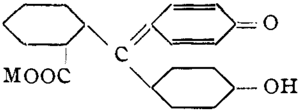
[10] *Ibid.*, 39, 1959, 4237.

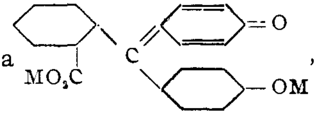
compound in salt formation with colorless metal atoms is to be ascribed to an intramolecular rearrangement." Such a phenomenon as indicated here he calls *chromotropy*, and the isomeric substances, *chromoisomers*.

An interesting application of this chromotropic theory is to those compounds, like phenolphthalein, methyl orange, aminoazobenzene, and others, which rapidly undergo color changes in salt formation in solutions.

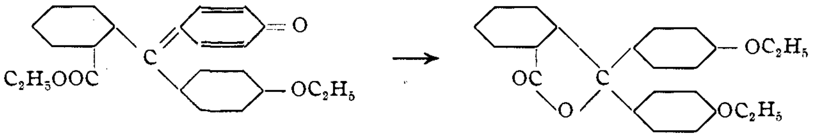
The formula 

shows Baeyer's lactone structure for phenolphthalein.

The well-known violet-red color of a phenolphthalein solution, when alkali is added, was supposed by many to be due to a monobasic salt, 

In 1905 Meyer and Spengler[1] succeeded in separating and analyzing the red salt and found it dibasic, but considered its color due to halochromy. Baeyer[2] who also held this view of color rejected it in 1907, as did also Richard Meyer[3] last July in favor of the quinoid structure and tautomerism in the salts, as a cause of the color in phenolphthalein solutions. This idea had previously been suggested by Stieglitz and Acree.[4] Friedlander[5] had in 1893 assumed the presence of a red dibasic salt and had suggested the formula 

, which contains a quinoid ring, as the cause of color. Richard Meyer and Marx[6] showed, two years ago, that the production of color in colorless phenolphthalein solutions was due to a molecular rearrangement and the formation of a quinoid group. They were not able to show this in the salts, but with the corresponding esters. These they obtained in isomeric form and assigned the following structure to the yellow unstable one, which easily changes over to the colorless stable form, which contains no chromophore group:



Yellow crystals, labile Colorless crystals, stable

In this they indicated the tautomeric character of the change during color formation with phenolphthalein solutions. The color reactions and

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[1] *Ber.*, 38, 1318; 41, 2446.

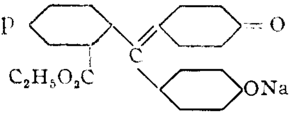
[2] *Ann.*, 354, 152.

[3] *Ber.*, 42, 2832.

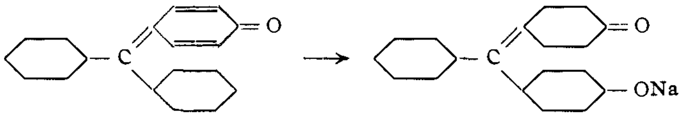
[4] *Am. Chem. J.*, 39, 543, 650 and 651.

[5] *Ber.*, 26, 172.

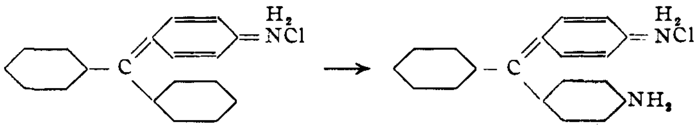
[6] *Ibid.*, 40, 3603.

formation of colored esters in phenolphthalein cannot, however, be fully explained by the mere *presence* of the quinoid ring alone as chromophore. Arthur Green[1] in a recent paper (June last) has called attention to the fact that if, in this yellow quinoid ester, sodium be substituted for the ethyl radical in the phenol group  a very deep violet-red color is produced. This decided deepening of color cannot be due to the sodium atom as such, as it is not a chromophore, but in some way to its interrelation to the neighboring quinoid ring; in other words *the phenol and quinoid groups interact* as a strong chromophore. Such interaction of groups was proposed by Dr. Stieglitz[2] in his quinhydrone theory, to explain color formation, not only in phenolphthalein, but also in the rosanilines, rosolic acids, and eosins. He believed the presence of a quinone and a phenol group gave color by virtue of an intra- or intermolecular condensation, forming quinhydrones, compounds whose salts have intense colors, as we shall soon note below.

