RELATIONSHIPS BETWEEN ABSORPTION SPECTRA AND CHEMICAL CONSTITUTION OF ORGANIC MOLECULES

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A brief historical account of theories concerning the origin of color in organic compounds is given. Correlations between the wave length of absorption bands and the chemical constitution of organic molecules are reviewed and present-day quasi "classical quantum-mechanical" concepts on color are discussed. The influence on color of such factors as resonance, steric hindrance, the conjugation and insulation of chromophores, and linearly conjugated chromophores is illustrated. The effects of stereostructural changes on the position and the number of absorption bands are described. Several quantitative relationships between the wave length of the maximum absorption band and chemical constitution are presented.

CONTENTS

I. INTRODUCTION

One of the long-range goals of organic chemists has been the determination of the chemical constitution of organic substances from a study of their physical properties and, conversely to a limited degree, the prediction of certain physical properties of organic substances from a knowledge of their structure. One such physical property is color as recorded by the measurement of absorption spectra. For over three-quarters of a century, organic chemists have been studying the color and structure of organic compounds and have drawn a large number of qualitative and, more recently, quantitative correlations between them. Several theories to interpret absorption spectra have been proposed; however, few have been of sufficient generality to apply to more than one or two classes of dyes.

It has been difficult for organic chemists through classical theories to learn just what causes color in organic substances. With the application of quantum mechanics the chemical physicists[1] have been more successful in this direction. As a result of qualitative and semiempirical quantitative applications of approximation methods much is now understood about the absorption peaks in terms of the characteristic electronic energy levels of various atomic groupings. It is now possible to calculate the frequencies and, in some instances, the intensity of light absorbed by simple molecules, and to obtain values which agree remarkably well with the experimental ones. Eventually, the same may be possible for all substances. There are several reasons,[2] however, why organic chemists should, in the meantime, continue their search for correlations between molecular structure and spectra until, through a fusion of empirical and theoretical methods, it will be possible to define all the laws for the absorption of light by organic molecules. For instance, qualitative relationships between the color and the chemical constitution of organic molecules serve as a wieldy tool to elucidate the structure of and to characterize new compounds. Many cases are found in the literature where the structure of a compound was selected from among several possibilities on the basis of its absorption spectra. In this respect, Jones (140) has found that systems of condensed aromatic rings have associated with them a characteristic spectrum by means of which a particular ring system may be recognized. Further, an accurate compilation of quantitative data on the spectra of pure compounds will provide material for the quantum theorists.

Although a large number of more or less detailed reviews (4, 34, 52, 75, 114, 133, 189, 190, 195, 201, 212, 228, 249, 266, 295, 304) have appeared on this subject, Lewis and Calvin (182) have probably given the most general semiclassical treatment[3] of the absorption of light by organic substances. For complete understanding,[4] fluorescence, phosphorescence, and the emission of light should be considered over the spectral range from the vacuum ultraviolet to the far infrared. However, this article will be limited to the absorption of light of wave lengths between 200 mμ and 800 mμ.

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[1] See, particularly, the publications by Mulliken (217, 220, 221), Forster (91), Sklar (277), Hückel (128), Price (239), Sponer (282), Herzfeld (120, 121), Bowen (31), Pauling (226), and London (196).

[2] Concerning the application of spectrophotometry in qualitative and quantitative analyses and in physicochemical investigations see references 22, 34, 39, 56, 111, 153, 213, 242, 258, 260, and 293.

[3] For a brief presentation see the discussion given by Branch and Calvin (32, pages 159 to 182).

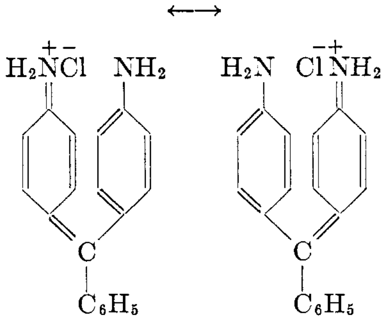
[4] The definitions of some useful spectrographic terms are as follows: *hyperchrome* = a group which causes an increase in the molecular extinction coefficient of an absorption band; *hypochrome* = a group which causes a decrease in the molecular extinction coefficient of an absorption band; *bathochrome* = a group which produces a shift of an absorption band toward longer wave lengths; *hypsochrome* = a group which produces a shift of an absorption band toward shorter wave lengths; *chromophore* = a group containing multiple bonds which are fundamentally responsible for the color of organic substances (Gr. *chroma*, color, + *phoros*, bearer); *auxochrome* = a group which does not confer color upon an otherwise colorless substance but does increase the coloring power of a chromophore (Gr. *auxo*-, increase);

II. HISTORICAL BACKGROUND

Graebe and Liebermann (99) were probably the first to report that there existed a relationship between the color and the chemical constitution of organic molecules. A few years later, in 1876, Witt (303) stated that for a substance to exhibit color its structure must possess unsaturated linkages such as C═C, N═O, etc., to which he gave the term "chromophore" (54, 55, 194), and that the color of such compounds is enhanced when they possess, in addition, certain groups such as NO_2, NH_2, or OH, which he called "auxochromes" (2, 55, 147). In 1879, Nietzki (223) formulated an empirical rule to which reference is still made occasionally by some authors: namely, that the colors of related compounds deepen with increasing molecular weights (color depth increases in going from yellow through red to green; that is, the complementary colors of the spectral ranges, violet to red). A simple example of an exception to this rule is the fact that alkylbenzenes, with alkyl groups containing from one to six carbon atoms, all have their maximum absorption bands at 269 $m\mu$ (229).

About this time there began to appear a series of theories attributing color to some type of valency change in the molecule. In 1888, Armstrong (7) proposed that all colored compounds contain a quinoid structure, or one that is changeable into such. Hewitt (123) showed that the color is deeper the longer is the conjugated system. In 1906, Baly (10) and his coworkers expressed the belief that color is due to a dynamic isomerism between atoms that are in the proper positions; they called this isomerism "isorropesis." This same idea was expressed in different words by Kauffmann (147), who ascribed color to the shattering of the principal valencies of the atoms and their resolution into scattered component forces, and also by Hantzsch (102), who attributed color to changes in the distribution of affinity without accompanying changes in the relative positions of atoms, a phenomenon which he called valency isomerism. Baly (11) stressed the idea that color is due not to a change in structure but to an opening up of the molecular fields of force.

Through this era there was a common belief, first advanced by Hartley (105), that absorption bands are characteristic of the parent compound and are merely altered by chromophores, auxochromes, or substituents. Overlapping this period with that of the next is the work of Baeyer (9), who stated in 1907 that the color of triphenylmethane dyes is due to an oscillating atom.



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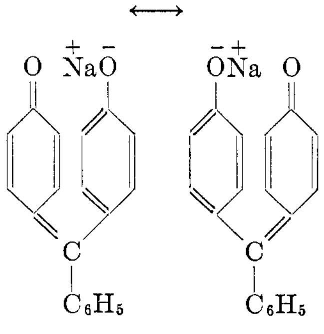
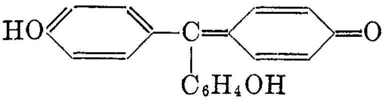
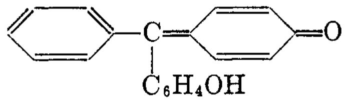


In 1913, Campbell (60) attributed the absorption of light to vibrating electrons, and in 1914, Adams and Rosenstein (1) stated that it may be due to either oscillating electrons or charged particles, such as ions. In 1916 Lewis (177), and later Wells (298), also attributed the absorption of light to electronic vibrations, while Meek (205) tried to determine the number of vibrating electrons. Baly (12) applied the old quantum theory of Bohr to absorption spectra and attempted to calculate absorption bands in the ultraviolet from bands in the infrared.

This period introduced the present-day belief that oscillating electrons within a molecular structure permit the absorption of light by the substance. Several proposals were advanced in the attempt to explain or describe these electronic vibrations in classical terms.[5] In 1921, Moir (211) postulated that color in organic substances is due to electrons revolving in oval orbits about the whole molecule with a period equal to that of the wave length of light absorbed by the colored substance. He stated that substitutions in a particular molecule affect the wave length of its maximum absorption band by altering the size of this orbit. From the wave length, λ_0, of the maximum absorption band of a reference molecule the absorption band for other substances λ_x, can be calculated by multiplying the fundamental wave length, λ_0, by substitution and structural "color constants" according to an equation of the form $\lambda_x = k_1k_2 \ldots k_n\lambda_0$. These "color constants," $k_1, k_2, \ldots k_n$, were obtained, for example, as follows: $k_{p\text{-OH}} = \lambda_{\text{aurin}}/\lambda_{\text{benzaurin}} = 0.9657$.



Aurin



Benzaurin

A structural "color constant" was similarly obtained; for instance, that for an oxo link, —O—, was determined from the ratio $\lambda_{\text{fluorescein}}/\lambda_{\text{phenolphthalein}}$, equal to 0.89. In this way, upon choosing *p*-hydroxybenzyl alcohol and two phenol molecules as reference compounds with λ_0 assumed to be 290 mμ and 138 mμ, respectively, and after determining "color constants" for various substituents and structural links, Moir calculated the absorption bands in water solution for a large number of colored substances and obtained values which agreed quite well with the observed ones. In 1923, Steiglitz (284) proposed that within molecules there is an oxidizing–reducing system which, by the process of oxidation and reduction, releases electrons from their intraatomic restraints and starts them vibrating. Dutt (78), in 1926, stated that strain within the molecule from multiple bonds and cyclization causes substances to be colored. Dilthey (74), and later Wizinger (304), implied that "ionoid" compounds are the strongest absorbers of light, although other types of substances may show a weak absorption extending into the visible region. Moir (210), in 1929, made a quantitative study of the triphenylmethane dyes and noted the effect of various auxochromes on both the production of two or three bands and the position of the band of maximum wave length. He concluded that their $\lambda_{\max}$ depends upon the path of the vibrating

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[5] For an example of the quantum-mechanical picture see Herzfeld (119).

electrons as influenced by the type and number of auxochromes in the resonating system.

In an attempt to form a mechanical picture of a conjugated polyene system, Rădulescu (245), in 1931, likened it to a vibrating string which was assembled from many similar units. Each unit has an independent characteristic tension and vibrational frequency but, by vibrating in phase, the units resemble a single oscillator. He discussed the effects of the number of units, and substituents, upon the frequency of vibration of the mutual oscillators.

In 1935, Bury (57) pointed out the important rôle that resonance plays in affecting the color of organic substances. It was about this time that quantitative relationships between absorption spectra and structure based on semiclassical theories began to show promise.[6] Hauser, Kuhn, Smakula, and coworkers (106, 107) measured the spectra of several types of linearly conjugated polyenes and illustrated how the frequency of the lowest-frequency band may be calculated with certain empirical equations, and how the height of this band and the strength of absorption $\left(\int \epsilon d\nu\right)$ (66) vary with the number of conjugated ethylenic groups in the system. In 1936, Clar (67, 76) presented empirical equations by which one can account for the positions of the several bands of condensed-ring hydrocarbons. In 1939 appeared the paper of Lewis and Calvin about which more will be said presently. In 1940, Henrici (115) set up an equation

$$\lambda = 334.2\sqrt{V \cdot s_i}$$

based on classical theories of electrical discharges through gases, to calculate the wave length of the absorption bands of unsaturated compounds. Here, V depends upon the volume of the electron cloud of oscillating p-electrons, which is estimated from interatomic distances, and s_i, the dampening coefficient, is proportional to the dielectric constant and hence the polarizability of the molecule in the direction i. Thus, with increasing number of conjugated unsaturated links the size of the electron cloud will increase and λ_{max} will move toward longer wave lengths. Henrici considered the spectra of condensed-ring hydrocarbons and the diphenylpolyenes. His calculations of λ_{max} for the latter compounds did not agree with the observed values as closely as did those of Hauser, Kuhn, *et al.*

In the past few years many other semiclassical, quantitative treatments of absorption have been given and some of these will be discussed later. From the foregoing brief historical account it can be observed that organic chemists have slowly arrived at the conclusion that the absorption of light is due to vibrating electrons and that a number of qualitative relationships have been molded into a working hypothesis from which, in the later years, there have been formulated a few quantitative generalizations as to the color of organic substances.

Over the past decade quantum-mechanical methods have been applied to the electronic spectra of simple organic molecules and fruitful results have been obtained. The approaches taken by the various workers to determine fre-

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[6] A remarkable mathematical attempt for their time to account for molecular spectra was made by Bielecki and Henri in 1913 (24, 112a).

quencies and intensities of absorption bands differ essentially in the relative degree of theoretical computation and the extent of substituting empirical data for exact integrals. Using approximate wave functions of the molecular orbital (MO) or of the atomic orbital (AO) type, calculations have been carried out on the spectra of unsaturated molecules whose exact energies, $\int \psi H \psi d\nu$, were determined (91, 96, 122, 277). Except for the time consumed in computing the value of the integrals the method shows considerable promise.

More lucrative have been the methods whereby the theoretically defined integrals are replaced by empirical parameters. The molecular orbital approximation method seems to have advantages over the atomic orbital method in that (*1*) the AO method must assign arbitrary formulations to describe the ground states of "resonating" molecules, while the MO method treats these the same as "normal" molecules, and (*2*) the MO method is usually simpler for the description of excited electronic states. From such information as excitation and ionization potentials, dipole moments, electronegativities, polarizabilities, interatomic distances, bond angles, and force constants, the energy of the ground and first excited states may be evaluated in terms of a single parameter. The value of the parameter is then chosen so as to fit the particular data best. To illustrate the results obtainable by quantum-mechanical methods the wave lengths of the maximum absorption bands for some hydrocarbons are listed in table 1 (91, 196, 277).

TABLE 1

Wave lengths of maximum absorption bands for some hydrocarbons

COMPOUND	λ max (CALCULATED)	λ max (OBSERVED)
Benzene	247	255
Biphenyl	240	252
Naphthalene	295	275
Anthracene	365	370
Naphthacene	450	460
Pentacene	545	580
Phenanthrene	300	295
Pyrene	345	330
Fulvene	365	365
Butadiene	190	210
Azulene	691	700

III. THEORY OF ABSORPTION OF LIGHT[7]

According to current electronic theories ethane and ethylene may have the homopolar electronic arrangements of I and II, or either of the two polar forms, I′ and II′, respectively:[8]

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[7] For a quantum-mechanical discussion see the articles by the authors listed in footnote number one.

[8] Diradical forms, such as that for ethylene, $\underset{\bullet}{C}H_2\text{—}\underset{\bullet}{C}H_2$, are given little consideration, because resonance among forms of different multiplicity is negligible. On the other

$$
\begin{array}{cccc}
H_3C : CH_3 & H_3C\ :CH_3 & & H_3C\!:\ CH_3 \\
H_3C\text{—}CH_3 & H_3\overset{+}{C}\quad \overset{-}{C}H_3 & & H_3\overset{-}{C}\quad \overset{+}{C}H_3 \\
\text{I} & & \text{I}' & \\
H_2C{=}CH_2 & H_2\overset{+}{C}\text{—}\overset{-}{C}H_2 & & H_2\overset{-}{C}\text{—}\overset{+}{C}H_2 \\
\text{II} & & \text{II}' &
\end{array}
$$

When a molecule is placed in an alternating electromagnetic field, such as that of radiations of wave length large compared with the dimensions of the molecule, there is an induced oscillation of electrons throughout the length of the molecule in which the displacement will be proportional to the polarizability of the molecule. It is assumed, as was done by Lewis and Calvin and by Mulliken, that in the electronically excited states as those of I′ and II′ produced by the absorption of light energy, there are oscillations within the molecule of the same character as the induced oscillations mentioned above. The absorption of light causes the transition of the molecule from its ground state to an ionic, electronically excited state and the difference in energy of these two states will determine the frequency of the light absorbed.[9] If it is assumed that the electronic displacements are harmonic oscillations, then the restoring force, according to Hooke's law, will be $-kx$, where x is the electronic displacement from the equilibrium position and k is the restoring force constant. Thus, the energy required for these displacements will be $-\frac{1}{2}kx^2$ and a plot of the potential energy against the electronic displacement will be that of a parabola. The anharmonicity of the less ideal, and more probable, case will be considered later. If the energy is quantized, then the energy levels associated with the successive energy states will be given by $E_v = (v + \frac{1}{2})h\nu_0$; ν_0, the fundamental frequency, is given by $\nu_0 = \frac{1}{2\pi}\sqrt{k/m}$, where m is the effective reduced mass of the vibrating electrons. If E_0 and E_1 are the energies of the ground and first excited states, respectively, then the frequency of the light causing this transition will be

$$E_1 - E_0 = (3/2 - 1/2)h\nu_0 = h\nu_0 \tag{1}$$

and for its wave length,

$$\lambda = C/\nu_0 = 2\pi C/\sqrt{k/m} \tag{2}$$

This means that the chromophoric power of different bonds will vary inversely with their restoring force constants, k. Single bonds with a large k will absorb in the far ultraviolet (152a). Polarization of the second bond of the double bond need not be considered, since it has an extremely large restoring force constant and its absorption would appear in the region where ionization and dissociation take place.

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hand, if the unpaired electrons have their spins antiparallel, then essentially they form a covalent bond. Furthermore, it is not reasonable that an electric field would cause the electrons to migrate in opposite directions simultaneously.

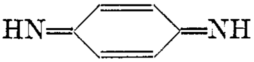
[9] The absorption of light of wave lengths in the region 180–400 mμ corresponds to energy differences of between 70 and 160 kg.-cal./mole, intermediate between those required for the photoionization of single covalent bonds (240, 241) and those required for vibrational or rotational transitions. Energy increments of this magnitude are sufficient to allow the displacement of *mobile electrons* (174) (π or *unsaturation electrons*) of multiple bonds.

