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## **Color and Chemical Constitution**

**L**ight is electromagnetic radiation (that is, it has both electrical and magnetic components) vibrating in transverse wave packets, or quanta. The vibration may occur in all planes or in one only (plane polarized light), each plane having right and left circular vector components. We may measure the amplitude of the wave quantum (intensity of the light), its frequency,  $\nu$ , and/or wavelength,  $\lambda$  (color or tone), and its velocity in a given medium,  $v$ . The last is mainly of interest in differential refraction or separation of vibrations of different frequencies for spectral determinations. There are other important characteristics of light: spectral distribution or purity, brightness and variation (flicker, sparkle, etc.), reflection and absorption of specific light frequencies (most important to this discussion), refraction or the "rainbow" effect, and scattering, or the Tyndall effect. The latter, for example, has been used to explain (1) why the sky is blue—Rayleigh's Law states that the intensity of the scattering varies inversely with the fourth power of the wavelength—that is, because the atmosphere scatters the shorter wavelengths to us more efficiently. This effect is also found in the blue color of lakes and in the blue color of the rump of a species of chimpanzee that possesses no colored compounds in that region of its anatomy.

Light is composed of waves of varying wavelengths, not all of which are visible to the human eye. We can see those having wavelengths between 4000 Å and 8000 Å, approximately. In general, an object appears colored when it transmits or reflects light of the visible region non-uniformly. The band of waves having a wavelength of about 4250 Å appears violet; waves from 5450 Å to about 5850 Å appear yellow; and those longer than about 6200 Å are red. Light is absorbed selectively by all organic materials, but most of them appear colorless because they absorb in the ultraviolet region of the spectrum. Molecules which contain conjugated double bonds in certain arrangements, or which contain specific systems of delocalized electron wave quanta, however, absorb some of the frequencies of visible light. If they absorb all the wavelengths except those in the red region, for instance, the material will appear red in color. If they absorb only the waves of the color completely complementary to red, i.e.

blue-green, the material will appear to be red in this case also, but it will usually be of a lighter tint, because of the greater amount of total reflection or transmission (see Table 1).

**Table 1. Relationship of Frequency Absorbed to Color Transmitted**

$\lambda$ Wavelength absorbed (Å)	Color observed (transmitted)
4000 (violet)	greenish-yellow
4250 (dark blue)	yellow
4500 (blue)	orange
4900 (blue-green)	red
5100 (green)	purple
5300 (yellow-green)	violet
5500 (yellow)	dark blue
5900 (orange)	blue
6400 (red)	bluish-green
7300 (purple)	green

The principles involved in this interaction of the electronic constituents of matter with light have been the subject of careful mathematical scrutiny. It is the purpose of this discussion to present an unsophisticated non-mathematical model-system approximation of these principles and of their useful application. For those who wish to pursue a more rigorous investigation involving quantum mechanics, any competent text for advanced physical chemistry published in the last five years will provide an excellent starting point. The advent of "bega-stage" digital and analogue computers, taken with a number of simplifying assumptions proposed in recent years, has extended the direct application of wave mechanical calculations to ever larger molecules.

Light is received at the retina and in the region of the rods and cones. Although definitive work to conclusively establish the mechanism of the transfer of color information, as to nature and quality, to the brain from the receptors has not yet been reported in the literature, many investigators now agree that an energy-deficient system may be the transfer agent, employing delocalized electrons that may be excited in the manner to be discussed below. Last year (2) an ATP-acetylcholine synergistic combination was suggested that would operate both as an energy-transfer agent and as an influence on the conductivity of the synaptic fluid at the ganglia. Considerable investigation has yet to be carried out in this interesting area of the chemical basis of color perception.

In nature the major colored compounds in plants

include the carotenoids, the basic structure of which is derived from isoprene units and may be represented by  $\beta$ -carotene, which is yellow in color when pure, and from the flavonoids which are based structurally on the flavonoid nucleus (especially with —OH substitution). In animals, melanin is the basis for color; it is a mixture of quinonoid dyes and enzymes in a protein base. Other biological colored compounds include sclerotin, haemochromes like haemoglobin and haemocyanin, porphyrins, guanins, pterins, flavins and quinone pigments. We shall later refer to these structures and especially to their electronic distributions to explain the color they exhibit. In the non-organic area, the colors of certain elements and ions (e.g., transition metals) and ion complexes are also of interest and may be derived from the same principles employed in the case of organic substances.

