

THE COLOR OF ORGANIC SUBSTANCES

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The absorption of light by organic molecules has been the subject of an enormous amount of successful experimentation, and yet very few fundamental principles have been discovered, as may be seen in the numerous reviews that have been published (40, 46, 57, 60, 71). The connection between the finer structure of absorption bands and the known bands of atomic vibration is being very satisfactorily established, but the position and intensity of the main electronic absorption bands can rarely be predicted. Yet the prediction of these bands, and thence the color, from the structure of the molecule, should be one of the chief goals of chemistry.

Despite the great importance of dyes, which absorb intensively in the region of visible light, exact and systematic data are at present available chiefly for the relatively simple organic substances that absorb in the ultraviolet only. Because of the great success in the interpretation of the spectra of atoms and diatomic molecules, it has been natural to study first the simpler molecules. Moreover, to the simpler molecules quantum mechanics may be applied by methods of approximation which are not excessively arduous and which represent a reasonable extrapolation from the known into the unknown. Recently numerous attempts have been made to extend the quantum-mechanical methods (20, 33, 49, 65) to molecules of some complexity, such as benzene and butadiene.

Such studies will undoubtedly continue to be prosecuted and may lead to the discovery of generalizations applicable to even more complex molecules. But it appears unlikely that in the near future these means alone will permit the interpretation of the absorption of light by such complex structures as the organic dyes.

For this reason it has seemed to us that it might be useful to reexamine the data of light absorption and to see whether, by applying the more inductive methods of chemistry, together with such general results of quantum theory as are applicable to all systems, we may obtain a better understanding of the data. Starting with the idea that in the absorption of light the energy is taken up by electronic oscillations, we have considered these oscillations as analogous to classical oscillations, but subjected

to the rules of simple quantization. As we have tested this quasi-classical model with the various known facts relating to light absorption, we have found that it affords in many cases a qualitative, and in a very few cases a quantitative, interpretation of the experimental facts.

When we consider a heavy diatomic molecule such as I_2 , we speak of the rotation and vibration with the feeling that these words, and the implied analogy to rotations and vibrations of large objects, will be useful in the understanding of the properties of such a diatomic molecule. When we apply similar words and analogies to a molecule composed of light atoms such as H_2 , it is realized that the picture is a less adequate one, and when we proceed to the very light particles, the electrons, the analogy has not even been attempted. It is, however, to be noted that it is not the mass alone that determines the degree of approximation to the classical picture. Hydrogen held to another atom by a very loose bond may undergo motions nearer to the classical than iodine held by a strong bond. So if even so light a particle as the electron is in a field of small constraints, the various electronic excitations may be called vibrations. We shall therefore attempt to interpret the absorption of light by dyes, and even by substances which have only ultraviolet bands, in terms of such a quasi-classical model; and thus consider the molecules as containing vibrating electronic systems, which are subject to the rules of quantization applicable to an oscillator. We must consider not only the various possible modes of vibration and the laws governing them, but also the interaction between electronic and atomic vibrations in the molecule.

Our first task must be to attempt a simplification of the complex band system that is found in many dyes. Even the individual broad electronic bands frequently show a finer structure, which has successfully been attributed to atomic vibrations associated with electronic transitions. This structure may be accentuated by various means. One method is to work at low temperatures where the initial vibrational state of all of the molecules is at the same (or nearly the same) energy. Figure 1 shows the absorption of dodecapentaenic acid (25) in a mixture of ether and alcohol, at room temperature (above) and at liquid air temperature (below). We shall see later that the more pronounced structure in the second case, while it may be partly due to lower temperature, is probably chiefly attributable to a change in the physical character of the solvent.

Even when a broad band is resolvable into narrower bands, the latter often have half-widths of several hundred Ångström units. As far as existing experimental material goes, this may be explained in either of two ways. One explanation is that, in addition to atomic vibrations of high energy, such as are brought out in figure 1, there are in a complex molecule

many types of vibration (and rotation) of much smaller energy. It may therefore be that the narrow bands are themselves resolvable into still narrower ones. The other explanation also assumes these vibrations of small energy, but assumes that the main excitation is to one of the widely spaced energy levels, and that the energy is almost immediately transmitted to the vibrations of smaller energy. If this process is so nearly instantaneous that the mean life in the initial excited state is only of the order of 10^{-13} to 10^{-14} sec., the "natural" broadening would account for the observed widths of the bands.