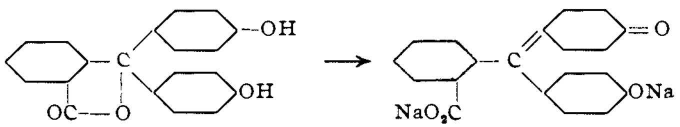
Baeyer[3] has recently discussed similar cases of color intensification. Oxo- and imino-triphenylmethane (the former called fuchsone) are only faintly colored orange, but an intense deepening of color is produced by simply introducing an hydroxyl, and an amine group respectively, in an adjacent phenyl group, and forming salts.



Fuchsone, orange Benzaurin, violet-red



Iminotriphenylmethane (salt), orange Döbner's violet, violet-red



Phenolphthalein, colorless Salt, violet-red

The mere presence of these added groups can neither explain this deep color change, nor the remarkable fact that the red salts have indentical absorption spectra—and therefore, identical color. They are also, in this respect, identical with the red salts of phenolphthalein. This is a very strong argument in favor of like structure in all three compounds. Such similarity of structure is not shown in the above formulas. Baeyer

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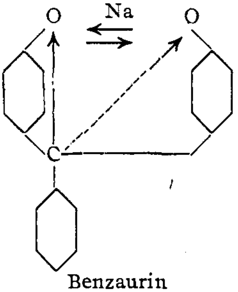
[1] *J. Chem. Ind.*, 28, 638.

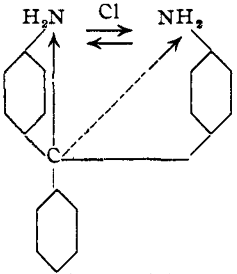
[2] *Am. Chem. J.*, 39, 651, 529, 431.

[3] *Ann.*, 354, 152.

has, however, sought to indicate it[1] by assuming a rapid oscillatory change of the quinoid structure from one ring to the other, involving a corresponding movement of both the sodium or chlorine atom from oxygen to oxygen or nitrogen to nitrogen, respectively—and likewise an oscillation of a carbon to oxygen, or nitrogen, valence, as shown below:



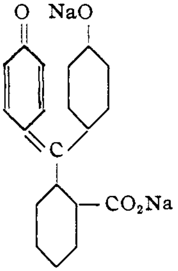
Benzaurin



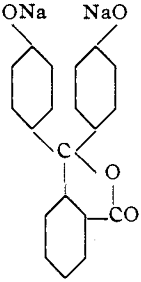
Döbner's violet

An auxochrome group is here shown to act not by its presence only, but by its interrelation or action with the rest of the molecule. This has also been clearly shown by Hantzsch[2] in the colored salts and esters of the colorless nitrophenols.

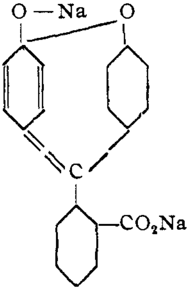
In interesting papers in the *American Chemical Journal* of April, 1908, and July of the present year on the subject of indicators, Acree and Slagle[3] assert that in addition to such quinoid and lactoid dibasic salts of phenolphthalein as shown here,



Quinoid



Lactoid

a third form exists, , to which the color may be largely

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[1] *Ann.*, 354, 152.

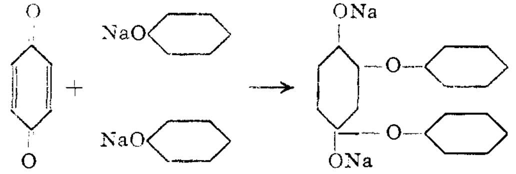
[2] *Ber.*, 39, 1073, 1084; 40, 1535.

[3] *Am. Chem. J.*, 42, 122.

due. They assert all three exist in solution in tautomeric equilibrium and that the cause of the color is probably an inter- or intramolecular change of the various salts into each other such as Acree[1] and his co-workers found to be the case in the urazoles, where they isolated three tautomeric but colorless salts.

The quinhydrone theory of Stieglitz, the recent work of Willstätter and Piccard[2] on Würster's colored salts, that of Baeyer, Richard Meyer, Acree, and others on this subject, are all in general accord in ascribing as a cause of color in this whole class of compounds the interrelation of a phenol (or amine) and a quinoid group.

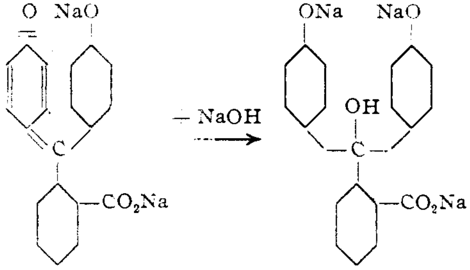
My honored friend Professor C. Loring Jackson, and his co-workers, in their interesting and valuable researches on the quinones, found[3] in 1895 that sodium salts of phenols give with quinone intensely colored addition products, called quinhydrones, to which I have referred above.