On the basis of the relative chromophoric powers (34) of the various double bonds, the order of decreasing k must be:

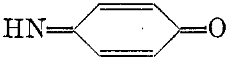
	$H_2C{=}CH_2$	$(CH_3)_2C{=}NCH_3$	$(CH_3)_2C{=}O$
λ_{max} =	200 mμ	230 mμ	280 mμ
	$CH_3N{=}NCH_3$	$(CH_3)_2C{=}S$	$C_4H_9N{=}O$
λ_{max} =	347 mμ	400 mμ	665 mμ

Simple compounds containing these bonds exhibit a maximum wave-length absorption band, λ_{max}, approximately as indicated. Additional examples are the following compounds with their approximate absorption maxima:

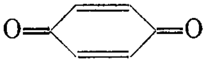
$CH_2{=}CHCH{=}CH_2$	$CH_2{=}CHCH{=}O$	$O{=}CHCH{=}O$
220 mμ	350 mμ	460 mμ (198)



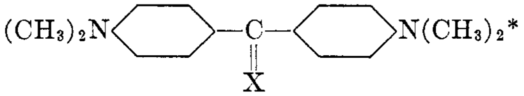
colorless (302)



pale yellow

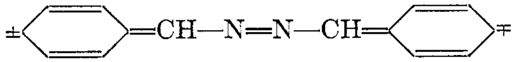


deep yellow



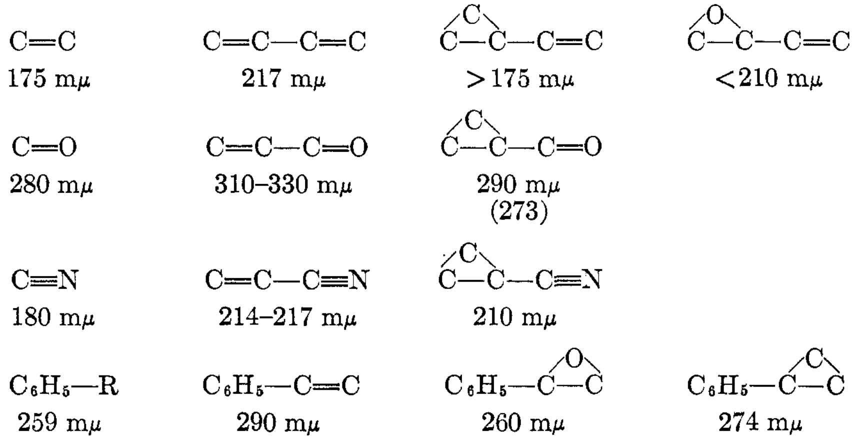
*λ_{max} increases in the order given, where X is CH_2, NH, O, S (54).

The order of increasing chromophoric power for these double bonds is due to the increased strain within the bonds (151). With increasing strain there results a less stable ground state, causing a smaller difference in the potential energies of the ground and first excited states, and hence an absorption of light (excitation) of longer wave lengths. An interesting corollary was noted by Lewis and Calvin (182). They pointed out that although benzalazine, $C_6H_5CH{=}NN{=}CHC_6H_5$, contains two stronger chromophores ($C{=}N > C{=}C$) than 1,4-diphenylbutadiene, $C_6H_5CH{=}CHCH{=}CHC_6H_5$, the former compound ($\lambda_{max}$ = 265 mμ) absorbs light at shorter wave lengths than does the latter (λ_{max} = 334 mμ). In the predominant form of the excited state of benzalazine,



there is an N=N bond and because of this highly strained bond there is a resistance to the complete conjugation throughout the molecule, that is, a less stable excited state. This increases the energy required for excitation to the extent that the maximum absorption band for the azine occurs at shorter wave lengths. Ferguson and Goodwin (86) found this to be true in a number of cases containing the C=N—N=C and the —N=C—C=N— structural systems.

The cyclopropyl group may be considered a chromophore but weaker than an ethylenic bond, since in cyclopropane the bonds are under less strain. This viewpoint (15, 63, 78, 193) is supported by the fact that the color deepens in going from cyclohexane to cyclopropane and also for the series cyclohexanone, cyclopentanone, cyclobutanone, and ketene (20, 89, 93). In this connection a number of studies (61, 109, 155, 200a, 257a) have shown that the cyclopropyl ring and the epoxy group have chromophoric powers approaching that of an ethylenic bond. When these two small saturated groups are adjacent to an ethylenic bond or a carbonyl bond the resulting systems are found to have absorption maxima in between those of a monoene, or carbonyl compound, and a diene, or an α,β-unsaturated carbonyl system. This is illustrated below, where the $\lambda_{\max}$ for skeleton structures are indicated.



$C{=}C$ 175 mμ	$C{=}C{-}C{=}C$ 217 mμ	$\overset{\diagup C \diagdown}{C{-}C}{-}C{=}C$ >175 mμ	$\overset{\diagup O \diagdown}{C{-}C}{-}C{=}C$ <210 mμ
$C{=}O$ 280 mμ	$C{=}C{-}C{=}O$ 310–330 mμ	$\overset{\diagup C \diagdown}{C{-}C}{-}C{=}O$ 290 mμ (273)	
$C{\equiv}N$ 180 mμ	$C{=}C{-}C{\equiv}N$ 214–217 mμ	$\overset{\diagup C \diagdown}{C{-}C}{-}C{\equiv}N$ 210 mμ	
$C_6H_5{-}R$ 259 mμ	$C_6H_5{-}C{=}C$ 290 mμ	$C_6H_5{-}\overset{\diagup O \diagdown}{C{-}C}$ 260 mμ	$C_6H_5{-}\overset{\diagup C \diagdown}{C{-}C}$ 274 mμ

In line with the above concept, acetylene is found to absorb at longer wave lengths than ethylene (283). On the other hand, when it is conjugated with other unsaturated bonds it closely resembles the ethylenic bond spectrographically. This is perhaps due to the increased strain in the excited molecule, where one carbon atom forms two double bonds,

$$R{-}C{\equiv}C{-}CH{=}CHR \qquad R{-}\overset{\pm}{C}{=}C{=}CH{-}\overset{\mp}{C}HR$$

counterbalancing the greater strain in the ground state of the triple bond over that of the double bond. For instance, cumulated double bonds, $C{=}C{=}C$, $C{=}C{=}O$, $N{=}C{=}N$, etc., are found to absorb light at longer wave lengths than when these bonds are conjugated, owing to a less stable ground state and hence a smaller difference between the energies of the ground and excited states (56, 64, 173). The resemblance between the spectra of vinylacetylenes and those of α,β-dienes was pointed out and illustrated by Heilbron, Jones, and coworkers (108).

Since auxochromes, like chromophores, are found to exhibit high-intensity absorption in the far ultraviolet and the conjugation of two auxochromes produces bathochromic as well as hyperchromic effects, and since saturated groups like the cyclopropyl and epoxy groups are found to be spectroscopically similar to double bonds, Braude (34) suggests a redefinition of the classical terms *chromophore* and *auxochrome* to "covalently unsaturated" and "covalently saturated" groups, respectively. For instance, it is found that the introduction of an amino group, long recognized as one of the principal auxochromes, at the terminal carbon atom of a conjugated system causes a greater bathochromic effect than the addition of another ethylenic or other unsaturated group (25; see also reference 300, page 1986).

There are two points concerning spectra about which little will be said: (*1*) the effect of the solvent; (*2*) the intensity of absorption bands. It is commonly known that the shape and position of the peaks of absorption bands greatly depend upon the solvent. Several authors (46, 66, 159, 171, 191, 244, 265, 270) have attempted to determine the way in which the solvent influences the spectrum and causes a deviation from the Beer–Lambert law. Shepard and his coworkers (274) have found a number of trends in the effect of the solvent with such properties of the solvent as its dielectric constant, its dispersion or index of refraction, and with the type of solvent, whether it is polar or non-polar, acidic or basic, aromatic or aliphatic, or is an associating solvent, but no one of these correlations has been rigid. There is little doubt that the effects are caused through aggregation between solvent and solute or solute and solute molecules, and also dissociations and associations (28, 32, 79, 103, 154, 169, 170, 180, 183, 187, 216, 291); nevertheless, regardless of the several theories proposed (127, 207, 265, 274, 280), a general fundamental explanation is still lacking.

According to classical electromagnetic theory (35) and quantum mechanics it seems reasonable to say that the intensity of absorption bands depends partly upon the probability of the transition from the ground to the ionically excited states of the molecule (31, 34, 220), upon the polarity of the excited states, and upon the magnitude of the electronic displacements involved in passing from the normal to the excited states (238). The transition probability is calculable for certain simple substances by quantum mechanics, but experimentally the organic chemist has learned little to help him predict the band intensities. Theoretical considerations lead to the conclusion that small absorption coefficients of the order of that of benzene usually indicate "forbidden" transitions (281). Strong absorption occurs only when there is a large electric moment connected with the transition. It can be shown for symmetrical molecules, such as benzene and mesitylene, that when an unsymmetric vibration is singly excited with the electronic transition, a small transition moment is produced and the spectrum will appear with weak intensity. That is, instead of a 0–0 band (electronic transition without vibration) as in allowed transitions, there will be a 0–1 band which corresponds to a transition from the vibrationless ground state to the upper state in which that particular vibration is excited with one quantum. Thus, Sponer (281) found in the long-wave region of the spectrum of 1,3,5-trichlorobenzene small absorption coefficients like those of benzene. On the other hand, the unsymmetrical isomer, 1,2,4-trichlorobenzene, shows moderately strong absorption in the same region.

Several correlations have been found (34, 38, 40, 70, 119, 230, 243, 290) concerning the effect upon λ_{max} of substituents in the aromatic nucleus but fundamental generalizations (34, 43, 68, 90, 101, 102, 118, 133, 238, 288) are limited in scope. Very recently Doub and Vandenbelt (76a) made an excellent study of the ultraviolet absorption spectra of mono- and di-substituted benzenes, from which a remarkable systemization was possible. Doub and Vandenbelt have considered absorption to be primary when the molar extinction coefficient, ϵ, is equal to or greater than 6×10^3, while secondary absorption results in ϵ being less than 2.6×10^3, usually much less. Thus, the absorption band of benzene near 200 mμ ($\epsilon_{max} = 7400$) is the first primary band, and the long-wave band near 250 mμ ($\epsilon_{max} \sim 200$) is the first secondary band. From their work it appears that greater success will be achieved in understanding the absorption of aromatic compounds by focusing attention on the primary bands rather than on the low-intensity secondary band.

When the substituent groups were divided into electron-donating (ortho and para directing) and electron-attracting (meta directing) types, and arranged in order of increasing $\Delta\lambda$ (displacement of the primary band relative to the 203.5 mμ band of benzene) values, the following series was obtained by Doub and Vandenbelt:

ortho and para directing

$$CH_3 < Cl < Br < OH < OCH_3 < NH_2 < O^-$$

meta directing

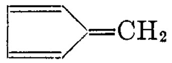
$$NH_3 < SO_2NH_2 < COO^- = CN < COOH < COCH_3 < CHO < NO_2$$

In both series, the largest bathochromic shift is with the groups which exhibit the greatest amount of electronic interaction (mesomerism or resonance rather than coulombic force) with the ring. In the case of the disubstituted compounds, when the two substituents are of the same type the red shift is close to the displacement that is the larger for the two groups, and when the two substituents are of different types, and ortho or para situated, the bathochromic shift is much larger than the combined displacements from the single groups.

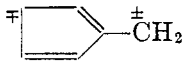
IV. RESONANCE AND COLOR

According to equation 1, the smaller the difference in energies of the ground and excited states the lower is the frequency, or the longer is the wave length, of the light absorbed. One can only predict the effects of resonance and other influences by considering separately the energy changes brought about in the ground and excited states (240, 294). It is not the magnitude of the resonance energy of a substance which determines λ_{max} (199, 299) but whether the resonance stabilizes the excited states more than the ground state (256).

The relationship between color and resonance can be clearly disclosed by regarding the fact that benzene and naphthalene are colorless, while their isomers, fulvene (299) and azulene (237, 292), are yellow and blue, respectively. According to well-founded resonance theories, structures involving a separation of charge contribute chiefly to excited states. The Kekulé and Dewar resonance of benzene and naphthalene accounts for most of their resonance energies, while the chief resonating forms of fulvene and azulene are of the polar types IIIa and IVa.[10]

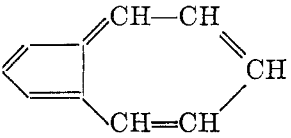


III

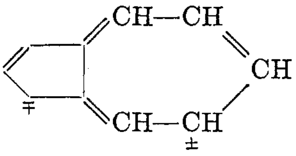


IIIa

Fulvene



IV

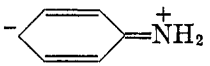


IVa

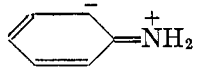
Azulene

Although benzene and naphthalene have large resonance energies the resonance is predominantly between forms that stabilize the ground state, increasing the difference in energy between the ground and first excited states, such that they absorb below 300 mμ. On the other hand, the resonance of fulvene and azulene lowers the potential energy of the first excited states with respect to the ground state to the extent that their absorption occurs in the visible. For the same reason, cyclooctatetraene, whose resonance energy is less than that of benzene, absorbs at longer wave lengths than benzene (200).

It is apparent that, in general, the color of a molecule will be deeper the greater is the resonance among ionic forms or forms involving a separation of charge.[11] Many authors have shown that λ_{max} is larger for compounds exhibiting the greatest amount of resonance but, in general, such resonance has involved polar structures (57, 125, 126, 269, 273, 290). For instance, the values of λ_{max} for aromatic amines are greater than those of the corresponding compounds without the amino group, owing to the resonance among such ionic forms as



and



while in acid solution such resonance is inhibited and the spectra revert to those of the parent compounds (72, 112, 136, 170, 289, 305). The resonance of enols, phenols, and naphthols is less than that of their ions and, accordingly, a bathochromic shift occurs in passing from neutral to basic solutions (28, 84, 173a). Schwarzenbach and coworkers (271) have correlated the color of phthalein-type indicators with the symmetry of the ions present at various pH values and have pointed out that the greater the equivalence in resonating forms the deeper is the color of the ion.

---

[10] The non-coplanarity of azulene decreases the contribution from the two equivalent forms of type IV, while there are a number of forms of type IVa.

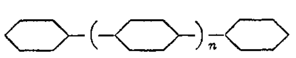
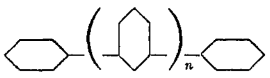
[11] Mulliken (219) and others have stated from wave-mechanical considerations that absorption of light takes place predominantly through transitions to charge-resonance structures.

V. CONJUGATION AND INSULATION OF CHROMOPHORES

It was very early recognized that the longer the conjugation within a molecule the deeper will be its color (73, 123). The effect of conjugation, or of insulation, of chromophores is strikingly revealed by observing the spectra of two compounds one of which has two chromophoric systems conjugated, while the other has the same two chromophoric systems separated by one or more saturated carbon atoms[12] (250) or meta-oriented about a benzene ring. For instance, the spectrum of 1,5-hexadiene, $CH_2{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2$, is identical with that of 1-pentene except for a twofold intensity, while 1,3-pentadiene has a larger λ_{max} by about 20 mμ (64). Then too, although the rubber hydrocarbon molecule contains thousands of unconjugated carbon–carbon double bonds, its λ_{max} is near that of ethylene (267).

TABLE 2

Wave lengths of the maximum absorption bands of the meta and para "polyphenyls" (97)

PARA 		META 	
n	λ_{max}	n	λ_{max}
	mμ		mμ
0	251.5	0	251.5
1	280	1	251.5
2	300	7–12	253
3	310	13	254
4	317.5	14	255

Numerous examples of this conjugation and insulation effect are reported in the literature (18, 94). To mention a few:

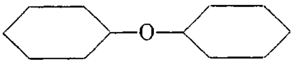
(*1*) The absorption of propenylbenzene, $C_6H_5CH{=}CHCH_3$, extends to longer wave lengths by 20 to 30 mμ beyond that of the corresponding allylbenzene, $C_6H_5CH_2CH{=}CH_2$, and with much greater intensity; the allyl group has the same auxochromic effect as a saturated side chain (61, 73, 124, 141, 214, 231, 248, 249).

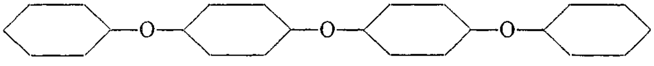
(*2*) *Insulation:* The following compounds all have λ_{max} at 262 mμ (97, 192, 251):

$C_6H_5CH_2CH_2C_6H_5$ $(C_6H_5)_2CH_2$ $(C_6H_5)_3CH$ $(C_6H_5)_4C$

---

[12] Not necessarily saturated carbon atoms for, regardless of the oxonium properties of the oxygen atoms, the compounds

, ,

and 

all have similar spectra (203; see also reference 130).

TABLE 3

Wave lengths of the maximum absorption bands of some similarly conjugated or insulated chromophoric systems

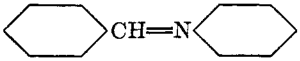
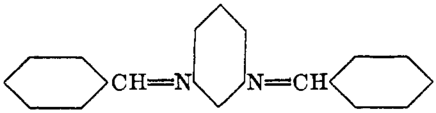
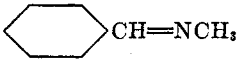
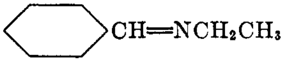
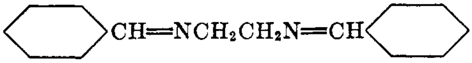
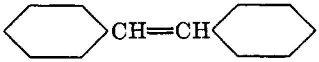
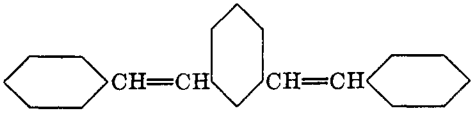
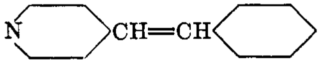
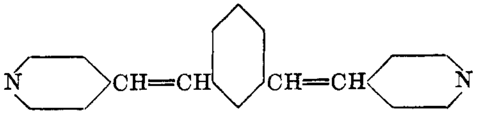
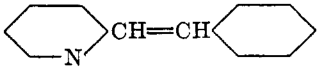
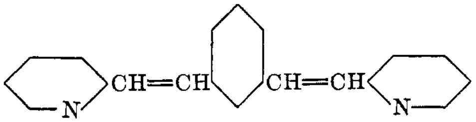
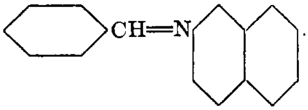
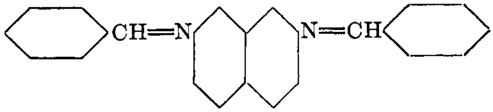
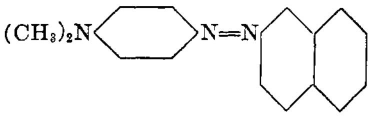
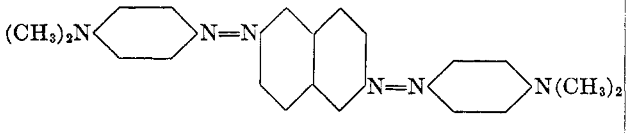
COMPOUND	λ_{max}	ϵ_{max}	REFERENCES
	$m\mu$		
	263	16,800	(85)
	267	33,800	(85)
	247	17,200	(85)
	245	15,900	(85)
	247	29,800	(85)
	295	26,300	(26, 87)
	298	53,700	(26)
	307	29,700	(26)
	308	46,800	(26)
	310	27,600	(26)
	314	50,100	(26)
	323	10,000	(117)
	313	22,000	(117)

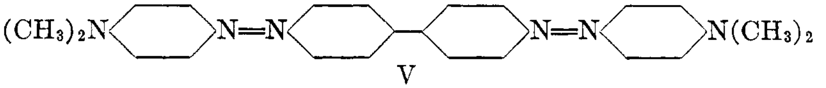
TABLE 3—*Concluded*

COMPOUND	λ max	ε max	REFERENCES
	mμ		
	422	36,000	(117)
	450	73,400	(117)
$CH_3(CH{=}CH)_2CHOHC{\equiv}CH$	230	28,500	(110)
$CH_3(CH{=}CH)_2CHOHC{\equiv}CCHOH(CH{=}CH)_2CH_3$	229	74,000	(110)
$CH_3(CH{=}CH)_3CHOHC{\equiv}CH$	267.5 278	55,000 44,500	(110)
$CH_3(CH{=}CH)_3CHOHC{\equiv}CCHOH(CH{=}CH)_3CH_3$	269 281	100,000 81,000	(110)

(*3*) Consider the para and the meta "polyphenyls" reported by Gillam and Hey (97), which are listed in table 2. For the para series, in which there is conjugation throughout the molecules, λ_{max} increases with increasing length of the molecules, while in the meta series where, starting with biphenyl, each additional phenyl ring is placed meta to the rest of the chain, the conjugation extends only through any two adjacent rings and is thus of the same lengths as in biphenyl. For as many as sixteen phenyl rings so attached, λ_{max} is practically the same as for biphenyl.