### Historical Background

The original work on color and chemical constitution that formed the basis for our modern understanding was first reported by O. N. Witt (3) in 1876. He observed that every one of the structures of the various dyes known at that time contained at least one group found frequently in other dyes and to which he assigned the color-bearing function. He named these groups *chromophores* (from the Greek, *chroma*-color and *phoros*-bearer) and noted that they are not all equally potent; some organic molecules need to possess one of these groups in order to be colored while others require two or more. These combinations of atoms we now know represent different types of unsaturation centers. Witt later (3) divided the chromophores into *chromogens* (color-generating groups) like  $-\text{N}=\text{O}$ ,  $-\text{NO}_2$ ,  $-\text{N}=\text{N}-$ ,  $-\text{CH}=\text{CH}-\text{CH}=\text{CH}-$ , quinone, etc., and *auxochromes* (color-augmenting groups), mostly salt-forming combinations like  $-\text{OH}$ ,  $-\text{NH}_2$ ,  $-\text{OR}$ , and others. We will discuss this work more fully below. In 1888, H. E. Armstrong (4) showed that the quinoid grouping is a strong chromogen. This discovery was useful to early color theory, as a basis for predicting the existence of other chromogens. It stimulated research in the area of color versus structure, but the theory based on it had too many exceptions and was soon discarded. From 1879–1892, R. Nietzki (5) reported “color-deepening,” which was a shift of the frequencies of absorbed light toward longer wavelengths, as directly related to an increase in the molecular weight of chromogens (5). This was termed a “bathochromic shift” (6). Here, too, closer investigation disclosed too many exceptions to the rule. From the lofty eminence of our present knowledge we note that the rule was followed only when increased electron-delocalization went with increased molecular weight. The terms “bathochromic” shift or group are used today in their fundamental sense, as are their antonyms, “hypsochromic” shift or group. This view was foreshadowed in 1907 when J. T. Hewitt and H. V. Mitchell (7) noted that the bathochromic shift could be tied to an increase in the length of a conjugated chain. Then A. J. Evans (8), in 1913, postulated that the roots of chromophoric activity lay in a “lack of valence saturation” in all colored organic compounds.

Thus, the empirical data needed for color theory were compiled and the fact that selective absorption of visible light was associated with conjugated unsaturation was recognized many years ago. However, it remained for G. N. Lewis and others (9, 10), upon the development of the electronic theory of bonding, to explain the color phenomenon in terms of electron (particle) vibrations. In 1916 Lewis wrote (9):

“When a particle is held in position by definite constraints, it is capable of vibrating with a definite frequency or wavelength, and this frequency is determined solely by the mass of the particle and the magnitude of the constraints. When such a particle is electrically charged and subjected to alternating electromagnetic forces, which constitute a beam of light, and when the frequency of the light is near to the characteristic frequency of the particle, the latter is set to vibrating . . . and the energy of the light is absorbed. There are two kinds of charged particles which exist in chemical substances, charged atoms and charged electrons. The former, on account of their relatively large mass, have low characteristic frequencies which are . . . far below the frequencies of visible light and therefore cause absorption only in the infrared spectrum. The electrons . . . because of their relatively small mass and the rigid constraints by which they are ordinarily bound, usually have frequencies higher than those of visible light and therefore absorb only in the ultraviolet. When . . . by a change in constitution of the molecule . . . the constraints acting upon an electron become weaker, the frequency of that electron becomes less. It may begin to absorb visible light of the highest frequency, namely the violet and blue, and the transmitted light is therefore yellow. If the changes are made more pronounced, and the frequency of the electron(s) concerned is still further lowered, so that the maximum of absorption is in some other part of the visible spectrum, different colors will be produced.

In the 1930's and 1940's, Wheland (11) and Brooker (12) tied color theory and chromophores to resonance and to the old, but still useful, concept of resonance-contributing forms. This has led today to the idea (based on molecular orbital theory) that colored substances are ones in which the electrons are least firmly held in a constant location; they are rather delocalized (“smeared”) electrons from *p*, *d* and *f* sublevels. Another important factor is the number of electrons involved. Thus, modern color theory rests on the early work and concepts described above and on quantum wave mechanics and the MO theory evolved from it, on the work of Syrkin and Dyatkina (13), Wheland (11), Dewar (14) and others (15, 16), mainly from the 1930's on.