Quinone, yellow   Quinhydrone, deep blue

This work has suggested that such a structure as shown in the above third form of phenolphthalein salts of Acree may be a very probable cause of color in the salts of this series. The tautomerism of such a salt is very similar (as a benzaurin carboxylic acid) to that rapid oscillating change of structure suggested by Baeyer in the benzaurin formula above.

The well-known loss of color of a red phenolphthalein solution by excess of alkali has been explained by the hydration of the quinoid ring:



Red   Colorless

Green and King[4] have assumed this structure for all colorless salts of phenolphthalein. Since such salts have not been separated the question remains open.[5]

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[1] *Am. Chem. J.*, 42, 123.

[2] *Ber.*, 41, 1458.

[3] *Am. Chem. J.*, 17, 589; 18, 1.

[4] *J. Chem. Soc.*, 85, 398; *Ber.*, 39, 2365; 40, 3724; also v. Baeyer, *Ann.*, 202, 73; K. Meyer and Hantzsch, *Ber.*, 40, 3481.

[5] Acree, *Am. Chem. J.*, 42, 127.

In summarizing the probable cause of color in all of these classes of compounds, it is noticeable that every colored compound contains within its molecule a series of points of unsaturation, or *double bonds.* It is very important to note that these are also the *points of chemical activity.* They act in conjunction with each other, or with the auxochrome groups, to produce or deepen color. In cases where an extreme change of color is induced, as in salt formations in the rosaniline and phthalein series cited above, and in many other cases, a more powerful chromophore is produced by a *molecular rearrangement.* Further, a rapid *oscillatory change of structure* is assumed in extreme cases of color deepening. The final cause of color cannot be in the mere presence of a chromophore group as Witt supposed, but must be sought in some peculiar dynamic condition of the molecules, or atoms, wherein resides the power to stop or transmit the ether vibrations.

Valuable as are such results as I have discussed, they are, however, insufficient to fully solve this great problem of the cause of color. All the powers of the physicist as well as chemist will be required.

I have considered very incompletely and superficially some of the chemical aspects of this question.

As we all know a colored substance is one which has absorbed ether vibrations of certain definite wave length in the white light falling upon it. The absorption spectrum formed by the light which has passed through such a colored substance therefore has shadows, or dark absorption bands, in the exact position which would be illuminated by these light waves, were they not taken up by the compound. The absorption spectra of very many organic compounds have been quite fully studied, especially by Hartley,[1] of England. He showed that many chemical compounds which, like benzene, appear colorless, absorb wave lengths of a shorter period than those which affect the eye and therefore give absorption bands in the ultraviolet. The form of these bands is characteristic for each pure substance producing them. Thus benzene shows six characteristic dark bands in the ultraviolet. Therefore, to an eye of greater sensitiveness than ours benzene would show color. We must then extend our ideas of color to include compounds like benzene, whose absorption bands in the ultraviolet are only discernible by their actinic effect on the photographic plate. Hartley assumed[2] that there were, within such a molecule—benzene for instance—ntramolecular vibrations, which, when synchronous with ether vibrations of a certain amplitude, destroyed them, and thus caused dark bands to appear in their place in the spectrum of the compound. By introducing into the benzene ring, chromophores like the carbonyl group, these peculiar intramolecular vibrations are slowed down, and the absorption bands in the spectrum are pushed toward the position of longer wave lengths and first become visible in the violet. This brings a yellow color into the compound. Further substitution in the molecule may cause the bands to be moved still further toward the red, with production of a corresponding color in the compound, as shown in the chart.

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[1] See *Kayser's Handbuch d. Spectroscopie, Bd.* III, 149 to 315.

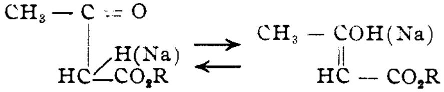
[2] *J. Chem. Soc.*, **39**, 165, 153; **41**, 45; **47**, 685; **51**, 152; **53**, 641; **87**, 1796, 1822.

Absorption bands in	Color of substance is
Ultraviolet	———
Violet	Green-yellow
Indigo	Yellow
Blue	Orange
Blue-green	Red
Green	Purple
Green-yellow	Violet
Yellow	Indigo
Orange	Blue
Red	Green-blue
Purple	Green
Ultrared	———

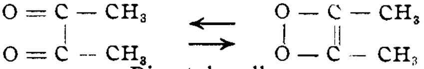
The absorbed color is the complement of the color apparent to eye.