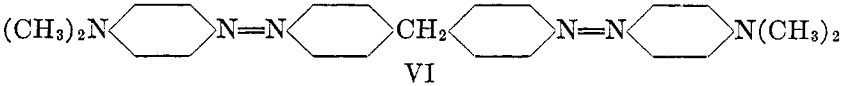
(*4*) Molecules with two insulated chromophoric systems will absorb light of near the same wave length as a molecule containing only one such chromophoric system, but the intensity of the light absorbed by the former molecule will be approximately twice that of the latter. This is brought out in table 3.

This phenomenon can further be observed in figure 1 for monoazo and biszao dyes, as measured by Piper and Brode (236; see also 41). Here is plotted the intensity for the bisazo dyes,



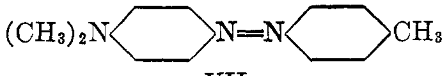
V

and



VI

and twice the intensity for the monoazo dye:



VII

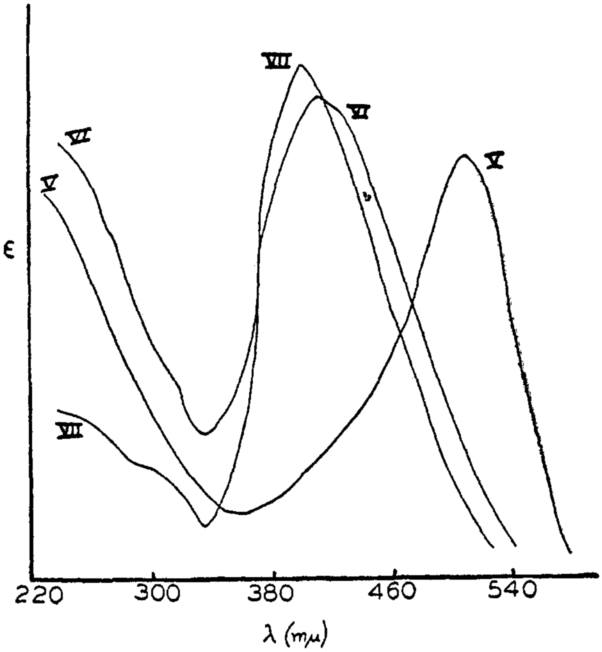
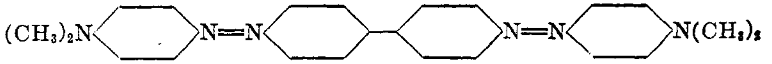
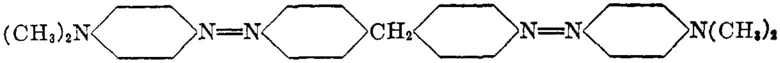


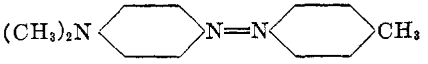
FIG. 1. Absorption spectra of V and VI and 2 × ε for VII, measured by Piper and Brode (236).



V



VI



VII

It can be seen that twice the molar absorption for the monoazo dye VII corresponds well to that of the insulated bisazo dye VI, but the conjugated bisazo dye V shows a new band at longer wave lengths.

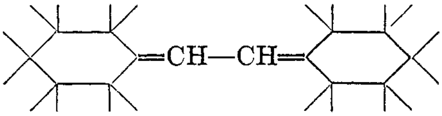
To cite another excellent example, the curve for 2 × ε for acetone is identical with the curve of ε for 3,6-diketoöctane, $C_2H_5COCH_2CH_2COC_2H_5$, while biacetyl, $CH_3COCOCH_3$, has a much larger λ_{max} (249).

These examples serve to illustrate how λ_{max} is greatly affected by the conjugation or insulation of the chromophoric systems. This fact is often used to decide upon the structure of compounds (167, 227) for which there is a question as to the location of certain double bonds.

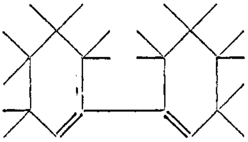
VI. SPECTRA OF COMPOUNDS CONTAINING TWO CONJUGATED CHROMOPHORES

A. Dienes

Many authors (8, 30, 68, 90, 209, 229) have observed the increase in λ_{max} upon replacing a hydrogen atom by an alkyl group on a carbon–carbon double bond. Mulliken (218, 222; see also 155) has attributed this to hyperconjugation, that is, a coupling between the σ-electrons of the adjacent C—H bonds of an alkyl group with the bonding electrons of the C—C_{alkyl} linkage (compare the conclusions of Price and Walsh (241) and of Bateman and Koch (17, 18)). Furthermore, the bathochromic shift is approximately the same for all substituents attached by a saturated carbon atom. Upon inspection of substituted α,β-dienes Woodward (306) noticed that substitution apparently is not the sole factor affecting λ_{max}. For example,

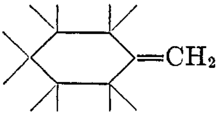


has a λ_{max} of 247 mμ while both

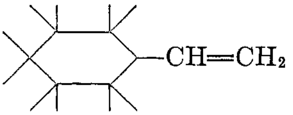


and $(CH_3)_2C{=}CHCH{=}C(CH_3)_2$

have λ_{max} at 237 mμ, i.e., 10 mμ lower. It is known from heats of hydrogenation (169) that a double bond exocyclic to a six-membered ring,



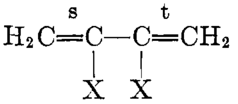
is under greater strain than an endocyclic double bond:



Also it was pointed out above that strain within a molecule will cause it to absorb at longer wave lengths. These two facts led Woodward to the conclusion that a diene with exocyclic double bonds will have a λ_{max} greater than that anticipated from the number of substitutions on the system.

On this basis Woodward started with the λ_{max} for 1,3-butadiene and, for each substitution and for each exocyclic double bond, assumed a bathochromic shift of 5 mμ. With these three constants he calculated the λ_{max} for eleven symmetrically substituted α,β-dienes with an average deviation of 1 mμ from the observed values.

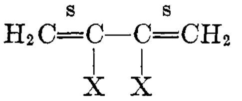
Woodward gave a somewhat different treatment to unsymmetrical α,β-dienes, but one that will hold as well for the symmetrical dienes. Consider an unsymmetrical α,β-diene (X) with double bonds designated as s and t:



$$H_2C\overset{s}{=}\underset{\substack{|\\ X}}{C}-\underset{\substack{|\\ X}}{C}\overset{t}{=}CH_2$$

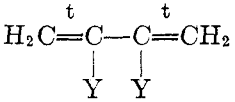
X

X may be thought of as a composite of two symmetrical α,β-dienes, VIII and IX.



$$H_2C\overset{s}{=}\underset{\substack{|\\ X}}{C}-\underset{\substack{|\\ X}}{C}\overset{s}{=}CH_2$$

VIII



$$H_2C\overset{t}{=}\underset{\substack{|\\ Y}}{C}-\underset{\substack{|\\ Y}}{C}\overset{t}{=}CH_2$$

IX

It would be reasonable to expect λ_{max} for X to be the mean of the values of λ_{max} for the two related dienes, VIII and IX. That is,

$$\lambda_{st} = \frac{\lambda_{ss} + \lambda_{tt}}{2}$$

where λ_{st}, λ_{ss}, and λ_{tt} are the calculated wave lengths for the maximum absorption bands of the unsymmetrical and symmetrical α,β-dienes, respectively. In this manner Woodward calculated λ_{max} for several unsymmetrical α,β-dienes, again assuming that each exocyclic double bond causes a 5-mμ bathochromic shift in λ_{max}. Several examples are taken from Woodward's table and listed in table 4. Woodward's calculations for eighteen compounds have an average deviation of 3.5 mμ from the observed values.

It is possible, then, to calculate with reasonable accuracy the position of the maximum absorption band for α,β-dienes containing no other chromophores and having the two double bonds not within the same ring (21).

B. α,β-Unsaturated carbonyl compounds

It was early noted (23, 206, 262) that α,β-unsaturated ketones have characteristic spectra. An isolated carbonyl group gives a low-intensity band ($\epsilon = 10$–100) near 275 mμ, while an ethylenic group gives a high-intensity band ($\epsilon \simeq 10^4$) near 195 mμ. When these two groups are conjugated, producing an α,β-unsaturated carbonyl compound, the two bands, referred to as *K* and *R* bands following Burawoy's (54) terminology, occur at longer wave lengths (81).

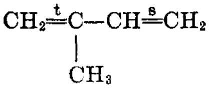
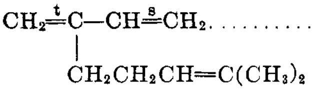
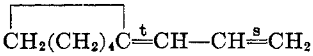
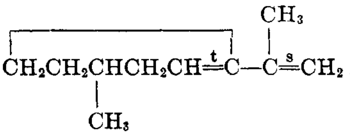
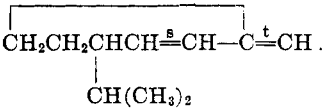
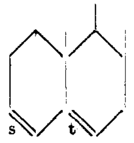
K band	220–260 mμ	$\epsilon = 10^4$
R band	310–330 mμ	$\epsilon < 100$

Since the *R* band is of such low intensity, most attention is focused upon the *K* band.

After studying a number of α,β-unsaturated carbonyl compounds, Woodward (307) found that the values of λ_{max} for such compounds can be approximated in fair agreement with the observed values if one assumes that a carbon-attached substituent on the conjugated system causes a bathochromic shift of 10–11 mμ and an exocyclic double bond causes a shift of 5 mμ. His table of values of λ_{max} to be expected on this basis for mono-, di-, and tri-substituted α,β-unsaturated ketones is as follows:

TABLE 4

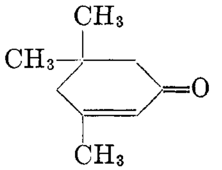
Woodward's (306) calculated and observed values of λ_{max} for some unsymmetrical α,β-dienes

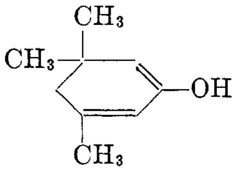
COMPOUND	λ_{ss}	λ_{tt}	$\frac{\lambda_{ss} + \lambda_{tt}}{2}$	$\lambda_{obsd.}$
	mμ	mμ	mμ	mμ
$CH_3CH\overset{t}{=}CHCH\overset{s}{=}CH_2$	217	227	222	223.5
 $CH_2\overset{t}{=}\underset{\displaystyle CH_3}{\underset{\vert}{C}}-CH\overset{s}{=}CH_2$	217	227	222	220
 $CH_2\overset{t}{=}\underset{\displaystyle CH_2CH_2CH{=}C(CH_3)_2}{\underset{\vert}{C}}-CH\overset{s}{=}CH_2$	217	227	222	224.5
 $\overline{CH_2(CH_2)_4C}\overset{t}{=}CH-CH\overset{s}{=}CH_2$	217	247	232	236.5
 $\overline{CH_2CH_2\underset{\displaystyle CH_3}{\underset{\vert}{C}H}CH_2CH\overset{t}{=}C}-\overset{\displaystyle CH_3}{\overset{\vert}{C}}\overset{s}{=}CH_2$	227	237	232	235
 $\overline{CH_2CH_2\underset{\displaystyle CH(CH_3)_2}{\underset{\vert}{C}H}CH\overset{s}{=}CH-C}\overset{t}{=}CH$	227	237	232	232
$\Delta^{3,5}$-Cholestadiene 	237	247	237	235

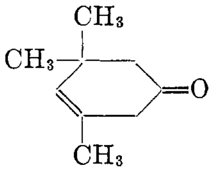
SUBSTITUTION		λ_{max} TO BE EXPECTED
		mμ
α or β		225
α,β or β,β	no exocyclic bond	235
	one exocyclic bond	240
α,β,β	no exocyclic bond	247
	one exocyclic bond	252

Evans and Gillam (81, 82, 98) and other investigators (14, 93, 300) have measured the spectra of many α,β-unsaturated ketones and aldehydes and found additional evidence to substantiate Woodward's table. However, Evans and Gillam found that the aldehydes have a λ_{max} only 5 mμ lower than that of the corresponding ketones, rather than 10 mμ. In this connection, Evans and Gillam (83) measured the spectra of dienones and dienals, C=C—C=C—C=O, to find that their λ_{max} fall between 269 and 317 mμ; here too they found that a substitution causes roughly a 10-mμ shift znd that the aldehydes absorb light of 5 mμ shorter wave length than the corresponding ketones. Also, they found that there is a slightly larger substitution effect the farther away is the substitution from the carbonyl carbon atom. Wilds *et al.* (300) find that a phenyl group exerts approximately the same bathochromic effect on the λ_{max} of α,β-unsaturated ketones as does a second double bond.

Klotz (153) has pointed out an excellent illustration of how these generalizations about the position of the wave length of the maximum absorption band may be of use. In the reaction of isophorone (XI) with methylmagnesium bromide, Kharasch and Tawney (149) could not decide from chemical tests whether the structure of the product was XII or XIII.


XI


XII


XIII

If it were XII, it should have a λ_{max} just a little larger than that of 1,3-hexadiene, while if it were XIII it should have a spectrum characteristic of a saturated ketone, i.e., $\lambda_{max} \backsim 275$ mμ, $\epsilon < 100$. Kharasch and Tawney (150) recorded the spectra of isophorone and of the product; from figure 2 one can easily decide that the latter has the structure of XIII and is $\Delta^{3,4}$-3,5,5-trimethylhexenone Notice, too, that isophorone has the spectrum of an α,β-unsaturated ketone.

C. α,β-*Unsaturated imino compounds*

Evans and Gillam (82) chose the semicarbazones of α,β-unsaturated carbonyl compounds, RCH=CHCH=NCONH$_2$, as the simplest class of compounds containing the C=C—C=N system. For these compounds they noted four effects (typical spectra are drawn in figure 3): (*1*) a bathochromic and hyperchromic effect in the maximum absorption band over the corresponding carbonyl compound; (*2*) a disappearance of the α,β-unsaturated carbonyl *R* band; (*3*) a loss in difference between the aldehyde and ketone derivatives; (*4*) the lack of a regular substitution effect and the fact that all the of λ_{max} fall within the range 267 ± 7.5 mμ (53, 100, 118, 152). The authors turned to the oximes of α,β-unsaturated carbonyl compounds, but again could not detect a regular substitution effect on the C=C—C=N system.

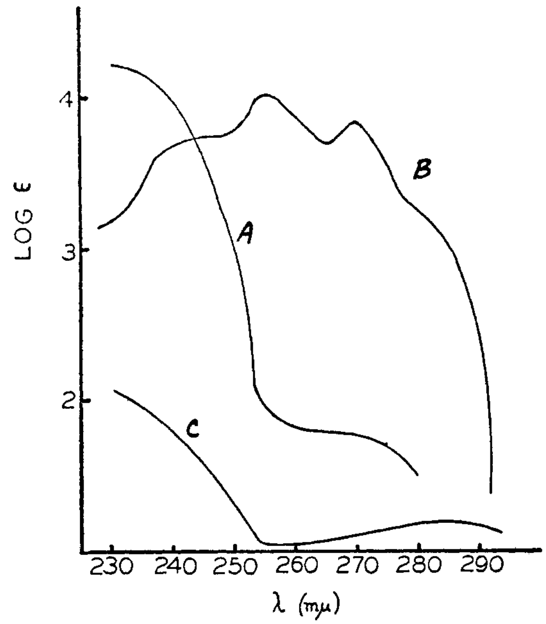


FIG. 2. Absorption spectra of isophorone (XI) (A); 1,3-cyclohexadiene (B); $\Delta^{3,4}$-3,5,5-trimethylhexenone (XIII) (C). Redrawn from reference 153 through the courtesy of the Editor, Professor Norris W. Rakestraw.

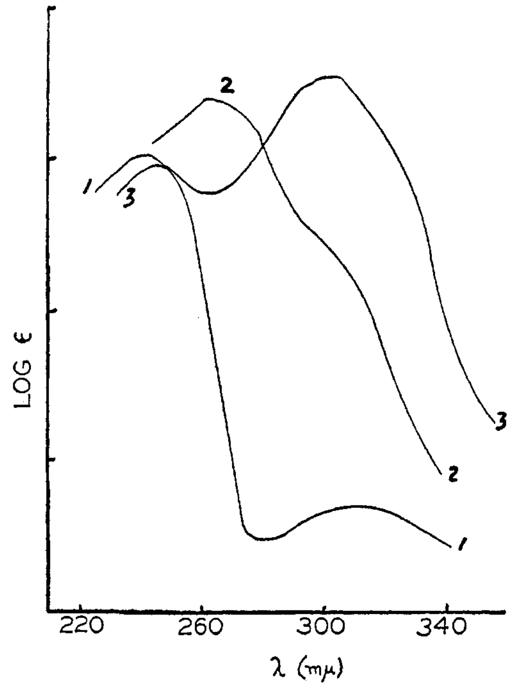
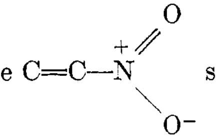


FIG. 3. Absorption spectra of a typical α,β-unsaturated carbonyl compound (curve 1), an α,β-unsaturated carbonyl semicarbazone (curve 2), and an α,β-unsaturated carbonyl thiosemicarbazone (curve 3).

Upon studying the thiosemicarbazones, RCH=CHCH=NCSNH$_2$, Evans and Gillam found that all of them have two bands; one in the region of 245 mμ and one in the small range of 301.5 ± 2 mμ. Nevertheless, an orderly substitutive effect was not observed. Since the thiosemicarbazones of saturated carbonyl compounds have their two bands near 230 mμ and 271 mμ, the authors point out that the thiosemicarbazones offer another means of spectroscopic detection of isolated and α,β-unsaturated carbonyl compounds. That is, the absorption bands for the saturated and unsaturated compounds fall in different regions (109).