### Principles of Color Production

Early spectrographic work, interpreted by Max Planck (8, 10), led to the conclusion that when energy (heat, light, or other wave forms) is absorbed by matter the energy gain is directly proportional to the frequency. Thus,  $E_2 - E_1 = h \nu$ , where  $E_1$  and  $E_2$  are quantum energy levels (usually ground state and excited state, respectively),  $h$  = Planck's constant and  $\nu$  is the frequency. The energy absorbed causes a quantum jump from  $E_1$  to  $E_2$  by electrons when the frequency of the impinging energy matches that described by Planck's equation for one or more “allowable” quantum jump(s), as determined by the nature of the substance involved; this frequency has been termed the “natural” or “resonant” frequency of the electron wave. The mechanism involved is simply an addition of electrical and magnetic vectors of the resonant light frequency with the molecular electron system. Let us consider

such a molecular electron system. A widely supported thesis which is derived from wave mechanics pictures conjugated unsaturation in a molecule as consisting of a delocalized electron wave pattern arising from the overlap of parallel *p*-orbital electrons to form a single polarizable pi-cloud (a molecular orbital). When, because of steric or other factors, the adjoining *p*-orbitals cannot be aligned in parallel fashion, such overlap does not occur and, in consequence, there can be no delocalization in such instance. In order to have the vector addition mentioned above, the impinging electromagnetic radiation must encounter electromagnetic vector forces in the molecule at the "natural" or "resonant" frequency. This occurs primarily when the molecule possesses a permanent dipole and/or a delocalized electron system that is (by its nature) polarizable by the interacting electromagnetic vectors.

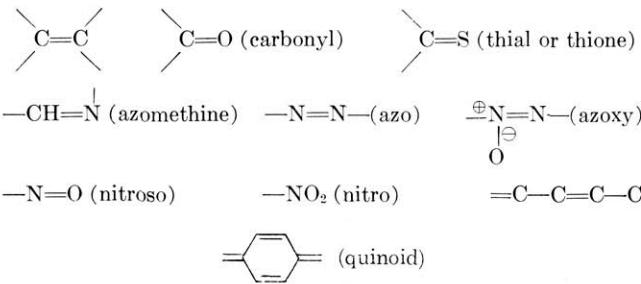
Subsequently the excited state returns to the ground state and the energy is relatively rapidly reradiated as heat (via collisions with other molecules), fluorescence and/or phosphorescence. Thus the frequencies that may be absorbed depend on the number and types of transitions possible for the molecule, including especially electron transitions (and the frequencies of the electron waves therein). The electron delocalization leaves the system at a lower quantum energy level, so that quantum jumps to the close-lying more localized excited states involve a greater number of smaller energy transitions. Thus a greater number of *lower* frequencies of light might be absorbed if such delocalization were not possible. Due to vibrational and rotational energies, the number of energy differences or quantum jumps (and hence frequencies) are increased by small amounts near the electronic state transitions. Because of the close spacing of the quantum level transitions there is also a fairly wide, but closely spaced, band of frequencies which can be absorbed. For gases and for liquids and solids at very low temperatures the frequencies may still be separated as individual absorption bands. At normal temperatures for liquids and solids the frequency bands merge and there results a region of continuous absorption. Thus, a substance will appear colored only if selective absorption occurs in the visible region of the spectrum; this is related to the resonant frequency of the molecular electron wave (i.e., the allowable quantum transitions based on the electronic pattern, or the energy content of the electron system). We can show, for example, that benzene absorbs in the ultraviolet because the first excited state is very far above the energy level of a ground state which is at an abnormally low level due to a node-free isotropic totally-delocalized pi-resonance system; thus, the quantum jump is very large and so is the resonant frequency. At ordinary temperatures most of the molecules are at an essentially zero-point of vibrational energy and in their lowest electronic state. As energy is absorbed they go to a higher electronic state, but not necessarily to the zero-point of vibrational energy for this state. This excess vibrational energy is quickly lost in collisions. In ordinary non-fluorescent and non-phosphorescent substances the transition to the lower electronic state is bridged by going from a low vibrational energy in the excited state to a high vibrational energy in the ground state ( $E_1$ ). The

result is a complete return without the emission of visible radiation (light is converted to kinetic energy at various stages).