Even if the band structure due to atomic vibrations is absent or has been accounted for, the system of electronic bands of a colored substance is often bewilderingly complex. In some dyes the multiplicity of electronic bands is due to the fact that the dyes are mixtures. Even if the dye is carefully purified it may be subject to reversible changes in composition; thus an indicator molecule may add or lose hydrogen ion, or other acid,

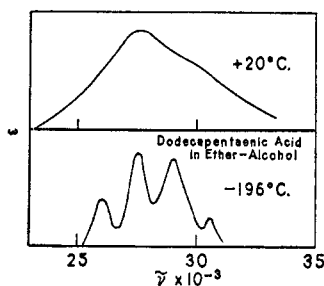


FIG. 1. Absorption curves of dodecapentaenic acid in a mixture of ether and alcohol¹

in one or more stages. In rarer cases, such as trinitrobenzene, the indicator may add a base.

One of the first careful analyses of the spectrum of an indicator was carried out in this laboratory by Adams and Rosenstein (1), who were able to obtain the curve for the molar extinction coefficient of each of the ions that are present in aqueous solutions of crystal violet. These curves are reproduced in figure 2. The central band is due to the simple ion; that on the left is due to the addition of one hydrogen ion, and that on the right to the addition of two hydrogen ions.

Moreover, the solvent, especially if it is a substance like water, may

¹ All of the figures used in this paper have been redrawn. Clerical assistance of the Works Progress Administration (OP-465-03-3-147) is gratefully acknowledged. In all of the figures the molar extinction coefficient, ϵ , or some function thereof, is plotted as ordinate; as abscissa the wave number $\bar{\nu}$ (in cm.^{-1}). The extinction coefficient, if in arbitrary units, is designated by α .

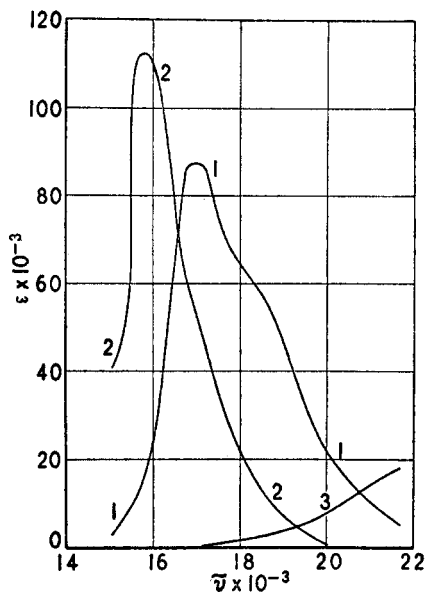


FIG. 2. Absorption curves of the several ions of crystal violet in water

Curve 1, absorption curve for $[(\text{CH}_3)_2\text{NC}_6\text{H}_4)_2\text{C}]^+$

Curve 2, absorption curve for $[(\text{CH}_3)_2\text{NC}_6\text{H}_4)_2(\text{CH}_3)_2\text{NHC}_6\text{H}_4\text{C}]^{++}$

Curve 3, absorption curve for $[(\text{CH}_3)_2\text{NC}_6\text{H}_4)(\text{CH}_3)_2\text{NHC}_6\text{H}_4)_2\text{C}]^{+++}$