	SATURATED	α,β-UNSATURATED
	mμ	mμ
Carbonyl	275 ($\epsilon < 100$)	220–250 ($\epsilon \backsim 10^4$)
Thiosemicarbazones	230 and 271	245 and 301.5

D. *Nitroölefins*

Braude, Jones, and Rose (37) found that although an isolated nitro group gives rise to a low-intensity band near 270 mμ (34), the  $C{=}C{-}\overset{+}{N}(=O)O^-$ system exhibits a high-intensity band at 225 mμ but none at longer wave lengths as do the α,β-unsaturated carbonyl compounds. Lengthening of the conjugated chain as in α-nitrobutadiene and β-nitrostyrene, i.e., CH$_2$=CHCH=CHNO$_2$ and C$_6$H$_5$CH=CHNO$_2$, respectively, results in a high-intensity band appearing near 300 mμ. In addition, the shorter wave-length band near 225 mμ persists, which is peculiar to the nitro compounds. Substituents attached to the α,β-ethylenic bond of the nitroölefins cause auxochromic effects; thus $\Delta\lambda_{\text{alkyl}}$ = *ca.* 10 mμ and $\Delta\lambda_{\text{Br}}$ = *ca.* 30 mμ.

VII. LINEARLY CONJUGATED SYSTEMS

It was shown above how $\lambda_{\max}$ is affected by the conjugation of chromophores and, in general, $\lambda_{\max}$ is larger the longer is the conjugated system. One may consider molecules containing many chromophores conjugated in a linear fashion such that the molecule has essentially only one axis. There are several types of such linearly conjugated systems, among which may be included the following (possible resonating forms are indicated):

1. *Polyenes* (*163*):

$$R(CH{=}CH)_nCH{=}CHR,\ R\overset{\pm}{C}H(CH{=}CH)_n\overset{\mp}{C}HR$$

Examples: diphenylpolyenes (71, 107), carotenoids (165, 309), dialkylpolyenes (166), and dyes of the malachite green type in strong acid

2. Polyenals and polyenimines:

$R(CH{=}CH)_nCH{=}O$, $R\overset{+}{C}H(CH{=}CH)_n\overset{-}{O}$

Examples: polyenaldehydes

$R(CH{=}CH)_nCH{=}NR$, $R\overset{+}{C}H(CH{=}CH)_n\overset{-}{N}R$

Examples: polyenal Schiff bases (anils (118), phenylhydrazones (36), etc.)

$R(CH{=}CH)_n CH{=}NN{=}CH(CH{=}CH)_mR$,

$$\left\{\begin{array}{l} R\overset{+}{C}H(CH{=}CH)_n\overset{-}{N}N{=}CH(CH{=}CH)_mR \\ R\overset{-}{C}H(CH{=}CH)_nN{=}\overset{+}{N}{=}CH(CH{=}CH)_mR \\ R\overset{\pm}{C}H(CH{=}CH)_mN{=}N(CH{=}CH)_m\overset{\mp}{C}HR \end{array}\right\}$$

Examples: polyene-azines (85)

3. Amide type (simplest member is an amide)

$R_2N(CH{=}CH)_nCH{=}O$, $R_2\overset{+}{N}{=}CH(CH{=}CH)_n\overset{-}{O}$

Examples: merocyanines (46, 55)

4. Amidinium type

$R_2N(CH{=}CH)_nCH{=}\overset{+}{N}R_2$, $R_2\overset{+}{N}{=}CH(CH{=}CH)_nNR_2$

Examples: polyene-azomethines (44, 55, 156) and dyes of the malachite green type (197)

5. Carboxyl ion type (simplest member is the ion of formic acid)

$^-O(CH{=}CH)_nCH{=}O$, $O{=}CH(CH{=}CH)_nO^-$

Examples: polyenedicarboxylic acids and esters (16, 285)

These five types of dyes fall into two classes:[13]

Class I: Dyes to be included in this class are those for which there is one predominant canonical structure, such as is found for those of types 1, 2, and 3, above. These compounds give rise to ionic resonating forms of higher potential energy than the normal classical structures.

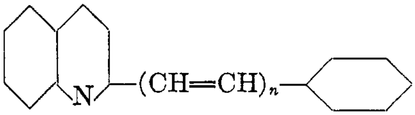
According to equation 2 the wave length of light absorbed by a unit vibrating chromophore can be given by the equation $\lambda = 2\pi C/\sqrt{k/m}$. If n such chromophores are joined, each with the same restoring force constant, k, and effective mass of vibrating electrons, m, and if they vibrate in phase such that the system resembles a single oscillator, one can express the wave length of the absorbed light by a similar equation, $\lambda = 2\pi C/\sqrt{k/nm}$. By squaring both sides,

$$\lambda^2 = \frac{4\pi^2 C^2 m}{k} \cdot n$$

---

[13] See a similar classification by Schwarzenback, Lutz, and Felder (272).

one gets an equation for a straight line, $\lambda^2 = A + Bn$, where B is a constant, equal to $4\pi^2C^2m/k$, and A is the intercept value when n is zero. Therefore, the square of the wave length of the maximum absorption band, λ^2_{max}, should vary linearly with the number of chromophores.[14] Lewis and Calvin (182) showed that this equation holds true for the diphenylpolyenes, $C_6H_5(CH{=}CH)_nC_6H_5$, whose spectra were measured by Hauser, Kuhn, and coworkers (107). Compton and Bergmann (71) found this same relationship to hold for the α-(α-quinolyl)-ω-phenylpolyenes:



The latter authors point out the very close similarity between the spectra of the n^{th} member of this series and that of the $(n + 1)^{\mathrm{th}}$ member of the diphenylpolyene series, giving evidence that the chromophoric character of the α-quinolyl group is equivalent to that of a styryl group.

From the measurements recorded by Hauser, Kuhn, *et al.* (106, 107) for the polyenals, and their own for the polyenimines, Ferguson and Branch (85) illustrated that, although there are different types of chromophores (C═O, C═C, C═N) in the conjugated chains of dyes of types 2 and 3, above, there still exists essentially the same type of oscillator, in that λ^2_{max} varies linearly with the number of chromophores, n. A plot of λ^2 *vs.* n for these compounds, and also for the diphenylpolyenes, is shown in figures 4a and 4b.

Measurements with the simple polyenes, $R(CH{=}CH)_nR$, are not completely satisfactory, in that the few known values of λ_{max} were determined in different solvents and, too, close agreement between values reported by different authors is lacking. However, a plot of λ^2_{max} against the chain length approximates a straight line. It is of interest to notice, as Heilbron, Jones, and their collaborators have pointed out (108), that the conjugated polyenyne molecules closely resemble the polyenes spectroscopically. For example, from the value of λ_{max} for butadiene (217 mμ) and an assumed value for hexatriene, 265 mμ, a straight line can be drawn whose equation, $\lambda^2 = (0.09 + 2.31n) \times 10^4$ mμ, can be used to calculate the λ_{max} for longer molecules, both polyenes and polyenynes. This has been done and the calculated values are compared with observed values in table 5. Little significance should be attached to these calculated values since solvent effects, which may cause changes in λ_{max} by 20 mμ, and substitution effects have not been considered.

The results are interesting when one groups the conjugated polyene and polyenyne series together and calculates λ_{max} by making substitution corrections as Jones did for the α,β-dienes. Here, values of λ_{max} (calculated) were obtained for the dienes by adding, to the λ_{max} of butadiene, 5 mμ for each alkyl and 6 mμ for each RCHOH— substituent, and for the vinylacetylenes, 6 mμ for each

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[14] Several investigators have expressed this same relationship by similar equations (4, 5, 114, 165).

RCHOH— and 1 mμ for each alkyl substituent. In the case of the $n = 3$ compounds, the base value for a triene was taken as 265 mμ, for a C═C—C═C—C≡C system as 259 mμ, and for a C═C—C≡C—C═C system as 253 mμ. With the trienes, 6 mμ for each RCHOH— and 5 mμ for each alkyl substituent was added to the base value, and for both of the other two systems

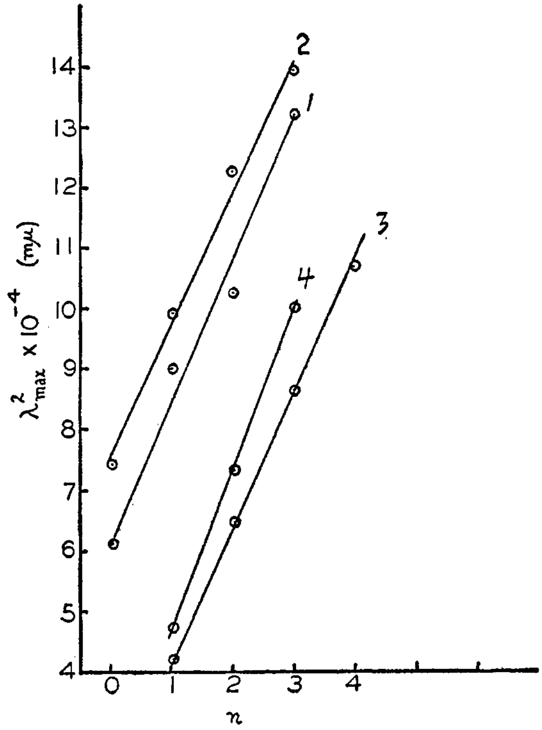
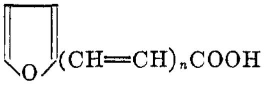
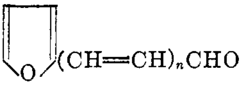


FIG. 4a. A plot of λ^2_{max} against the number of ethylenic bonds, n, in the linearly conjugated series:



Curve 1



Curve 2

$CH_3(CH{=}CH)_nCOOH$
Curve 3

$CH_3(CH{=}CH)_nCHO$
Curve 4

each alkyl and each RCHOH— substituent was set equal to an increase of 2 and 6 mμ, respectively. In this manner the values of λ_{max} for a number of such compounds were calculated; a comparison with the observed values is shown in table 6. Although there are a few deviations of 10–15 mμ, many calculated values agree very closely with the observed ones.

There are a few exceptions among dyes of Class I: for instance, the *p*-dimethylaminophenylpolyenals, $(CH_3)_2NC_6H_4(CH{=}CH)_nCHO$ (158), the *p*-phenylenediamine Schiff bases of phenylpolyenals,

$$C_6H_5(CH{=}CH)_nCH{=}NC_6H_4N{=}CH(CH{=}CH)_nC_6H_5$$

(85), and the *p*-polyphenyls (97). For these three series it is found that a plot of λ^2_{max} against the number of ethylenic groups in the chain, n, gives a curve that is convex upward (figure 5). This is understandable in the case of the polyphenyls when one considers the resonance involved. The structures concerned in the absorption of light are of the type:

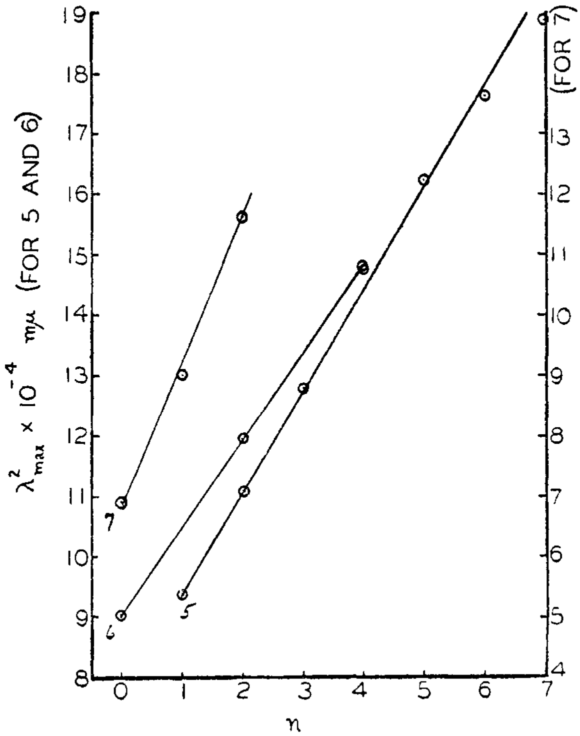
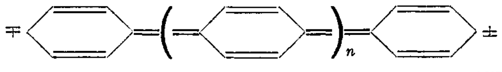


FIG. 4b. A plot of λ^2_{max} against the number of ethylenic bonds, n, in the linearly conjugated series: $C_6H_5(CH{=}CH)_nCHO$ (curve 5), $C_6H_5(CH{=}CH)_nCH{=}NN{=}CH(CH{=}CH)_nC_6H_5$ (curve 6), and $C_6H_5(CH{=}CH)_nCH{=}NC_6H_5$ (curve 7).



which contribute at the expense of the Kekulé resonance. When the number of phenyl groups is small, the percentage increase in length and contribution of these polar forms is sufficient to outweigh the additional energy required to overcome the Kekulé resonance, but as the number of phenyl groups increases, the percentage of contribution from polar forms (only two forms for each molecule while the number of Kekulé forms is 2^n) decreases. Hence, an increase in λ_{max} can be expected for each additional phenyl group, but the increase will diminish with increasing chain length. This amounts to an increase in the restoring force constant, k, with increasing n; this is contrary to the assumption that k is a constant.

TABLE 5

Observed and calculated values of λ_{max} for polyenes and polyenynes

n	λ_{max} (OBSERVED)	λ_{max} (CALCULATED)	COMPOUND	REFERENCE
	$m\mu$	$m\mu$		
1	190	155	$CH_2{=}CH_2$	(279)
2	217	(217)	$CH_2{=}CHCH{=}CH_2$	(278)
	219		$CH_2{=}CHCH{=}CH_2$	(172)
3	260	(265)	$CH_2{=}CHCH{=}CHCH{=}CH_2$	(161)
	257		$CH_2{=}CHCH{=}CHCH{=}CH_2$	(160)
	264		$CH_3CHOHCH{=}CHC{\equiv}CC(CH_3){\equiv}CHCH_3$	(110)
	253		$CH_2{=}C(CH_3)C{\equiv}CC(CH_3){=}CH_2$	(15)
4	302	305	$CH_2{=}CH(CH{=}CH)_2CH{=}CH_2$	(161)
	320		$CH_3(CH{=}CH)_4CH_3$	(20, 166)
	305		$CH_3CHOH(CH{=}CH)_3C{\equiv}CH$	(110)
	311		$CH_3(CH{=}CH)_4CH_2OH$	(110, 253)
5	341	341	$CH_3CHOH(CH{=}CH)_2C{\equiv}C(CH{=}CH)_2CHOHCH_3$	(110)
6	375	372	$CH_3(CH{=}CH)_6CH_3$	(166)
	386		$HOOCCH(CH_3)CH{=}CHCH{=}C(CH_3)(CH{=}CH)_2{-}C(CH_3){=}CHCH{=}CHCH(CH_3)COOH$	(110)
7	392	403	$[CH_3CHOH(CH{=}CH)_3C{\equiv}]_2$	(110)
8	431	431	$[CH_3OOCCH_2(CH{=}C(CH_3)CH{=}CH)_2]_2$	(110)
	420 (445)		Dihydro-β-carotene	(142)
9	466 (497)	457	β-Carotene	(80)
	502		*trans*-Bixindialdehyde	(165)
10	445 (475)	482	α-Carotene	(142)
	474 (507)		Violaxanthin	(143)
11	517	505	Lycopene	(80, 107, 165)
	495		γ-Carotene	(165)
	521		β-Carotene	(142)

Class II: Dyes to be included in this class are those for which there are two

TABLE 6*

Observed and calculated values of λ_{max} *for compounds containing two or three conjugated* $C{=}C$ *or* $C{\equiv}C$ *bonds*

λ_{max} (OBSERVED)	λ_{max} (CALCULATED)	COMPOUND
		Two conjugated groups†
mμ	mμ	
230	228	$CH_3(CH{=}CH)_2CHOHC{\equiv}CH$
229	228	$CH_3(CH{=}CH)_2CHOHC{\equiv}CCHOH(CH{=}CH)_2CH_3$
225	225	$CH_3CH{=}CHCHOHC{\equiv}CC(CH_3){=}CHCH_3$
224	223	$CH_3CH{=}CHCHOHC{\equiv}CCH{=}CH_2$
225	224	$CH_3CH{=}CHCHOHC{\equiv}CC(CH_3){=}CH_2$
223	223	$CH_3CHOHCH{=}CHC{\equiv}CH$
228	229	$CH_3(CH_2)_2CHOHC{\equiv}CCH{=}CHCHOHCH_3$
224	229	$C_6H_5CHOHC{\equiv}CCH{=}CHCHOHCH_3$
225	229	$CH_3OC_6H_4CHOHC{\equiv}CCH{=}CHCHOHCH_3$
229	229	$CH_3CH_2C(OH)(CH_3)C{\equiv}CCH{=}CHCHOHCH_3$
228	229	$CH_3CH{=}CHCHOHC{\equiv}CCH{=}CHCHOHCH_3$
228	225	$CH_3(CH_2)_3C{\equiv}CC(CH_3){=}CHCH_2OH$
228	225	$CH_3(CH_2)_3C{\equiv}CC(CH_3){=}CHCHOHCH_3$
228	225	$CH_3(CH_2)_3C{\equiv}CC(CH_3){=}CHC(OH)(CH_3)_2$
223	223	$(CH_3)_2C(OH)CH{=}CHC{\equiv}CH$
224	224	$CH_3CHOHC(CH_3){=}CHC{\equiv}CH$
220	220	$CH_3CH{=}C(CH_3)C{\equiv}CH$
227	227	$CH_3CH{=}CHCH{=}CHCH_3$
226	224	$CH_3(CH_2)_3C{\equiv}CCH{=}CHCHOHCH_3$
228	225	$CH_3(CH_2)_2CHOHC{\equiv}CC(CH_3){=}CHCH_3$
225	225	$CH_3CH{=}CHCHOHC{\equiv}CC(CH_3){=}CHCH_3$
223	223	$CH_3CHOHCH{=}CHC{\equiv}CH$
226	224	$CH_3CHOHCH{=}CHC{\equiv}C(CH_2)_3CH_3$
		Three conjugated groups
260	(265)	$CH_2{=}CHCH{=}CHCH{=}CH_2$
272	275	$CH_2{=}C(CH_3)CH{=}CHC(CH_3){=}CH_2$ (148)
276	275	$CH_3(CH{=}CH)_3CH_2OH$
278	275	$CH_3(CH{=}CH)_3CHOHC{\equiv}CH$
260	270	$CH_3CHOH(CH{=}CH)_2C{\equiv}CH$
264	263	$CH_3CHOHCH{=}CHC{\equiv}CC(CH_3){=}CHCH_3$
280	265	$CH_3CHOHCH{=}CHC{\equiv}CCH{=}CHCHOHCH_3$
281	276	$CH_3(CH{=}CH)_3CHOHC{\equiv}CCHOH(CH{=}CH)_3CH_3$
264	263	$CH_3CHOHCH{=}CHC{\equiv}CC(CH_3){=}CHCH_3$
259	259	$CH_3CHOHCH{=}CHC{\equiv}CCH{=}CH_2$
259	261	$CH_3CHOHCH{=}CHC{\equiv}CC(CH_3){=}CH_2$
279	265	$CH_3CHOHCH{=}CHC{\equiv}CCH{=}CHCHOHCH_3$
264	263	$CH_3CHOHCH{=}CHC{\equiv}CC(CH_3){=}CHCH_3$
255, 269	259	$CH_2{=}CHC{\equiv}CCH{=}CH_2$ (78)

* Values for compounds not listed in table 5 are from reference 110.