When the energy level available in the ground state is very much lower than the zero vibrational energy level in the excited state, visible radiation (fluorescence) results. Because of the initial loss of vibrational energy before the transition involving radiation, the frequency of the emitted radiation is lower than that of the absorbed radiation and nearly independent of it (e.g., the blue component of violet light or ultraviolet causes green fluorescence in the yellow dye fluorescein when seen against a white background; when a blue filter is used, only the green fluorescence may be seen). If the molecule in the ground state has a high vibrational energy when absorption occurs, the frequency of the emitted radiation may be higher than that of the absorbed radiation. In phosphorescence, the molecules in the excited state lose vibrational energy and reach a semistable level from which a transition to a lower level does not occur readily. It ordinarily leaves this level by first absorbing energy from outside, usually from molecular collisions, then going to a slightly higher energy level and finally emitting radiant energy to return to the ground state. The length of time it remains in the semistable level determines the time lag between absorption and emission. On the basis of quantum calculations for allowable energy transitions, some specific molecules have been tailored successfully for the first time to provide specific color tints and shades and even fluorescence. The artist may soon be in the enviable position of being able to work with single-compound (truly homogeneous) colors of any desired hue and quality.

### **Color, Chromophores, Chromogens, and Auxochromes**

Empirical examples of the relations described above can be found in the area of organic dyes. The following is a list of some common chromogens, in increasing order of general potency



The carbonyl and ethylene (vinyl) groups have chromophoric properties only when they are present in the molecule in multiple conjugated order. Thus, acetone is colorless ( $\text{CH}_3\text{COCH}_3$ ), while diacetyl ( $\text{CH}_3\text{CO}-\text{COCH}_3$ ) is yellow, as is benzil  $\text{C}_6\text{H}_5-\text{CO}-\text{CO}-\text{C}_6\text{H}_5$ , which is deeper yellow, and triketopentane ( $\text{CH}_3-\text{COCOCOCH}_3$ ) is yellow-orange. Since it is the delocalization of pi-electrons that is related to the production of color, it is evident from these examples that such delocalization accompanies multiple conjugated unsaturation. The greater the accumulation of conjugated centers of unsaturation in an organic molecule, the greater will be the opportunity for consecutive overlap of parallel orbital p-electrons to

provide a delocalized electron wave (molecular orbital) pattern for each such region in the molecule (see Fig. 1.) This in turn will give rise to multiple absorption centers resulting in a complex absorption spectrum made up of several bands. Such a substance might absorb light over a wide range of the spectrum and give either a broad rounded absorption band or one resolvable into a series of peaks, instead of absorbing light in a single major or narrow region, as does a compound composed of molecules having only one delocalized pi-wave center. There are various types of pi-electron delocalization in organic compounds, and one type may absorb light at a longer or shorter wavelength than another. We have seen that since it is known that color will deepen as the absorption bands are shifted to longer wavelengths it is possible to determine what centers of electron delocalization will produce such shifts and to establish a relative basis of comparison between the different types of electron delocalization found in molecules.

Suppose we examine four compounds in which two phenyl groups are joined by different unsaturated groups, producing definitely different delocalization patterns and resulting in a progressive shift in absorption to light rays of longer wavelength: (wavelength absorptions and colors transmitted are shown) *stilbene*, C<sub>6</sub>H<sub>5</sub>—CH=CH—C<sub>6</sub>H<sub>5</sub>, 2950 Å, colorless; *benzal-aniline*, C<sub>6</sub>H<sub>5</sub>—CH=N—C<sub>6</sub>H<sub>5</sub>, 3300 Å, colorless; *azobenzene*, C<sub>6</sub>H<sub>5</sub>—N=N—C<sub>6</sub>H<sub>5</sub>, 4500 Å, orange; and *thiobenzophenone*, C<sub>6</sub>H<sub>5</sub>—(C=S) C<sub>6</sub>H<sub>5</sub>, 6200 Å, blue. The phenyl groups include, of course, total pi-electron delocalization which overlaps that in the chromophoric groups. The behavior seen in these examples is indicative of the greater delocalization of the pi-electrons by the four different types of unsaturation between the phenyl groups. The thione is apparently an exception to the general order of potency of chromogens shown above, but the anomaly can be understood when it is realized that the sulfur octet can expand and thus contribute more to the delocalization pattern of phenyl groups than can sterically smaller atoms with fewer possible energy transitions.