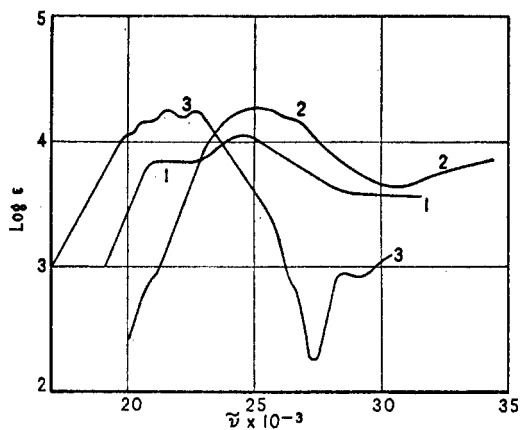
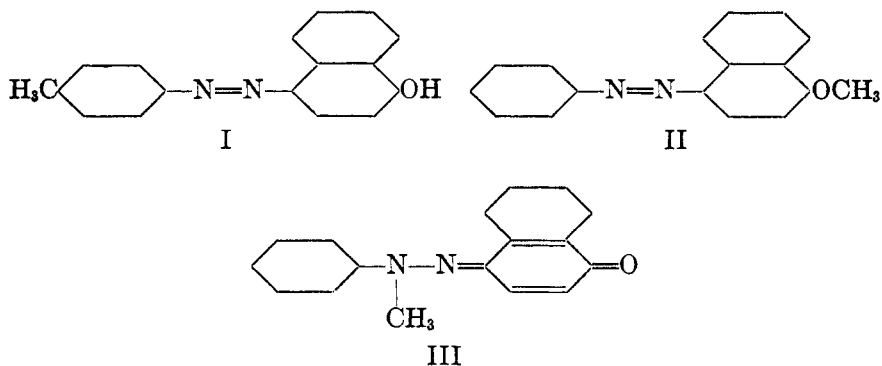


FIG. 3. Curve 1, absorption curve of *p*-methylbenzeneazo- α -naphthol; curve 2, absorption curve of benzeneazo- α -naphthol methyl ether; curve 3, absorption curve of naphthoquinone *N*-methylphenylhydrazone. The solvent in each case was benzene.

combine with the colored solute to produce a number of definite molecules, each of which has its own absorption. These compounds are ordinarily the result of a hydrogen bond between solvent and solute, but sometimes aromatic solvents like benzene form compounds with aromatic solutes, especially those containing the nitro group, when another type of resonance binding is manifest. It is our belief that all pronounced changes in color, when passing from one solvent to another, are due to such definite solvates, except in the single type of substance exemplified by *p*-nitroaniline, which we shall discuss later. The colored solute may combine with itself to form polymers which have their own characteristic absorptions, as we shall later illustrate.

If the solute is capable of tautomerism this may give rise to a complex spectrum, as illustrated by the work of Shingu (64) on a substance, one of whose tautomeric states is expressed by formula I, the other state being produced when the hydrogen is transferred from oxygen to nitrogen. Its complex absorption curve, curve 1 of figure 3, is due to these two substances, as was demonstrated by the author when he prepared the two corresponding methyl derivatives II and III, which give rise to the simpler curves 2 and 3 of the same figure.



Geometrical tautomerism also gives rise to mixed spectra, as, for example, in the azo dyes. Brode (6) found in benzeneazophenol two band systems which he suggested might be due to two modifications. Now a similar pair of band sets can be found in all azo compounds and, since the discovery of *cis-trans* isomerism (21) in such substances, they can definitely be ascribed to the *cis*- and *trans*-forms. In the case of stilbene the *cis*- and *trans*-forms have long been known, each in the pure state, and the two absorption curves (67) are given in figure 19.

When all pains have been taken to prepare a substance in a single

molecular form, and solvates are largely eliminated by the use of such a solvent as hexane, we still frequently find in an absorption spectrum, taken through the visible and well into the ultraviolet a number of separate electronic bands.

We shall attempt to classify these bands as (*A*) fundamental bands, or bands of electronic oscillation within the molecule as a whole, and (*B*) bands of partial or localized oscillation. The fundamental *A* bands may be further subdivided as follows: (1) Fundamental bands of the first order, that is, bands due to a transition to the first excited state. These are further classified as (*a*) a single band (*x* band) corresponding to oscillation in a single direction, (*b*) two bands (*x* and *y* bands) due to two mutually perpendicular oscillations, and (*c*) three bands (*x*, *y*, and *z* bands) which are to be found only in molecules in which the conjugating system has considerable extension in three dimensions. (2) Fundamental bands of the second order, due to a transition from the zero state to the second excited state of the fundamental oscillator.