† Braude (34) reports three maxima for a conjugated diacetylenic compound, 2,7-dimethylocta-3,5-diyn-2,7-diol, at 229, 241, and 256 mμ.

or more nearly equivalent canonical structures, such as is found for those of types 4 and 5 above. The dye molecules will resonate chiefly among the two or more

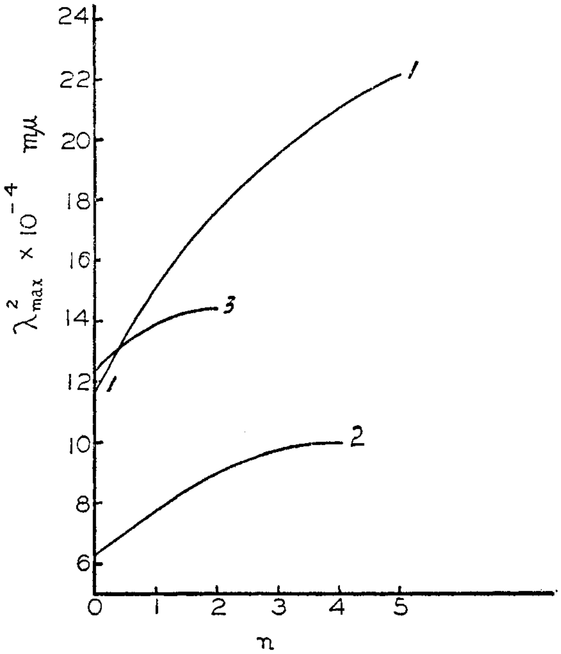
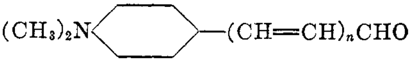


FIG. 5. A plot of λ^2_{max} against the number of ethylenic groups for the homologous series:



Curve 1

Curve 2

Curve 3

nearly equivalent structures but only by passing through many less stable structures (226), such as, for example, forms XV.

$$R_2N—CH{=}CH—CH{=}CH—CH{=}\overset{+}{N}R_2$$

XIV

$$\left\{\begin{array}{l} R_2N—CH{=}CH—CH{=}CH—\overset{+}{C}H—NR_2 \\ R_2N—CH{=}CH—\overset{+}{C}H—CH{=}CH—NR_2 \\ R_2N—\overset{+}{C}H—CH{=}CH—CH{=}CH—NR_2 \end{array}\right\}$$

XV

$$R_2\overset{+}{N}{=}CH—CH{=}CH—CH{=}CH—NR_2$$

XVI

The transition of the molecule from one extreme structure—say, for example, XIV—to the other nearly equivalent structure, XVI, involves a great motion of electrons and this amounts to two facts: (*1*) that the molecule will be easily polarizable; (*2*) that the electronic oscillations will extend practically to the ends of the molecule. Lewis and Calvin (182), in their summary on the rules for absorption, point out that the determining factors of color are (*1*) the number of electrons involved (which is dependent upon the length of the conjugated system and the amount of effective charge transported) and (*2*) the electron mobility, i.e., the induced polarization (polarizability) rather than the permanent dipole moment.[15] Several authors have shown that there is no simple relationship between λ_{max} and the polarity of chromophores (116).

For dyes of Class II the color will deepen rapidly with increasing length of the molecule. When the molecule passes from one of the equivalent classical structures to the other, each carbon–carbon bond changes from a double to a single bond or from a single to a double bond, and since both structures are equally probable each carbon–carbon bond is identical. Therefore, the electronic oscillations throughout the molecule can be treated as a longitudinal wave along a string for which the frequency will be inversely proportional to the length. Lewis and Calvin (182) illustrated that this is so by obtaining a straight line when they plotted the number of double bonds in several cyanine dyes against λ_{max}, as measured by Brooker and coworkers (45) and Fisher and Hamer (19, 88; see also 157).

The difference, then, between dyes of Class I and dyes of Class II is the way λ_{max} varies with the length of the conjugated system. For Class I, the square of λ_{max} varies linearly with the length; for Class II, the first power of λ_{max} is a straight-line function of the length of the molecule.

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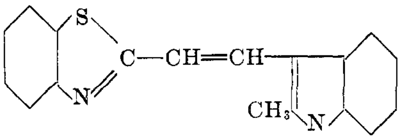
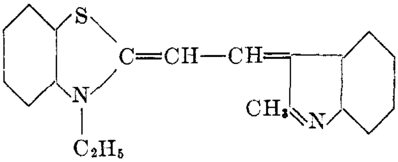
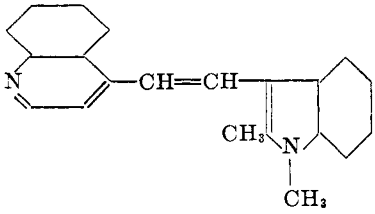
[15] Brooker and coworkers (48) have found for a pair of similar dyes that the more deeply colored have by far the larger dipole moment.



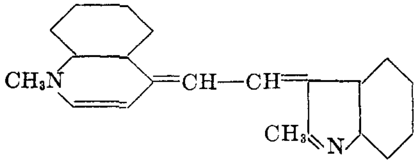
λ_{max} = 392 mμ
μ = 4.06 × 10^{18}



λ_{max} = 506 mμ
μ = 7.68 × 10^{18}

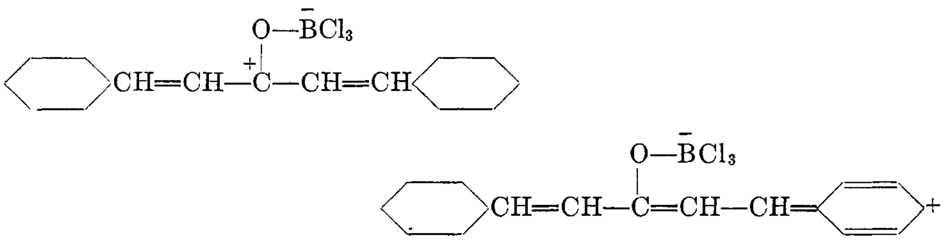


λ_{max} = 394 mμ
μ = 5.43 × 10^{18}

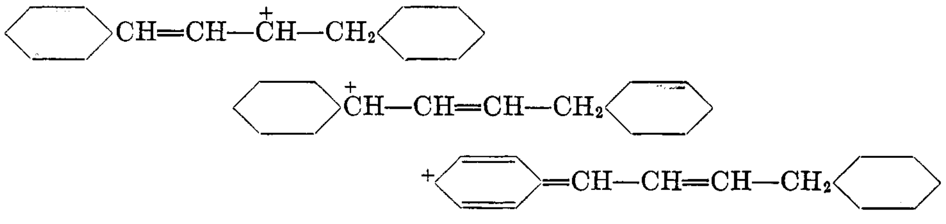


λ_{max} = 616 mμ
μ = 10.6 × 10^{18}

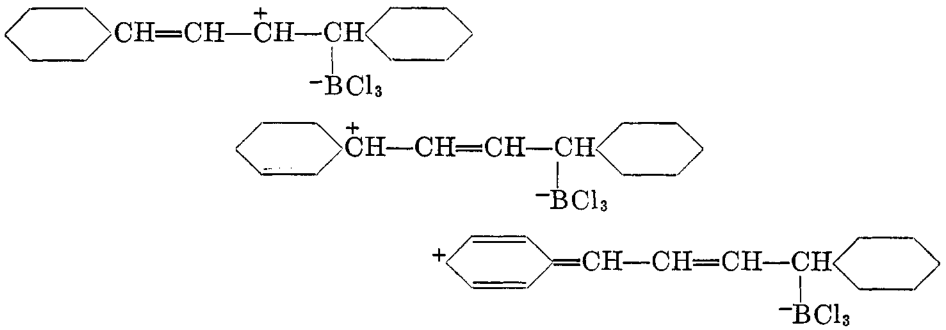
A dye of one class may change to become one of the other class. For instance, the polyenes (106, 166, 168, 188, 234), the polyenones (13, 233), and the carotenoids (80, 208) of Class I fall into Class II when placed in acid media such as $H^{+}_{\text{concd.}}$, stannic chloride, boron trichloride, etc. This is probably due to resonance among structures of near equivalence, such as, for a ketone



or for a polyene,



and



which cause the molecule to have a large polarizability. The anhydrobases of the benzothiazine dyes change from Class II to Class I upon removal of the alkyl halide. This change is quite prominent in figure 6.

Brooker (44) has spoken of dyes which are classified here in Class I as belonging to convergent series, since with increasing number of ethylenic groups the difference in $\lambda_{\max}$ between each successive member decreases, while dyes of Class II, he has said, form non-convergent series, for the difference in $\lambda_{\max}$ between successive members remains constant. This point is illustrated in figure 6.

The discussion so far of dyes of Class II has been limited to those dyes which have two classical structures of nearly equal potential energy. One may also

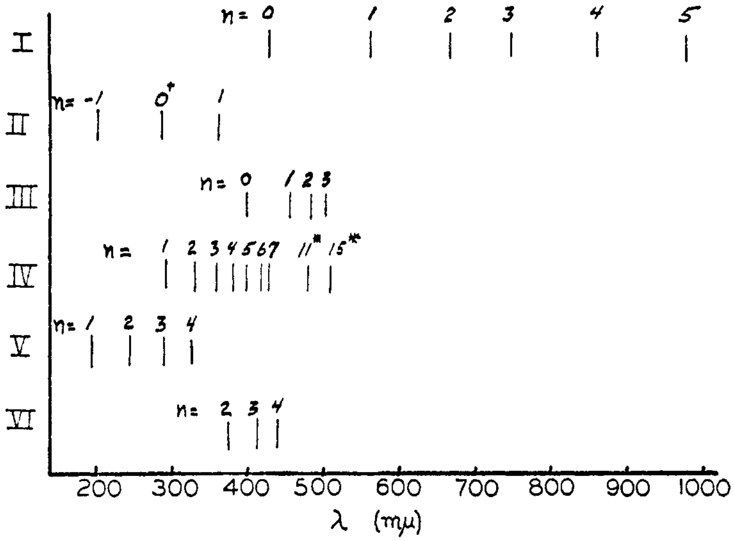
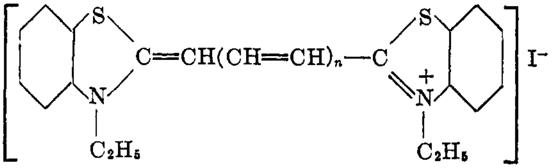


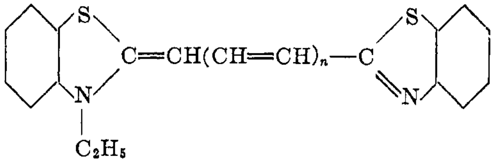
FIG. 6. Absorption maxima of homologues of dyes I (275) and II (272) in Class II and of dyes III (48), IV (107), V (107), and VI (144) in Class I.



I

$CHO(CH{=}CH)_nCH{=}CH{-}O^-$

II



III

$C_6H_5(CH{=}CH)_nC_6H_5$

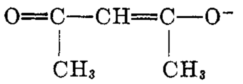
IV

$CH_3(CH{=}CH)_nCOOH$

V

$C_6H_5(CH{=}CH)_nCOCO(CH{=}CH)_nC_6H_5$

VI

+, value for 

$O{=}\underset{CH_3}{C}{-}CH{=}\underset{CH_3}{C}{-}O^-$

* Estimate by Henrici (115) for measurement by Kuhn (164).

consider examples where these two structures will not be equivalent. The λ_{max} of an unsymmetrical dye of type 4 above, $R''N(CH{=}CH)_nCH{=}\overset{+}{N}R'_2$, might be expected to be the arithmetic mean of the two related symmetrical dyes:

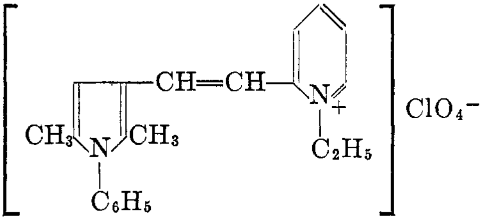
$$R''_2N(CH{=}CH)_nCH{=}\overset{+}{N}R''_2 \quad \text{and} \quad R'_2N(CH{=}CH)_nCH{=}\overset{+}{N}R'_2$$

Brooker (44) and coworkers, and also Fisher and Hamer (19), have found that this is not true in the case of a large number of cyanine dyes.

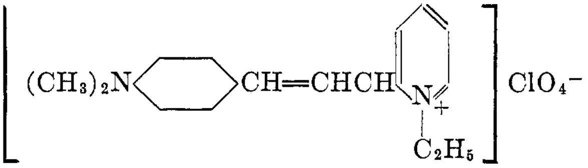
From one of the fundamental postulates of the resonance theory, that the more nearly equivalent are the resonant forms in potential energy the greater will be the resonance energy, one may state that the more equal in energy are the two end groups of the cyanine dyes when carrying the positive charge, the greater will be the resonance in the excited state and therefore the larger will be λ_{max}. Thus, if the two classical structures of the unsymmetrical dye

$$R''_2N(CH{=}CH)_nCH{=}\overset{+}{N}R'_2 \quad \text{and} \quad R''_2\overset{+}{N}{=}CH(CH{=}CH)_nNR'_2$$

are not nearly equivalent, its λ_{max} will fall short of the arithmetic mean of the λ_{max} of the two related symmetrical dyes, and further, the greater the difference in stability of the two forms the greater will be this deviation[16] from the mean. In this connection Brooker *et al.* (45) have measured the spectra of a number of cyanines which are of two families: one, the pyrrole dyes, wherein various groups are paired with the *N*-phenyl-2,5-dimethylpyrrole group and the other, the styryl dyes, in which these same groups are paired with the *N*,*N*-dimethylaniline ring. Two examples are:



Pyrrole dye



Styryl dye

Upon arranging the dyes in each family in order of their increasing *deviation* the sequence of the second end groups in each family is practically the same. This is illustrated in figure 7.

Brooker has given some justification for the observed order by considering the relative stabilities of these groups according to resonance theories, which he calls the "additional double-bond stabilization" factor, and also by comparing the relative basic strengths of two or three of these groups as determined by other physical measurements. Also in this connection, Brooker and his collaborators

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[16] Following Brooker's terminology reference has been made to this deviation of λ_{max} from the arithmetic mean of the λ_{max} of the two related symmetrical cyanines by simply calling it the *deviation.*

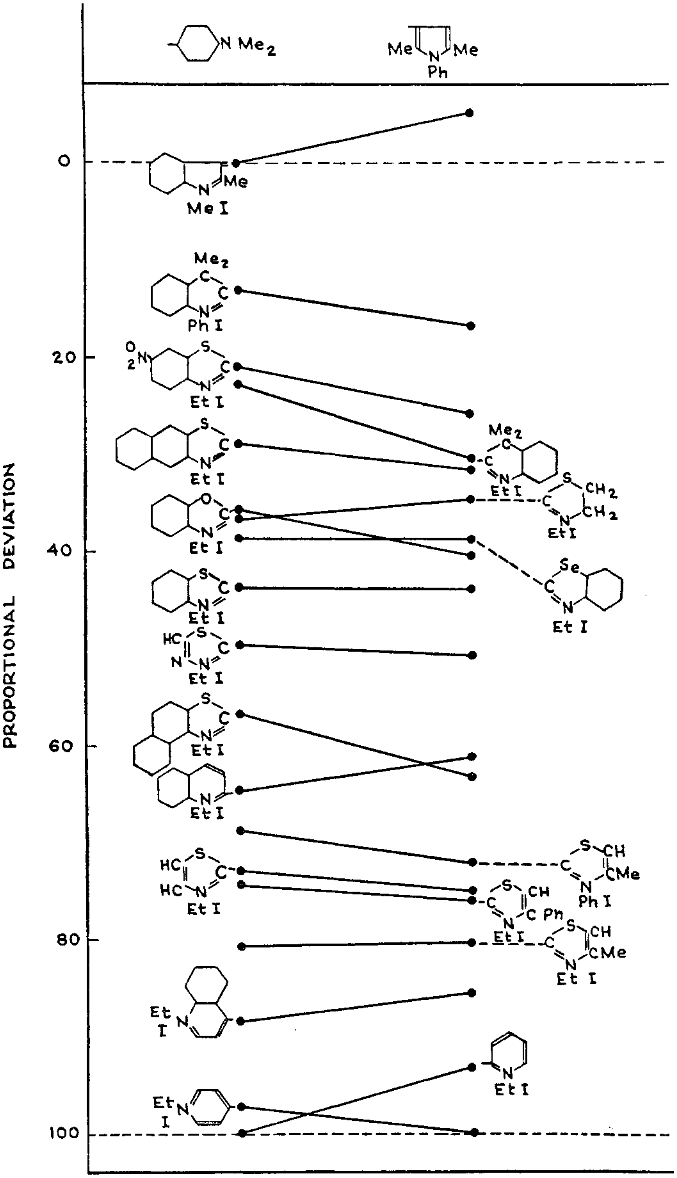
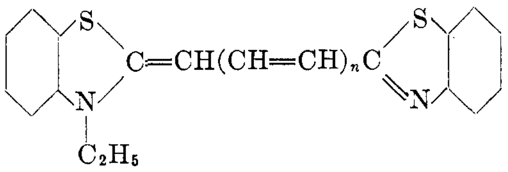
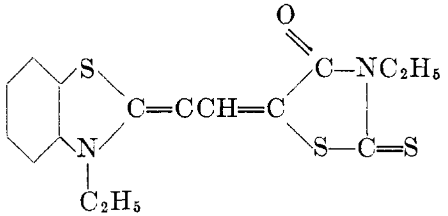


FIG. 7. Comparison of the *deviations* in two series of cyanine dyes. The relative *deviations* shown in the left-hand column are those of the styryl dyes; those on the right are of the pyrrole dyes. Reprinted from reference 44 through the courtesy of Interscience Publishers, Inc., and Dr. L. G. S. Brooker.