The characteristic color of the quinones, as well as of the quinonyl amines, may be ascribed to the presence of multiple delocalized electron patterns of conjugated chromophoric groups. In *benzoquinone*, O=C<sub>6</sub>H<sub>4</sub>=O, which is yellow, we have total delocalization of pi and p-electrons due to a similar conjugated order and this is also true of yellow *dibenzalacetone*, C<sub>6</sub>H<sub>5</sub>CH=CHCOCH=CHC<sub>6</sub>H<sub>5</sub>, which exhibits resonance delocalization. That delocalization through conjugated unsaturation is essential for color is shown by the fact that if the two carbonyl groups of *diacetyl*, CH<sub>3</sub>COCOCH<sub>3</sub>, and *benzil*, C<sub>6</sub>H<sub>5</sub>COCOC<sub>6</sub>H<sub>5</sub>, are separated by one or more carbon atoms, the color disappears because pi-orbital overlap is no longer possible. Thus, *acetylacetone*, CH<sub>3</sub>COCH<sub>2</sub>COCH<sub>3</sub>, and *dibenzoylmethane*, C<sub>6</sub>H<sub>5</sub>COCH<sub>2</sub>COC<sub>6</sub>H<sub>5</sub>, are both colorless.

The effect on color of increasing the number of chromophoric groups may be illustrated with a series of diphenyl polyenes, C<sub>6</sub>H<sub>5</sub>—(CH=CH)<sub>n</sub>—C<sub>6</sub>H<sub>5</sub>, by comparing the value of n with the absorption maxi-

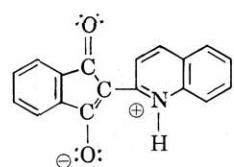
mum and the color transmitted (see Table 2). With the successive addition of ethylenic groups, the absorption maxima are shifted to longer wavelengths. However C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>—(CH=CH)<sub>4</sub>—CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub> is colorless, since the interposed methylene groups of the benzyl polyene break up the delocalization pattern, or the chances for p-electron orbital overlap, at the ends of the tetraene chain, thus isolating the phenyl groups which in themselves represent systems of delocalized pi-electrons. Lewis and Calvin (17) took the frequencies of the first absorption maxima and obtained wavelengths whose squares were plotted against the number of units, n, of the polyene chain. They obtained a very close approximation to a straight line. The linear relationship can be accounted for by assuming that delocalization for a conjugated series of pi-bonds spreads the electron system through the molecule so that it behaves as a single oscillating unit, with the frequency inversely proportional to the length of the delocalized system in the molecule (the square of this length can be related directly to "n").

**Table 2. Absorption and Color of Diphenylpolyenes**  
H<sub>5</sub>C<sub>6</sub>—(CH=CH)<sub>n</sub>—C<sub>6</sub>H<sub>5</sub>

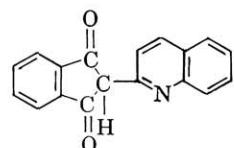
n	λ max Å	Color observed
1	3190	colorless
2	3520	colorless
3	3770	pale yellow
4	4040	greenish yellow
5	4240	orange
6	4450	brownish orange
7	4650	copper bronze
11	5300	violet black
15	5700	greenish black

Certain substituent groups, while they do not alone confer color, can augment the action of a chromophore by donating unbonded electron pairs to the resonance delocalization system. These auxochromes include such groups as —OCH<sub>3</sub>, —OH, —NH<sub>2</sub>, —NHR, and —NR<sub>2</sub>, in general order of increasing potency of function. Halogen atoms are also in this group, their effectiveness decreasing with atomic weight from iodine to fluorine. It has been seen that color and degree of polarity and/or polarizability are related since these phenomena arise from the same foundation, namely the extent of electron delocalization. In the case of the halogens just mentioned, the intensity and wavelength of the color observed varies with the polar character that results from the balancing of resonance contributions by the halogen (delocalization of p-electrons into the conjugated system) and the electronegativity effect (15). Other auxochromes could be the phenyl, naphthyl and conjugated heterocyclic groups like furyl or piperidyl, since they contribute appreciably to color by lengthening the resonance delocalization system and contributing their own pi-system electrons to the molecular orbital system. For example, mononitroparaffins are colorless but mononitrobenzene is definitely yellow. The relative effectiveness of the auxochromes is illustrated by the following three compounds: the base structure O<sub>2</sub>N—C<sub>6</sub>H<sub>4</sub>—N=N—C<sub>6</sub>H<sub>4</sub>—X, where the auxochrome X—X is —OH, deep yellow; X is —NH<sub>2</sub>, yellow red; X is —N(CH<sub>3</sub>)<sub>2</sub>, deep red. We must include with the auxochromes the salt groups (hydrochlorides, sodium