As we proceed we shall attempt to justify this classification and to give examples of each of the enumerated types.

ABSORPTION AND TYPES OF BOND STRUCTURE

According to the original theory of Witt (70) a colored substance must contain one or more unsaturated groups, such as the vinyl or carbonyl groups, which he called *chromophores*. He also spoke of *auxochromes*, which are groups that greatly enhance the color of a chromophoric substance.

Even a substituent that is not ordinarily regarded as an auxochrome may have a decided influence upon the position and intensity of absorption bands. Figure 4 (31, 58) shows the absorption curves of acetone and hexaethylacetone. Although the effect of the substituent groups is a large one, it appears to be the result of shifting and modifying the acetone curve, without introducing any new electronic band. The influence of the substituents may be said to be one of induction, which may be regarded as a perturbation in existing electronic paths without altering their essential character.

On the other hand, the effect of an auxochrome, which will be illustrated in numerous figures, may be described as providing, through resonance, entirely new electronic paths. Such a substituent causes, as we shall see, not only a shifting of old bands, but the appearance of entirely new electronic bands. These new bands we are going to consider as due to oscillations within the molecule as a whole, or, as Rădulescu (56) has put it, of the "résonateurs d'ensemble."

Auxochromes, as pointed out by Wizinger (71), are of two kinds, which

he calls positive and negative. The first kind, which we shall call basic auxochromes, is typified by the NR_2 group, which may enter into resonance by using its lone pair of electrons to form a double bond with the adjacent atom (37). The other kind, which we shall call acid auxochromes, is typified by the NO_2 group, which may enter into resonance through the formation of a double bond by means of a pair of electrons which is contributed by the adjacent atom. The important connection between color and resonance was first pointed out by Bury (10). Before proceeding further with the problem of color we must first consider simple structures, which absorb chiefly in the ultraviolet.

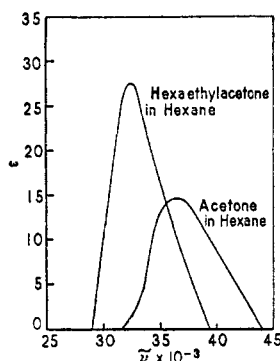


FIG. 4. Absorption curves of acetone and hexaethylacetone

The single bond

Molecules of the type called saturated do not ordinarily absorb light except in the extreme ultraviolet. It is true that methyl iodide absorbs down to 2700 \AA ., but, since this is approximately the absorption region of iodide ion, the absorption is probably to be attributed to the polarizability of the iodine itself. However, in the majority of organic molecules we shall be able to regard the bond as the seat of that mechanism which is responsible for the absorption of light, with occasional mention of the effect of non-bonding electron-pairs such as exist in the iodine atom. In our last section we shall consider systems containing odd electrons.

If we examine ethane, whose absorption spectrum is shown in figure 6, we see a continuous band beginning at about $62,000 \text{ cm.}^{-1}$. The lack of any structure, and the steady increase in intensity of absorption with increasing frequency, indicate either that the electronic excitation and the photodissociation of the molecule occur as a single act, or that the dissociation follows the electronic excitation after a very brief period of time. We do not know whether the first absorption is in the C—C bond or the C—H

bond. Presumably the two absorptions occur in very nearly the same region. We may assume then, for purposes of illustration, that the C—C bond begins to absorb at about $62,000\text{ cm.}^{-1}$

Let us begin now to develop our fundamental idea of the electronic excitation by light, realizing that while the cases that we must present first are the simplest of all, they are, on the other hand, the farthest removed from the conditions that best justify the employment of the quasi-classical method that we are adopting.

Let us assume that the pair of electrons in the C—C bond constitutes an oscillating unit, and think of its motion along the line joining the two carbon atoms. The electronic vibrations that we are going to consider are so rapid compared with atomic motions that we may regard the electrons as moving in a fixed frame of atoms. If, when the electron-pair is displaced from its equilibrium position, the restoring force is approximately proportional to the displacement, the potential is proportional to the square of the displacement, and we shall have a potential curve in the form of a parabola similar to those that we have drawn in figures 5 and 10. If we regard the electron-pair as a single unit, application of quantum mechanics leads to the familiar set of energy levels, $v = 0, 1, 2 \dots$, and we shall suppose that the value of $h\nu$ corresponding to light absorption is the difference in energy between $v = 0$ and $v = 1$.