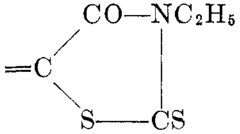
studied the spectra of two families of dyes which belong in Class I. These were the anhydronium bases, such as, for example:



and the merocyanines, as, for instance:



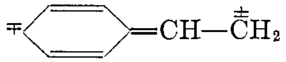
Both homologous series were found to be convergent, i.e., λ_{max} varies linearly with n, but only the merocyanines were studied to ascertain the *deviations*. The relative order of nine different groups paired with the



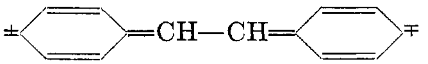
group agrees with that of the pyrrole and styryl dyes, with two exceptions.

VIII. STERIC HINDRANCE AND COLOR

The effects of steric hindrance upon the color of a substance are largely due to its interference with the resonance of the compound, either when the molecule is in its ground state or when it is in one of its excited states. Because of steric hindrance, the resonance may be limited to certain portions of the molecule and thereby affect its potential energy, and of course, its λ_{max}. For instance, consider the spectra of some substituted ethylenes, measured and discussed by Jones (135; see also 6). The λ_{max} for styrene, $C_6H_5CH{=}CH_2$ (240 mμ[17]) (87), is attributed to the resonance among such forms as



where one phenyl ring and the two ethylene carbon atoms are in the same plane (257). The resonance of *trans*-stilbene among such forms as



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[17] Although this λ_{max} is smaller than that of benzene its intensity (log $\epsilon \cong 4.0$) is large, while λ_{max} for benzene is of low intensity and, according to quantum mechanics, corresponds to a transition of low probability (220, 227, 281).

accounts for a larger λ_{max} (295 mμ) and requires that two phenyl rings and the ethylene carbon atoms be coplanar. On the other hand, since in *cis*-stilbene only one phenyl ring and the ethylene carbon atoms can be coplanar simultaneously, it would be expected to have a spectrum similar to styrene, or at least, λ_{max} would be smaller than that of the *trans* isomer; the latter expectation is found to be true. Also, α,β-dimethyl-*trans*-stilbene (6, 189) has a spectrum like that of styrene; this indicates that only one phenyl ring is coplanar with the ethylene carbon atoms. The same considerations apply to unsymmetrical diphenylethylene, and it is seen in figure 8 that interference between the ortho hydrogen atoms will force one phenyl ring to be rotated out of the plane of the paper. It should, and does, have a spectrum similar to that of styrene. Nevertheless, tri- and tetra-phenylethylenes may actually have two phenyl rings coplanar with the ethylene carbon atoms if one, or two, phenyl rings are simply rotated something less than 90° out of the plane (see figure 9). Hence, the two compounds would be expected to have, and do have, spectra similar to that of *trans*-stilbene. Jones (135) has divided these compounds into three groups: compounds which have spectra similar to that of styrene, compounds which have spectra similar to that of *trans*-stilbene, and compounds which have spectra intermediate between these two extremes.

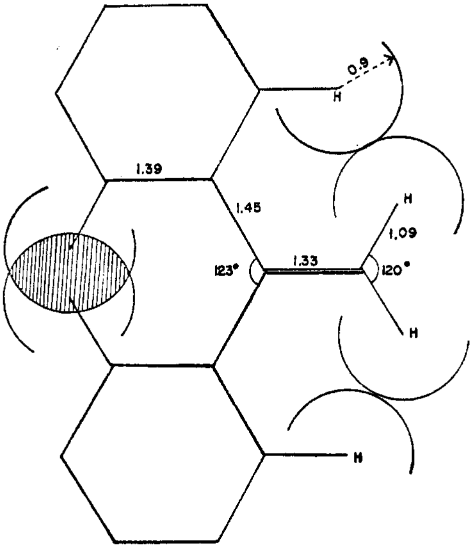


FIG. 8

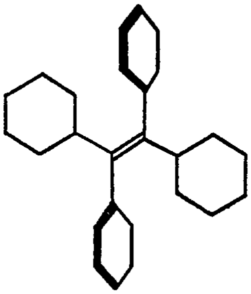


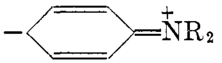
FIG. 9

FIG. 8. *as*-Diphenylethylene. Diagram illustrating interference between ortho hydrogen atoms. Reprinted from reference 135 through the courtesy of the Editor, Professor Arthur B. Lamb, and the Mack Printing Company.

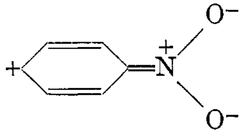
FIG. 9. Tetraphenylethylene

"STYRENE" TYPE OF SPECTRA	INTERMEDIATE SPECTRA	"*trans*-STILBENE" TYPE OF SPECTRA
Styrene	*cis*-Stilbene	*trans*-Stilbene
α,α-Diphenylethylene	α-Methylstilbene	Triphenylethylene
α,β-Dimethyl-*trans*-stilbene		Tetraphenylethylene

Steric strain, arising in the molecule when it is excited to the electronically excited states, would increase the potential energy of these higher states and therefore, according to equation 1, would increase the frequency of the absorbed light (225, 275). This has been illustrated by Remington (255) in the case of substituted *N*,*N*-dimethylanilines. Their ionic resonant forms are of the type

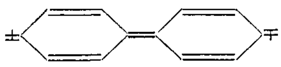


in which the ring, the nitrogen atom, and the methyl carbon atoms must be coplanar. When groups are situated in the ortho positions of the ring there is a spatial interference to such coplanarity and, as expected, there results a hypsochromic shift in λ_{max} (29, 136). Thus, 2-methyl- and 2,6-dimethyl-*N*,*N*-dimethylanilines have successively smaller λ_{max}, a fact which is illustrated in figure 10. Further, upon increasing the size of the ortho group these effects should become more pronounced. This is found true for *o*-*tert*-butyl-*N*,*N*-dimethylaniline, whose λ_{max} is close to that of the *o*,*o*-dimethyl-substituted derivative, and also for the *o*-halogenated *N*,*N*-dimethylanilines, whose values for λ_{max} decrease in the order of increasing size of the halogen atoms. Similar steric effects result when groups are ortho to the nitro group (40a, 209), causing a hindrance to the coplanarity of the oxygen atoms in such resonating structures as

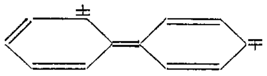


Remington found λ_{max} for *p*-nitro-*N*,*N*-dimethylaniline to diminish rapidly as one, and then two, methyl groups are placed ortho to the nitro group (see figure 10).

Several investigators (58, 113, 232, 235, 257, 276, 286, 301) have offered additional examples of steric hindrance occurring in the excited state of organic molecules, particularly the substituted biphenyls. It is found that 3,3′- or 4,4′-disubstituted biphenyls have spectra similar to that of biphenyl with, perhaps, anticipated substitutive effects. These spectra are thought to correspond to resonance among such forms as



and



where there occurs a double bond between the two rings. For 2,2′-disubstituted, and especially 2,6,2′,6′-tetrasubstituted biphenyls, the spectra are found to be similar to those of the correspondingly substituted benzenes. This is because the steric inhibition between the ortho groups prevents the coplanarity of the two phenyl rings, as would be required for the biphenyl-type resonance. As is to be expected, 9,10-dihydrophenanthrene (XIV) and 4,5-methylene-9,10-dihydrophenanthrene (XV), where the methylene bridges hold the two phenyl rings in a plane, have spectra similar to that of biphenyl (137).

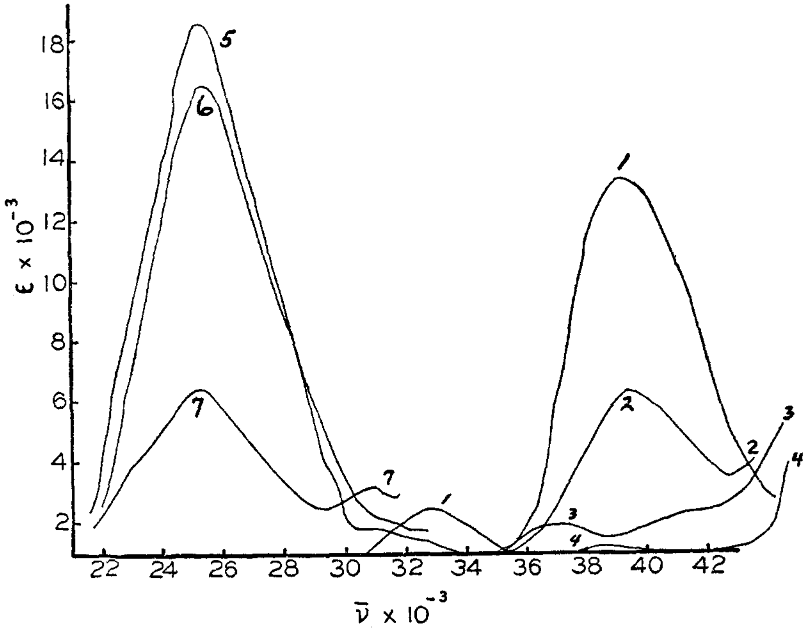
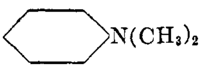
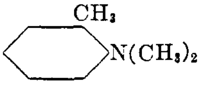


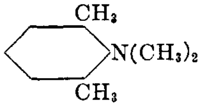
Fig. 10. Absorption spectra of dimethylanilines



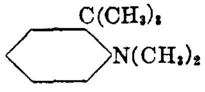
Curve 1



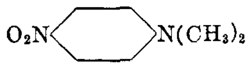
Curve 2



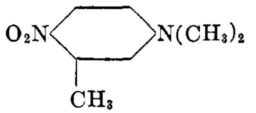
Curve 3



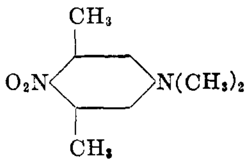
Curve 4



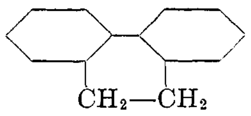
Curve 5



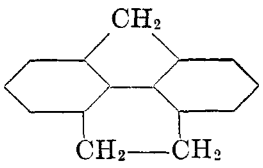
Curve 6



Curve 7

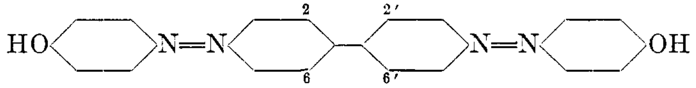


XIV



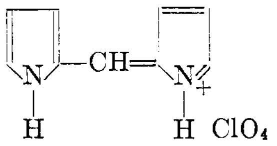
XV

Brode and Morris (42) have reported additional examples of this pinching off of the biphenyl conjugation in some bisazo benzidine dyes.

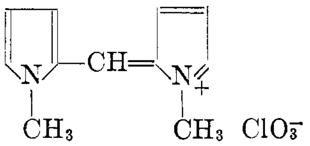


By introducing methyl groups into 2,2′-positions partial insulation of the two azo chromophoric systems was accomplished, and by tetrasubstitution into the 2,2′,6,6′-positions, complete insulation was effected, as evident from their absorption spectra.

Steric hindrance occurring in the ground state of the molecule will in general cause the molecule to absorb at longer wave lengths than a similar compound in which the steric strain does not exist. This is due to an increase in the potential energy of the ground state, bringing about a smaller difference in the energies of the ground and first excited states to allow a smaller excitation energy. An example of this was reported by Brunings and Corwin (50) and a number of additional examples were reported by Brooker *et al.* (47). For instance, Brunings and Corwin found that di-NH-dipyrrylmethene perchlorate (XVI) in chloroform has a λ_{max} at 470 mμ, while di-*N*-methyldipyrrylmethene perchlorate (XVII) in the same solvent has a λ_{max} at 510 mμ.



XVI



XVII

In dye XVI the two pyrrole rings could be coplanar only if there is a slight bending of the N—H bonds. When the hydrogen atoms are replaced by methyl groups, the methyl groups will overlap too much to allow the two pyrrole rings to lie in the same plane. This departure from planarity decreases the resonance in the ground state, bringing about a smaller difference in energies of the ground and first excited states and consequent absorption at longer wave lengths. Brooker and coworkers investigated this bathochromic effect due to crowding in several higher vinylogs of these two dyes and also with other symmetrical and unsymmetrical cyanine dyes. Just as it is found that the rate of racemization or the existence of optical isomers of ortho-substituted biphenyls does not depend solely upon the size of the ortho groups, so did Brooker and collaborators find that there is no simple relationship between the area of overlap in the projections of these cyanine dyes and the shift of λ_{max} to longer wave lengths.

IX. CHEMICAL CONSTITUTION AND THE SHAPE OF SPECTRA

The discussion, up to this point, has been confined to generalizations describing the position of absorption bands in the spectral range 200–800 mμ. Other points of concern about these spectra might be the number of bands appearing and the width, height, and shape of each band. It is worth while to review the correlations between chemical constitution and the shape and existence of several absorption bands for organic molecules.

A. Fine structure

It has been observed by a number of authors (204) that with a decrease in temperature the fine structure of absorption bands increases. This is illustrated in figures 11 and 12. This is in part due to a diminishing random distribution of the molecules in the various vibrational and rotational states by grouping in certain lower and lower vibrational states as the temperature falls. However, this is not the only factor, because in many instances a large decrease in temperature alters very little the fine structure, or broadness, of a band.[18]

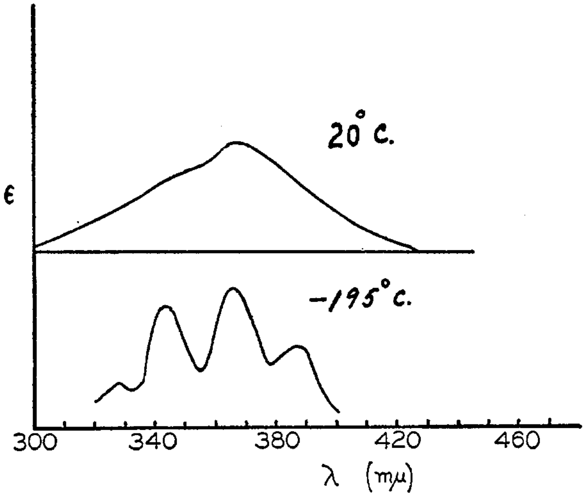


FIG. 11. Absorption spectrum of dodecapentaenic acid in ether–alcohol mixture at 20°C. and −196°C., measured by Hauser, Kuhn, and Seitz (107, page 403).

Suppose that immediately after the absorption of light the initial excited state passes into another excited state, or the electronic vibrational energy of the excited molecules is transformed into low-energy atomic vibrational, or rotational, energy; the probability of the latter process would be determined by the Franck–Condon principle. If this transformation takes place in 10^{-13} to 10^{-14} sec.,[19] then, according to Heisenberg's principle, there will be an uncertainty in

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[18] Compare the explanations given by Rădulescu and collaborators (246, 247).

[19] This value has been chosen because when one divides the resonance energy of a conjugated diene by Planck's constant, h, one obtains this number having the dimensions of time and, which one may consider, gives the order of magnitude of the time required to establish in the excited molecule the conditions of the resonance state (182).

The "natural width" of the band may also be due to a large number of low-frequency vibrational states in the upper electronic level so as to appear almost as a continuum of energy, or to perturbations upon the absorbing molecules from electric and magnetic fields of solvent molecules so as to greatly increase the number of neighboring excited states (32).

the observed frequency of absorbed light by several hundred wave numbers; hence, a diffuse band will be observed. In order for a group to pick up this energy it must, first of all, be attached to the chain of atoms whose electrons are participating in the electronic oscillations. Lewis and Calvin (182) have called this the "loose-bolt" effect, whereby mechanical energy is dissipated through a loosely held, vibrating body. The readiness with which groups will absorb the electronic vibrational energy will be greater the larger their mass and the weaker their restraining forces.[20] Thus, for example, the fine structure of the benzene spectrum gradually disappears in passing over the spectra for fluorobenzene to iodobenzene, pictured in figure 13. Also, it may be noticed that the spectra of phenyl-substituted ethylenes (135) have broad absorption bands without the fine structure characteristic of the ethylene spectrum. On the other hand, compounds containing methylene bridges, such as are found in fluorene, fluorenone, anthrone, and hydrindene, which hold the molecule rigid, show increased fine structure over similar compounds that do not have the bridges (136, 138, 252). Similarly, condensed-ring structures are too rigid to allow low-energy group vibrations and the spectra of such compounds exhibit much fine structure, while

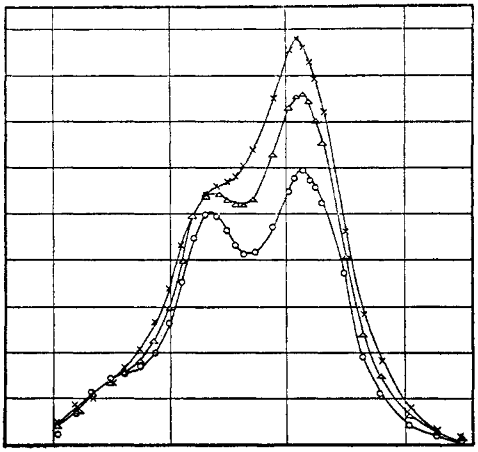
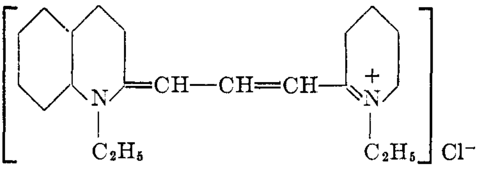


FIG. 12. Absorption spectrum of



at 298°K. (×), at 202°K. (△), and at 108°K. (○). Reprinted from an article by S. E. Sheppard and H. R. Brigham (J. Am. Chem. Soc. **66**, 381 (1944)) through the courtesy of the Editor, Professor Arthur B. Lamb.

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[20] Lewis and Calvin point out that the ability of substances to quench fluoresence closely parallels the absence of fine structure from their spectra.

the substituted derivatives may have spectra which resemble that of the parent hydrocarbon but with a slight broadening of the peaks (136).