salts, etc.), since color is usually greatly intensified when there is salt formation, and the frequencies absorbed are shifted to the low end of the spectrum. Examples include the anion salt of nitrophenol and the hydrochloride of a basic amine dye. This phenomenon can be explained by the fact that the resulting charge on the atom that is part of the conjugated system can be delocalized also by either the pi-cloud spreading over an electron-deficient atom or by absorbing the contribution from an electron-rich atom. Mention of the possibility for simple salt formation immediately focuses attention on a tremendous range of known dyes; but there exist many more which, although highly colored, are not capable of forming such simple salts. It was often found that the latter were dipolar molecules, with the polarity frequently the result of tautomeric shifts and/or induction. Such dipolar molecules may be formulated as inner salts. Such inner salt formation usually occurs when resonance delocalization can stabilize the molecule. For example, quinoline yellow exists primarily in the dipolar form,



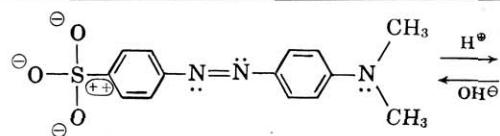
not in the non-polar form,



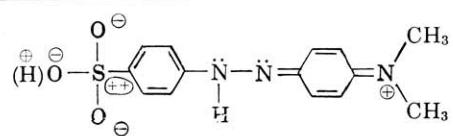
although the latter undoubtedly contributes slightly to the resonance hybrid resulting from delocalization of the pi-electrons in the fully conjugated form. That resonance through delocalization of electrons is essential for color formation has been emphasized throughout

this discussion. When such molecular hybrids are changed chemically so that the possibility of *p*-orbital overlap is restricted or eliminated the color diminishes or disappears, since the greater the delocalization of pi-electrons and the better the chance for all such electrons to act as a unified electron system, the longer the wavelength of light absorbed. In many cases, the effect of an electron donor-receptor system at the ends of a delocalized system provide just the push-pull effect for a strong enough dipole to provide or augment color. For instance, coumarin, and the naphthylamines, are colorless, while p-aminocoumarin is deep yellow. One is led to the conclusion that the cause of color in aminocoumarins is due to some relationship between the amino nitrogen atom and the unsaturated —O—CO— group present in the lactonic ring. The cause of the color can be found in the electron-delocalization between the auxochromic amino group and the chromophoric —O—CO— group whose carbonyl constituent greatly facilitates polarization of the entire molecular wave in the direction amino-to-carbonyl oxygen. When the amino group is absent, the carbonyl group is unable to promote sufficient polarization and delocalization by itself (in the adjoining benzene ring); the unbonded electrons of the nitrogen are needed for this. This concept of resonance can also be applied to the inner-salt type of formulation. The heteropolar character of such salts and greater delocalization of electrons which stabilize the polar charges results in increased intensity of light-absorption and in displacement of absorption maxima to longer wavelengths. Examples of this behavior can also be observed in that special class of dyes known as indicators, whose molecular structures and pi-electron wave patterns shift as a result of the chemical changes they are employed to indicate. This shift naturally results in an altered light absorption (different frequency) or color, and occurs at a given point in and over a narrow range of the reaction coordinate, in the manner of a quantum jump. See Table 3.