Baeyer's explanation of the intense color caused by salt formation in benzaurin and Döbner's violet as shown in the above formulas is an extension of Hartley's idea of intramolecular vibration and of the idea of isorropesis.

Equally interesting are the researches of Stewart, Baly and Desch.[1] They studied the absorption spectra of many unsaturated compounds, among them tautomeric substances which have a labile hydrogen atom capable of wandering to an adjacent carbon or oxygen atom. Such is acetoacetic ester, and its sodium salt, which have the tautomeric forms:



They found[2] in such compounds, and their tautomeric derivatives, that either form alone had little effect on the spectrum, but when light was passed through a solution in which both were present in tautomeric equilibrium, that characteristic absorption bands appeared. From this they concluded that it is not the fixed structure of a desmotropic molecule which causes absorption, but that it is due to the rapid oscillating change of atomic linking which occurs as a molecule changes from one form over to the other and reverses, which causes vibrations synchronous with certain light waves which thereby become absorbed, giving absorption spectra and consequently color. This rapid oscillating vibration of the valences, when unaccompanied by tautomeric atomic movement, they have called *isorropesis*[3] (equipoise). It can be most simply illustrated in the case of diacetyl or oxomalonic ester, in which the rapid oscillating change of double bonds between adjacent carbonyl groups is shown. It is not supposed that such isomeric forms really exist, but that the formulas represent the *limiting conditions* of such dynamic changes within a molecule of such a colored substance.



$$\begin{array}{c} O=C-CH_3 \\ | \\ O=C-CH_3 \end{array} \rightleftarrows \begin{array}{c} O-C-CH_3 \\ |\quad\| \\ O-C-CH_3 \end{array}$$

Diacetyl, yellow

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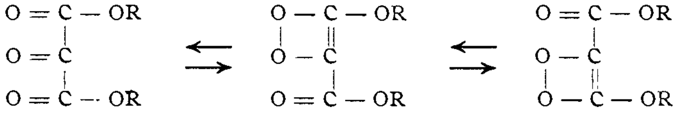
[1] *J. Chem. Soc.*, **85**, 1029; **87**, 766; **89**, 502, 514, 618; **91**, 426, 1572; *Proc. Chem. Soc.*, **22**, 33, 34, 35 (1906).

[2] *J. Chem. Soc.*, **85**, 1029, 1039; **89**, 489.

[3] *Ibid.*, **89**, 498, 513.



Oxomalonic ester, green.

If we consider, then, these interesting optical results in the light of our present ideas of the constitution of the atoms, we should seek the *final* cause of color, in a disturbance of the equilibrium of electrons within the atoms, induced by the breaking of the Faraday tubes of force between the atoms. This is represented by our bonds or valence lines undergoing rapid oscillatory changes as suggested in the formulas above. We might well expect such a disturbed equilibrium to produce or annul ether vibrations of the order of those which produce color, and thus account for the absorption bands in the spectra of numberless organic compounds showing visible as well as invisible color.

UNIVERSITY OF ILLINOIS,
URBANA, ILL.

NOTES.

The Instability of Alloxan.—On returning to the Chemical Laboratory after the summer vacation last year I found that an explosion had taken place in the case of specimens of organic chemicals in the lecture room. A pane of glass was pierced by a round hole as large as my fist and pieces of glass had been forcibly projected against the opposite wall of the room, ten feet from the case. Within the case quite a number of bottles were ruined. A careful examination of them showed very plainly that a bottle of alloxan containing 10 grams had been the cause of the wreck. This sample of alloxan had been in the case for several years and the past summer was an unusually cool one. I was not aware that alloxan had any such property and have been unable to find that it is subject to any such behavior. ALVIN S. WHEELER.

UNIVERSITY OF NORTH CAROLINA.

The above note by Professor Wheeler on the instability of alloxan is of peculiar interest to the writer.

Several years ago, upon my return to the laboratory at the close of the summer vacation, I found that an explosion had occurred in one of our cupboards for fine organic chemicals. The force of the explosion shattered all the neighboring bottles on that end of the shelf, so that it was impossible to tell which particular bottle was responsible for the trouble. We checked up all the missing bottles by our shelf list, but among those destroyed there were none that we had ever heard mentioned as likely to decompose with explosive violence, and the matter remained very much of a mystery. Prof. Wheeler's article seems to solve this mystery, for among the wreck and ruin of broken glass in our cupboard were found