It is interesting to consider the spectra of acetone, biacetyl, and triketopentane, measured and discussed by Calvin and Wood (59), among which only the spectrum of biacetyl shows fine structure (figure 14). First of all, the resonance of biacetyl which accounts for the bathochromic shift of its λ_{max} over the λ_{max} of acetone is due to the structures

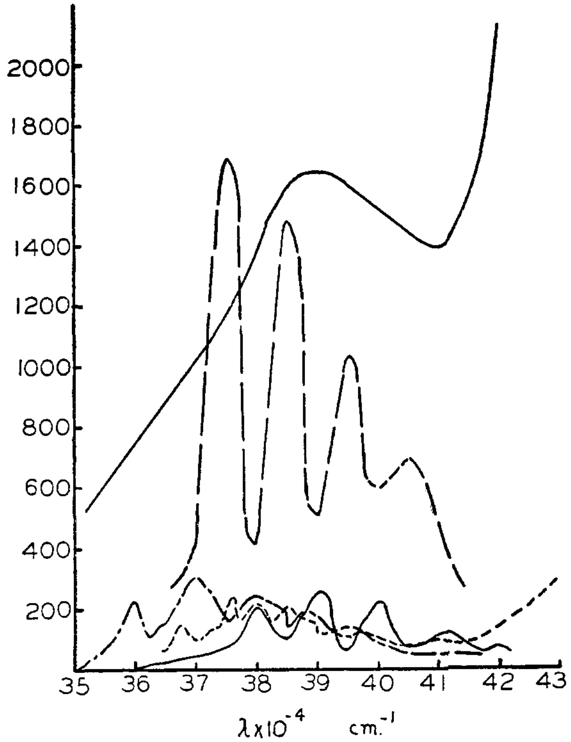
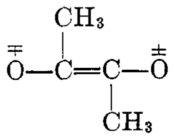


FIG. 13. Absorption spectra of benzene and halobenzenes



$$\overset{\mp}{O}-\overset{\overset{\displaystyle CH_3}{|}}{C}=\underset{\underset{\displaystyle CH_3}{|}}{C}-\overset{\pm}{O}$$

(supported by the fact that the distance between carbonyl carbon atoms is only 1.47 Å.). The acetone band does not exhibit fine structure because fo the "loose-bolt" effect of the methyl groups, whereby the electronic vibrational energy is transformed into low-energy rotational energy.[21] However, the excitational

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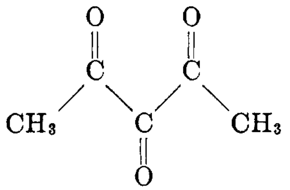
[21] The energy barrier to "free rotation" of the methyl groups of acetone has been estimated to be only about 1 kg.-cal. (268).

energy for biacetyl is presumably too low to cause group vibrations or rotations and the spectrum shows fine structure. On passing to triketopentane, Calvin and Wood have explained that its most stable coplanar configuration is



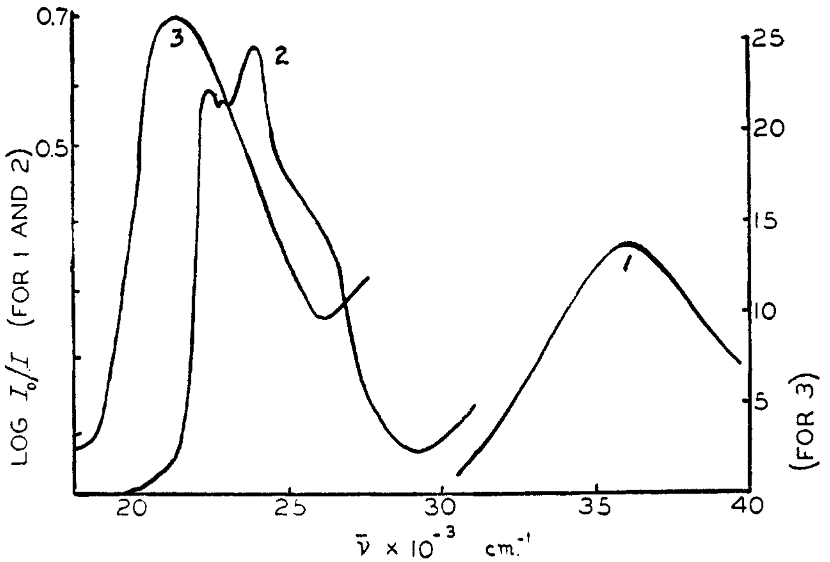
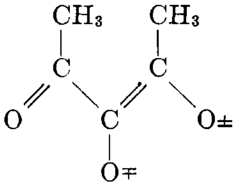
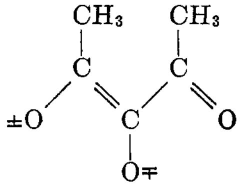


FIG. 14. Absorption spectra of acetone in hexane at room temperature (curve 1), biacetyl in hexane at room temperature (curve 2), and triketopentane in isoöctane at −50°C. (curve 3). Redrawn from reference 59 through the courtesy of the Editor, Professor Arthur B. Lamb.

Owing to the coulombic repulsion between the neighboring oxygen atoms there will be a tendency for one acetyl group to rotate out of the plane of the paper, resulting in a low energy for rotation. With a larger mass than just that of the methyl group, the acetyl group readily dissipates the electronic vibrational energy through group rotational energy and destroys any fine structure. Since the planar configuration necessary to permit the linear oscillation





is impossible, the electronic oscillation extends through only two carbonyl groups and gives a λ_{max} close to that of biacetyl.

The absorption spectra of all unsaturated hydrocarbons contain a group of narrow intense bands in the Schumann region which has been interpreted as the first member of a Rydberg series (64, 65, 241). In addition, these hydrocarbons have a long-wave-length absorption band. For a few hydrocarbons these bands show vibrational structure very similar to that in the Schumann region, and Miss E. P. Carr has found it possible to select comparable points for determination of the energy difference between the two electronic levels. These *Rydberg transition* bands differ from the usual molecular electronic transition bands and may be distinguished by the fact that the former are not appreciably displaced by conjugation of double bonds (64).

On the basis of her interpretation of these long-wave-length bands of the hydrocarbons as due to a Rydberg transition, Miss Carr was able to calculate resonance energies directly from spectra (62). The values for benzene and the cyclohexadienes are in satisfactory agreement with those calculated from thermal data, but there is a wide difference between the thermal and spectral values for cyclopentadiene.

B. Partials

Insulated resonating systems or insulated chromophores will have disjoined electronic oscillations, giving rise to excited states of different energies and, hence, separate absorption bands. Such bands from localized oscillations have been called *partials* (27, 182, 214, 215). This is somewhat related to the section above wherein the insulation of chromophores was discussed. In this respect, it has been observed that molecules of the type $A(CR_2)_nB$, in which A and B are insulated from one another, have spectra approximately the same as solutions of equimolar mixtures of ACR_2H and BCR_2H (39, 95, 139).

A noteworthy example of *partials* is found in the case of the carotenoids studied by Zechmeister and his coworkers (308–312). They found that when an all-*trans* carotenoid is isomerized into a mixture of *cis–trans* isomers, three spectroscopic changes occur: (*a*) the maximum in the visible shifts toward shorter wave lengths, (*b*) a new band appears in the ultraviolet region, referred to as a *cis* peak, and (*c*) the fine structure is diminished. If the double bond about which two portions of the molecule are *cis* acts as an insulating group, such that the electronic oscillations on each side are partially isolated from one another, then these *cis* peaks may be interpreted as *partials*. For short molecules the *cis* peak will be displaced not far from the band for the *trans* isomer but for long molecules it may. Thus, Sandoval and Zechmeister (259) found that the conversion of *trans*-diphenylbutadiene into the *cis* isomer is accompanied by the gradual disappearance of a band at 328 mμ, with the simultaneous appearance of a new one at 313 mμ. On the other hand, the *cis* peak for the long carotenoids appears at shorter wave lengths than the *trans* maximum by 100–150 mμ. Zechmeister, and his collaborators, have also reported that a stereoisomer showing a very high *cis* peak must possess a *cis* double bond near the center of the conjugated system and that as a rough approximation the intensity of the *cis* peak can be taken proportional to the square of the distance between the center of the chromophore and the midpoint of the straight line between its two ends (309). In addition, they find that each *trans* → *cis* rotation causes a decrease in the wave length of the fundamental band (311) by 5 $m\mu$ and that the difference in the λ_{max} for a stereoisomer and that of the all-*trans* form will give a rough indication of the number of *cis* double bonds (310).

A *cis* double bond is not a complete insulator but merely inhibits the electronic oscillation throughout the length of the conjugated system and sets up a shorter vibrating system which stops at the *cis* double bond. This means that the potential energy of the excited state, corresponding to the resonance of the completely conjugated system, is greater; hence there is a hypsochromic shift in the position of the fundamental band, but also there are created new, higher excited states corresponding to the "isolated" oscillating systems which give rise to new bands (*partials*) at shorter wave lengths.

The nitro group occasionally exhibits a *partial* band which may overlap with the main absorption band of the molecule. Several authors have noted this (169).

Often bands have a shoulder which Lewis and coworkers (187) attribute to (*1*) partial resolution of fine structure, (*2*) neighboring *partial* electronic levels, or (*3*) two isomers in rapid equilibrium. They point out that the shoulder on the long-wave band for methylene blue is due to the second, while that of crystal violet is due to the third.

C. y-Bands

If a molecule has a conjugated system extending in more than one dimension there may be two, or even three, optical axes. When such a molecule absorbs light there will be electronic oscillations along these optical axes giving rise to excited states of different potential energies and, hence, absorption bands of different frequencies. Lewis and Calvin[22] have associated the band of lowest frequency with the direction of longest extension in the molecule and called it the x-band. The band corresponding to the axis at right angles to this major axis has been called the y-band. Usually the x-axis for a molecule can be predetermined from its structural formula and frequently there will be just one axis, as is true for the linearly conjugated molecules. For dyes of the triphenylmethane and methylene blue type this may be a little less obvious.

The existence of x- and y-bands may be surmised when one considers the spectra of dyes related to malachite green (182).[23] The x- and y-bands for crystal violet should merge into one, since the two axes are identical.

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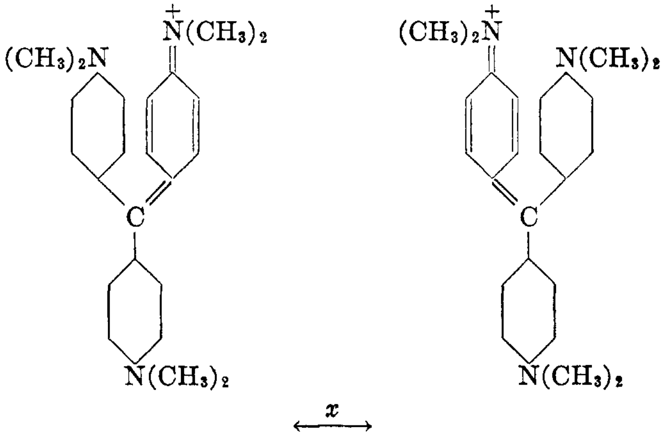
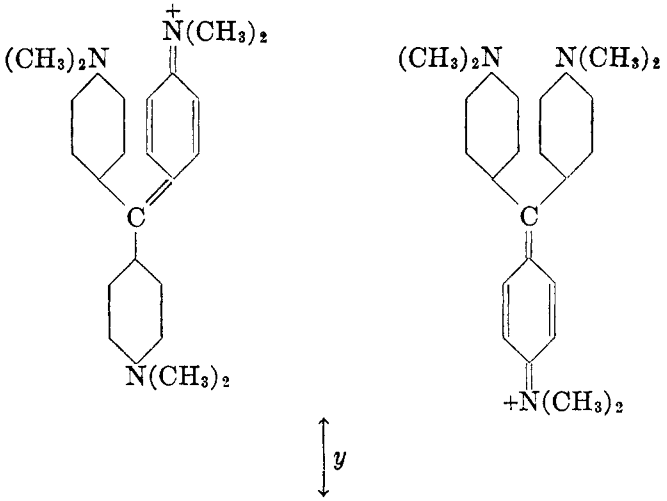
[22] See also the fine discussion of x-, y-, and x'-bands by Branch, Colbert, and coworkers (33, 145, 287, 288).

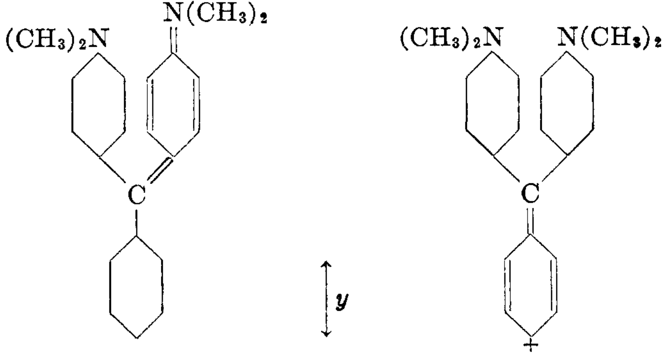
[23] From quantum-mechanical considerations Forster (92) has concluded that malachite green should have two bands to the one of crystal violet. Note also the discussion of Henrici (115) concerning optical axes normal to one another.



and



On the other hand, malachite green should have an x-band of about the same wave length as crystal violet but a y-band of smaller wave length, owing to the fact that the resonance in the y-direction involves a carbonium carbon atom which is of lower stability than an ammonium nitrogen atom.



Now if an auxochrome which readily accepts a positive charge (NR_2 or OCH_3) is placed on the lower phenyl group, this should not affect appreciably the position of the x-band but increase the wave length of the y-band; conversely, an auxochrome which prefers a negative charge (NO_2) should lower the wave length of the y-band to a lower value than is found for malachite green. Finally, the loss of the y-axis, by the removal of the lower phenyl group, as is the case for Michler's hydrol,

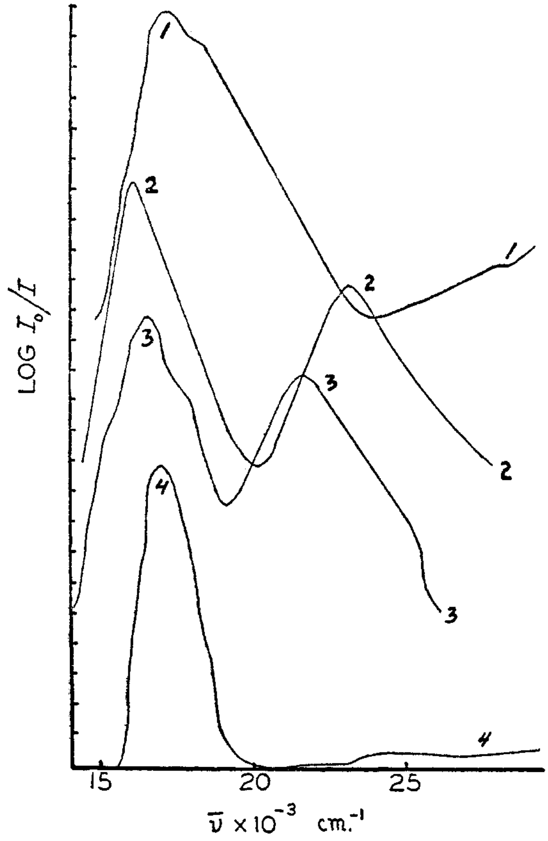
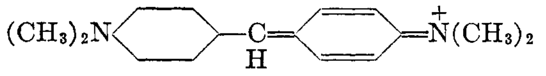


FIG. 15. Absorption spectra of crystal violet (curve 1), malachite green (curve 2), p-methoxymalachite green (curve 3), and the ion of Michler's hydrol (curve 4). 1, 2, and 3 in ethanol; 4 in glacial acetic acid; all at room temperature (179).



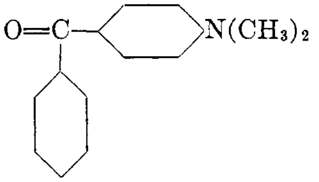
$$(CH_3)_2N\text{-}C_6H_4\text{-}\underset{H}{C}{=}C_6H_4{=}\overset{+}{N}(CH_3)_2$$

should result in the absence altogether of the y-band. These predictions are found to be correct and are illustrated in the spectra pictured in figure 15.

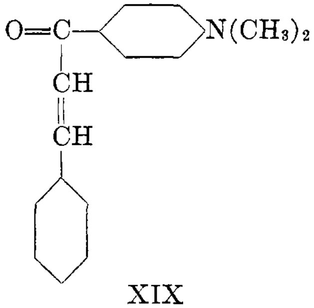
The strongest evidence for the existence of x- and y-bands is supplied through the use of polarized light. Lewis and Bigeleisen (179, 181) produced oriented dye molecules in a rigid solvent and found the absorption of light to be a maximum when light of the same wave length as that of the x-band of malachite green was polarized parallel to the x-direction and a minimum when polarized at right angles to this. The opposite was found true for light of the same wave length as the y-band. That is, when its plane of polarization was parallel to the x-axis, the intensity of absorption was a minimum and a maximum when the light was polarized parallel to the y-direction.

Lewis and Bigeleisen (179) were also able to show by a different method that these second absorption bands for malachite green and fluorescein were y-bands. Weigert (297) had earlier found that when one irradiates a fluorescent substance in a rigid medium with polarized light it reëmits light polarized in the same direction. Wawilow (296) later discovered that if one uses polarized light in the near ultraviolet (of higher energy) there results the same fluorescent bands but the fluorescent light is polarized normal to the exciting light. Lewis and Calvin interpreted this to be due to an excitation by light of sufficient energy to carry the molecule to a higher excited state where the electronic oscillations will be in the y-direction. Before the molecule has time to reëmit its ordinary fluorescence it suffers partial quenching to drop to the first excited state. As a result of this process the y oscillations will change to x oscillations and the molecule will now reëmit light polarized in a different sense to that of the exciting light. Lewis and Bigeleisen (179) found that the maximum of this negative polarization nearly coincides with the maximum absorption in y-bands.

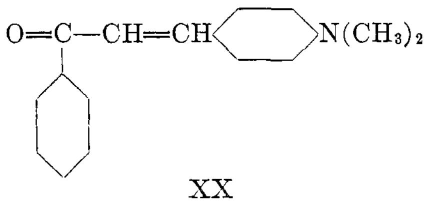
The direct demonstration of such oriented excitation offers considerable experimental difficulty, and more often the indirect approach is made as described above in the case of the crystal violet dyes. For example, Katzenellenbogen and Branch (146) studied the spectra of p-dimethylaminobenzophenone (XVIII) and two of its vinylogs, chalcones XIX and XX.



XVIII



XIX

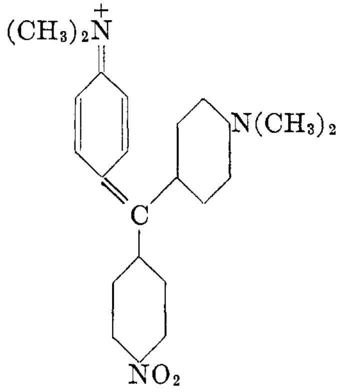


XX

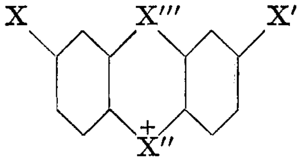
Katzenellenbogen and Branch point out that the direction parallel to the line joining the oxygen and nitrogen atoms in XVIII and XIX should be the axis of maximum polarizability in these molecules (x-band) and that one can say as a first approximation that in XX the ethylenic bond chiefly increases the polarizability along the x-axis, while in XIX it chiefly increases the polarizability along the y-axis. Hence, λ_x (λ_{max}) of XX should be greater than λ_x of XIX, and λ_y (λ'_{max}) of XIX should be greater than λ_y of XX. After studying the spectra of compounds XVIII, XIX, and XX, these authors observed that the interpolation of an ethylenic bond has the expected effect. They found λ_{max} for XX and XIX to be 419 and 387 mμ, respectively, and λ'_{max} to be 264 and 303 mμ, respectively. This same relationship between the wave lengths of the first and second absorption bands is found true also for several of the chalcones studied by Alexa (3).