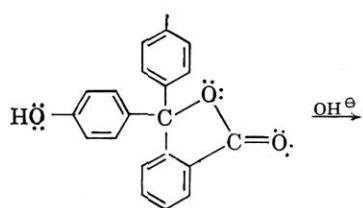
Table 3. Relationship Between Indicator Color Transitions and Structural Changes



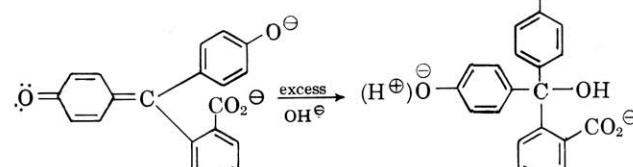
Basic methyl orange (yellow)



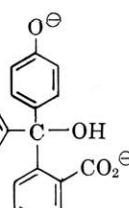
Acidic methyl orange, or helianthin (red-violet)  
(The electron-deficiency is delocalized by spreading of the pi-wave.)



Colorless phenolphthalein (phenyl rings are isolated)



Basic phenolphthalein (red) [note quinoid structure and delocalization over all 3 rings]



Colorless basic phenolphthalein [note the phenyl rings are isolated once again]

Among the inorganic compounds, light absorption by certain metal ions can be attributed to the transitions possible to *d*-electrons of an "inner" quantum level. When the ions are complex oxygenated, hydrated, or ammoniated ions, it is possible to show that the increased opportunities for a delocalized system—including overlapping *p*-electrons and metal *d*-electron orbitals—results in absorption at longer wavelengths. Examples include the color change from blue  $\text{Cu}(\text{H}_2\text{O})_4^{++}$  through green, yellow and colorless  $\text{Cu}^{++}$ ; the deep-blue color of  $\text{Cu}(\text{NH}_3)_4^{++}$  in which the less electronegative nitrogen nucleus allows greater delocalization of its unbonded *p*-electrons than does the oxygen in  $\text{H}_2\text{O}$  (hydrated ion); and the green color of the copper chloro complex which results from absorption at still longer wavelengths due to correspondingly smaller transitions possible with the additional unbonded electrons of the halogen and in spite of the electronegativity effect. We see these same principles at work in black anhydrous  $\text{FeCl}_3$ , yellow-orange hydrated  $\text{FeCl}_3$ , and red-orange  $\text{Fe}_2\text{O}_3$ . In addition, the change from yellow hydrated ferric ion to greenish hydrated ferrous ion can be attributed to the extra *d*-electron available to the latter, while the shift from blue cobalt(II) compounds to red ones (which have more  $\text{H}_2\text{O}$  or  $\text{NH}_3$  molecules complexed with the cobalt(II) ion) can be traced to complexing molecules which interdict delocalization of the higher-lying *d*-electrons. Thus, depending on the allowable transitions available, introducing complexing atom(s) may result in either increased delocalization with *p*-electrons or in an interdiction of delocalization with high-lying *d*-electrons, just like the introduction of a methylene group did for the diphenyl polyenes discussed above (see Table 2). The absorption of light is therefore shifted to shorter wavelengths.

Many other examples may be found and a satisfying explanation for the color observed and for color relationships may be deduced. Qualitative predictions can be made easily and many have been verified. Regardless of how the developments of the future will treat the present concept of color production discussed here, there is sufficient justification for it because it is useful now in bringing order to this phenomenon and in limited predictive work.

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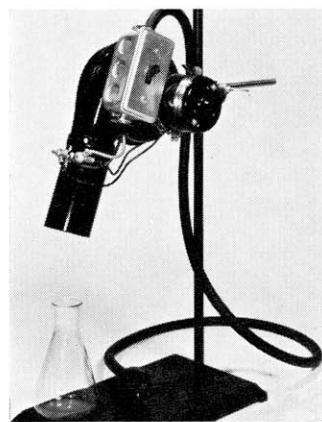
#### A Laboratory Blower-Dryer

**M. Benton Naff**

Dickinson College, Carlisle, Pennsylvania

A sturdy, efficient, and inexpensive hot-air blower may be assembled from readily available electrical supplies. The blower is useful for drying chromatographic strips, laboratory glassware previously rinsed with acetone, etc.

An electric switch-box is installed on the side of a Heinze blower No. DSH (55 cfm, 3000 rpm), 1000 w, 110 v. The ground wire is attached to a bolt on the blower which is also used to secure the switch-box to the blower. The assembly is fastened in a chain or Nestor clamp and mounted on a ring stand. Total cost of the parts, including a ground plug, switch-box, blower, and 6 ft of No. 16 type S cord, is under \$15. A replacement heater is available from the manufacturer. With general use in a student laboratory, an individual heater yields up to three years of service.



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