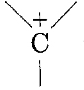
Another investigator to use this indirect method is R. N. Jones, who studied the spectra of derivatives of the polynuclear aromatic hydrocarbons (134, 136). Because of the closely packed structure of these molecules they do not exhibit such clearly defined x-bands and y-bands as do molecules such as triphenylmethyl ions and carotenoid dyes, in which the conjugated systems are along easily separated axes. Nevertheless, Jones finds in the spectra of these polynuclear compounds definite shifts in certain maxima so that one can correlate particular bands with electron excitations in a given direction.

Lewis (176) observed that the x-band of malachite green, λ_{max} = 621 mμ, increases for p-nitromalachite green



probably because the acidic nitro group reduces the amount of positive charge in the lower phenyl group, that is, increases the amount of positive charge oscillating horizontally in the two amino-substituted rings. On the other hand, a group like the NR_2 or OCH_3 group, attached to the lower phenyl ring, decreases the amount of positive charge oscillating horizontally by "side tracking" a portion of the positive charge into a vertical direction, and therefore λ_{max} will decrease. The order of this decrease is CH_3, OCH_3, NR_2. Meanwhile the y-band increases in wave length, until in crystal violet the x- and y-bands coincide. Lewis extended such considerations to other types of dyes the structures of which could be represented by the general structural formula,



and he set up a rule concerning the position of the x-band: namely, "since these molecules have approximately the same dimensions, the $\lambda_{\max}$ will be larger the greater is the amount of positive charge occurring on the auxochromes X and X'." Thus, with X and X' as OH, OR, O, NH_2, or NR_2, it is found that $\lambda_{\max}$ increases in the order given. If X''' is O, S, or NR, one observes a decrease in $\lambda_{\max}$ due to the acquisition of the positive charge part of the time by the oxygen, sulfur, or nitrogen atoms and consequent lowering of the positive charge on the auxochromes, X and X'. The replacement of CR by N at X'' is accompanied by a bathochromic shift, since  $\overset{\diagdown + \diagup}{\underset{|}{C}}$ is more stable than $\overset{+}{-N-}$, and upon adding a proton to the nitrogen a still larger bathochromic shift occurs, for practically all of the positive charge remains on the X and X' groups.

Lewis studied such dyes as the six following types: triphenylmethane (X''' absent, X'' = CR), diphenylmethane (X''' absent, X'' = CH), xanthene (X''' = O, X'' = CR), acridine (X''' = NR, X'' = CR), oxazine (X''' = O, X'' = N), thiazine (X''' = S, X'' = N), and azine dyes (X''' = NR, X'' = N). Choosing malachite green for the reference molecule and following the observed empirical rule that "any change in X and X', or X'', or X''' produces the same changes in $\lambda_{\max}$ regardless of the character of the rest of the molecule," Lewis determined empirical constants for the shift in $\lambda_{\max}$ when making the above indicated substitutions for X, X', X'', and X'''. Upon comparing the $\lambda_{\max}$ calculated from these constants with the observed values for seventy dyes, excluding the acridine dyes,[24] the average deviation is 5 mμ.

D. *z-Bands*

In certain cases there will be found molecules with an appreciable polarizability in three directions whose spectra, according to the discussion in the above section, should have at least three maxima. Scheibe (261), and also Jelley (132), has studied the spectrum of pseudoisocyanine, and the x-, y-, and z-bands have been assigned as shown in figure 16. The band at 530 mμ is the x-band corresponding to the major axis in the plane of the molecule, the band at 490 mμ is the y-band corresponding to the minor axis in the plane of the molecule and perpendicular to the major axis, while the band at 573 mμ is the z-band arising through a polarization along the length of the *threads* of molecules. This z-band does not appear in dilute solutions of pseudoisocyanine. These *threads* are due to a face-to-face polymerization occurring in concentrated aqueous solution, wherein there probably exists an intramolecular electronic resonance (234).

A similar interpretation may be applied to the observation of a number of authors (162, 224, 261, 263, 264), in working with crystals of anthracene, naphthacene, chrysene, and certain dyes, that absorption bands will appear when the exciting beam has its electric vector polarized parallel to the plane of the mole-

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[24] The acridine dyes show a large discrepancy and Lewis believed that what were calculated for x-bands were y-bands. That is, the oscillation corresponding to the lowest energy is vertical rather than horizontal.

cule, and that when the light is polarized normal to this plane a new band will arise.

E. x′-Bands

It has been shown that a molecule may have two optical axes and that excitation by light will produce an oscillation of an electron cloud along these two axes. Earlier, it was assumed that the whole system of quantized, mobile electrons moving in phase could be considered as a single oscillator analogous to a vibrating diatomic molecule. When such vibrations are harmonic, then the potential energy, V, will be proportional to the square of the displacement of what may be considered as the center of gravity of the electron cloud, x, and a plot of V against x will produce a parabola as, for example, in figure 17. The energy levels of the molecules may be indicated by evenly spaced lines parallel to the x-axis, whereby one lets the lowest represent the energy of the ground state and the next higher lines represent the energies of the succeeding excited states. The difference in energies of the first two lines will correspond to the main electronic absorption band of the molecule of frequency ν. When the molecule receives a higher excitation to the second excited state, resulting in an electronic oscillation of larger amplitude in the direction of greatest polarizability, one will observe a second absorption band of frequency ν', which Lewis and Bigeleisen have called an x'-band. Since the differences between energy levels are equal, the ratio of the two frequencies, ν'/ν, will be exactly 2; however, from selection rules, the probability of such a jump is zero. Therefore, the intensity, ϵ', of this second-order x-band will be zero and the ratio of the intensities of the two bands, ϵ'/ϵ, will be zero.

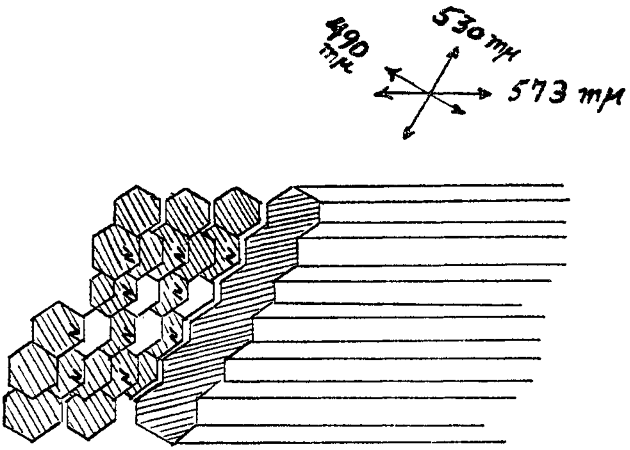

FIG. 16. Absorption and structure of the polymer of pseudoisocyanine. Redrawn from reference 32 through the courtesy of Prentice-Hall, Inc.

But then, if the electronic oscillations are anharmonic, the energy will rise less rapidly than the square of the displacement and the energy levels of the successive excited states will lie closer and closer together. In this case the ratio ν'/ν will be less than 2 and one might expect exceptions to the selection rules such that ϵ'/ϵ will be greater than zero. Lewis and Calvin (182) found in the spectra for the polyenes and carotenoids, and Lewis and Bigeleisen (178) observed in the spectra of several types of dyes, a set of bands where the ratio of the frequencies, ν'/ν, was less than 2 and that of the intensities, ϵ'/ϵ, greater than zero. Nevertheless, as Lewis and Bigeleisen demonstrated, the ratio ν'/ν may be greater than 2.

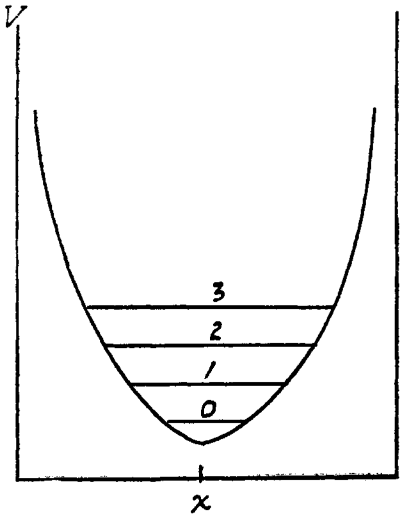

FIG. 17. Plot of potential energy, V, against electronic displacement, x

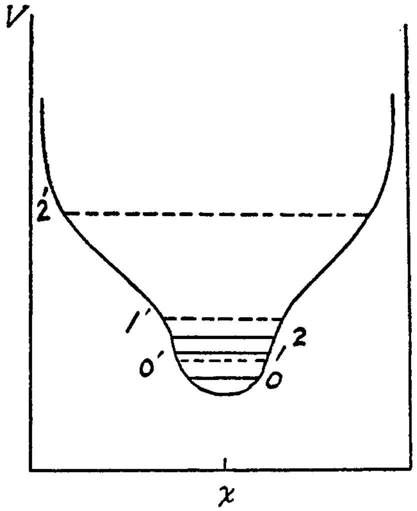

FIG. 18. Potential curve for electronic displacements in dye molecules

Lewis and Bigeleisen constructed a potential diagram as in figure 18 where the levels 0, 1, 2, . . . and 0′, 1′, 2′, . . . correspond to the energy levels for two different substances. If the electronic oscillations are harmonic for certain amplitudes and become anharmonic for other amplitudes, the first two energy states of the molecule may occur in regions indicated by 1 and 2, where the difference between the first and second excited states is smaller than the difference between the ground and first excited states. This would result in the ratio of the frequencies of the x- and x'-bands, ν'/ν, being less than 2. On the other hand, if the energy states occur as indicated by the set of lines 0′, 1′, and 2′, where the transition from the first to the second excited state involves a greater amount of energy than the jump from the ground to the first excited state, the ratio of the frequencies, ν'/ν, will be greater than zero. The only factor which determines by which type of diagram the molecule will be represented is the amplitude of the electronic displacements relative to the dimensions of the molecule.

It is customary to write resonance formulas for unsaturated compounds, for instance, for a polyene

$$CH_2{=}CH{-}CH{=}CH_2 \qquad \overset{\mp}{C}H_2{-}CH{=}CH{-}\overset{\pm}{C}H_2$$

in which each atom holds its full complement of eight electrons in its valence orbit (excepting, of course, hydrogen atoms). Such structures actually represent the limit of electronic displacement and hence must correspond to the boundaries in the potential diagram of Lewis and Bigeleisen, where the energy is increasing very rapidly with increasing x. In this region the energy levels are spaced farther apart than in the lower area of the diagram. For a long molecule with a small λ_{max}, as, for instance, β-carotene or 1,14-diphenyltetradecaheptaene, with λ_{max} 480 mμ and 465 mμ, respectively (167), the electronic displacements must be small compared to the dimensions of the molecules, so that the first two excited states occur in the lower region of the diagram. But if λ_{max} is relatively large for a short molecule, as for the triphenylmethane dyes or cyanines, one may expect the electronic oscillations to be approaching the limiting resonance distances. Therefore, even the first few excited states are found in the upper portion of the potential diagram and the ratio, ν'/ν, will be greater than 2. The amplitude depends upon the polarizability of the molecule, being greater for those dyes with large λ_{max}. One can say, therefore, that in a series of similar compounds, as the values of λ_{max} of the x-bands increase, the ratio of the frequencies of the x- and x'-bands, ν'/ν, will increase, even to exceed 2, and simultaneously the ratio of the intensities, ϵ'/ϵ, will decrease.

An excellent illustration to substantiate the existence of x'-bands in accordance with the above conditions was given by Kumler (169). He measured the spectra of eighteen compounds of the type AB, where A was an electron-donor such as the dialkylamino groups and B an electron-acceptor such as the NO_2, COOH, or SO_2NH_2 groups. His results are tabulated in table 7. Excluding the nitro compounds the trend agrees perfectly with the predictions of Lewis and Bigeleisen. Kumler explained the discrepancy in the case of the nitro compounds as due to the fusion of the nitro *partial* with the x'-band to make it unusually high and broad.

TABLE 7

Wave lengths and molar extinction coefficients of the absorption bands of some para-substituted aniline derivatives (Kumler (169))

COMPOUND IN 95 PER CENT ALCOHOL	λ_{max}	λ'_{max}	$\bar{\nu}$	$\bar{\nu}'$	ϵ	ϵ'	ν'/ν	ϵ'/ϵ
p-Nitrosodiethylaniline	428	275	23,300	36,400	31,100	5,470	1.56	0.176
p-Nitrosodimethylaniline	423	273	23,600	36,600	29,400	5,750	1.55	0.195
p-Nitrodiethylaniline	400	236	25,000	42,400	21,550	8,850	1.70	0.412
p-Nitrodimethylaniline	390	232	25,600	43,100	19,020	9,300	1.68	0.488
p-Nitroethylaniline	390	231	25,600	43,250	19,000	7,500	1.69	0.395
p-Nitromethylaniline	386	230	25,900	43,400	18,430	7,470	1.68	0.405
p-Nitroaniline	375	227	26,700	44,100	15,450	7,180	1.65	0.465
p-Diethylaminobenzaldehyde	348	243	28,700	41,100	32,800	6,010	1.43	0.183
p-Dimethylaminobenzaldehyde	342	241	29,200	41,500	29,800	7,390	1.42	0.248
p-Dimethylaminoacetophenone	337	239	29,700	41,800	25,600	6,340	1.41	0.248
p-Ethylaminoacetophenone	332	238	30,100	42,000	25,900	6,030	1.40	0.233
p-Aminoacetophenone	317	233	31,500	42,900	20,100	6,750	1.36	0.336
p-Diethylaminobenzoic acid	312	227	32,100	44,000	30,650	8,260	1.37	0.270
p-Dimethylaminobenzoic acid	308	227	32,400	44,000	25,400	7,450	1.36	0.293
p-Aminobenzoic acid	288	220	34,700	45,500	17,400	8,220	1.31	0.472
p-Diethylaminobenzenesulfonamide	280	213*	35,700	46,800	26,600	10,200	1.31	0.383
p-Dimethylaminobenzenesulfonamide	276	211*	36,300	47,300	24,500	9,400	1.30	0.384
p-Aminobenzenesulfonamide	262	204†	38,200	49,000	17,700		1.28	

* Kumler's estimate from curve.

† Kumler's estimate using Spekker and I. O. plates.

TABLE 8

Ultraviolet absorption characteristics of some p-disubstituted benzene derivatives

COMPOUND	λ_{max}	λ'_{max}	ϵ_{max}	ϵ'_{max}	ν'/ν	ϵ'/ϵ
p-Hydroxybenzoic acid	255	207.5	13,900	13,400	1.23	0.965
p-Anisic acid	256.5	208	15,900	14,750	1.23	0.928
p-Nitroaniline cation	258	208	8,700	7,800	1.24	0.896
p-Aminobenzonitrile	270	212	19,800	13,800	1.27	0.698
p-Hydroxyacetophenone	275	218.5	14,300	10,700	1.26	0.749
p-Methoxyacetophenone	276.5	219.5	15,500	10,600	1.26	0.685
p-Nitrochlorobenzene	280	217	10,300	7,150	1.29	0.694
p-Hydroxybenzaldehyde	283.5	221	16,000	12,000	1.28	0.750
p-Aminobenzoic acid	284	219.5	14,000	9,900	1.29	0.706
p-Nitrotoluene	285	217	9,250	6,700	1.31	0.725
p-Aminoacetophenone	311.5	231	17,100	6,950	1.35	0.406
p-Nitrophenol	317.5	225.5	10,000	6,900	1.41	0.690
p-Hydroxyacetophenone anion	324.5	236.5	23,100	7,500	1.38	0.325
p-Hydroxybenzaldehyde anion	330	238	27,900	7,500	1.39	0.269
p-Nitroaniline	381	226	13,500	6,700	1.69	0.497
p-Nitrophenol anion	402.5	226	19,200	6,500	1.78	0.338

Based on the criteria set up by Lewis and Bigeleisen, that in a series of similar compounds, as the values of λ_{max} of the x-bands increase, the ratio of the frequencies of the x'- and x-bands, ν'/ν, will increase and the ratio of the intensities, ϵ'/ϵ, will decrease, it seems that the two "primary" bands ($\epsilon < 2.6 \times 10^3$) (76a) for disubstituted benzenes are x- and x'-bands. Thus, for a number of compounds measured by Doub and Vandenbelt (76a), it is observed in table 8 that the trends in the ratios ν'/ν and ϵ'/ϵ are roughly as expected for x- and x'-bands. The agreement is not bad when one remembers that the exact values of λ_{max} are sometimes in doubt, because the absorption bands are broad and sometimes have very prominent shoulders.

X. SUMMARY

When a molecule absorbs light energy in the ultraviolet or visible region of the spectrum, electronic vibrations are set up within the molecule and it becomes excited to higher electronic vibrational levels. The difference in energies between the initial and final states determines the frequency of the absorbed light. A number of factors may influence the energy value of the initial and final states and thereby decrease or increase the energy difference between the two states. Thus it has been shown that the difference in energy, $E_1 - E_0$, between the ground state E_0 and the first excited state E_1 is diminished when there occurs resonance among structures which contribute chiefly to the excited state, thereby lowering the potential energy of the excited state, and also by steric hindrance existing in the ground state, thereby raising the potential energy of the ground state. Likewise, it has been shown that this energy difference is increased when the resonance occurs between structures which contribute primarily to the ground state, thus decreasing the energy of the ground state, and also by steric strain arising in the excited state which increases the potential energy of this state. With such an understanding, data from absorption spectra have been used to give information, sometimes unique, concerning the structure of an organic substance.

It has been shown further that the electronic vibrations produced by light excitation are oriented. Oscillations along the longest linear extension of conjugated multiple bonds cause the greatest stabilization of the excited state. This produces an absorption band of longer wave length than that arising from oscillations along any shorter conjugated system within the molecule.

A number of quantitative relationships between the wave length of the maximum absorption band and the structure of molecules have been presented. For instance, from absorption spectra one may determine the number of conjugated multiple bonds in a substance, the relative basic strengths of dyes, and the number of *trans* or *cis* ethylenic bonds in carotenoids.

Finally, through semiempirical approximation methods of quantum mechanics, the frequencies and intensities of light absorbed by simple molecules have been determined. Such calculations are of great value, because they give a large amount of information about the energies and electronic structures of organic molecules and their behavior under the influence of external fields.

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