One of the striking consequences of this point of view is that we are led to consider a *zero-point energy* of electronic vibration, corresponding entirely to the familiar zero-point energy of atomic vibration. Whether the consideration of this zero-point energy of the electrons will prove serviceable in this extreme case of the single C—C bond is perhaps doubtful, but we hope that it will become useful in dealing with the relation between the optical properties and the resonance energy of more complex chromophores.

We shall discuss frequently the correlation between color and chemical resonance. This phenomenon of resonance has often been given an interpretation which has never been found at variance with our chemical knowledge, and which may be stated as follows: A substance to which only one reasonable formula can be assigned has properties in accord with that formula. When to a substance two or more structures might be assigned, such that one may be derived from another merely by the shifting of electron-pairs, these structures are said to be in resonance with one another, especially if the energies corresponding to the several structures, as well as the relative positions of the atoms, are not widely different. Such a resonating substance is to be regarded not as a mixture of various molecules corresponding to the various structures, but rather as having a single kind of molecule which, however, partakes of the character of the

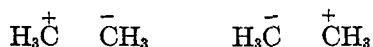
several contributing structures. Thus, for example, in different reactions it may behave in the various ways characteristic of the individual structures.

While we assign to a resonating molecule only a single set of properties, yet we must recognize that even in its state of lowest energy the molecule cannot be regarded as a set of atoms and electrons occupying fixed positions. The idea of zero-point energy, or the related principle of uncertainty of Heisenberg, leads to the consideration of some sort of flux which in its various phases may approach closely to some one of the electronic structures that are said to contribute to the resonance.

This concept, of which we shall make extensive use, may now be illustrated in its simplest, but perhaps least important, application. Considering the molecule $\text{H}_3\text{C}-\text{CH}_3$ we may write the two additional formulas that contribute to resonance in the single C—C bond, namely,



or



Now the contribution of these two forms to the actual state of the molecule is small; nevertheless, it is this very possibility of alternation of phase in the direction of the one form or the other, involving displacement of electric charge, that must be held responsible for the ability to absorb light. We need, however, devote no more attention to this simple type of resonance, since we have many more important types of resonance to discuss.

The double bond

When we come to the double bond, which is the most important unit in the mechanism of light absorption, we must differ at the outset from a conception that has been frequently advocated in recent years and is now generally accepted. According to this conception the electron-pairs of a double bond are different, one pair being designated as σ electrons and the other as π electrons. There is no objection, as a basis of some mathematical approximation, to the fiction that one pair still has the characteristics of a single bond while the other is loosely bound and is responsible for the phenomena of resonance and color. However, to the chemist who has not forgotten the brilliant strain theory of Baeyer, the two bonds of ethylene must be regarded as identical, and differing in degree, but not in kind, from the bonds of other ring systems. Without mentioning numerous facts of chemical behavior, it will be sufficient for our present purpose to point out that, even with respect to the absorption of light, the cyclopropyl group, in which all the electron pairs would certainly be regarded as σ electrons, is a chromophore of the same type as the ethylene

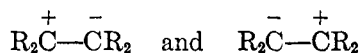
group, although less powerful. Thus Carr and Burt (12) have shown that in several types of compounds the absorption spectra of those compounds with a three-membered ring are intermediate between those with the double bond and those with ordinary single bonds.

When we ascribe the chromophoric character of ethylene to two electron-pairs held conjointly and symmetrically between the two carbon atoms, we already have a system which is far beyond the present powers of exact quantum mechanics. We are therefore forced at the outset to adopt some semi-empirical method.

As examples of double-bonded structure we may take the following types:



In the first compound, the formula, as written, is the major contributing structure, and the two symmetrical minor contributing structures are the ionic forms,



So may be written the corresponding contributors in the other cases. It will be noted that while there is no dipole moment in the first and fourth cases, because of symmetry, in the second, third, and fifth cases the molecule will have a dipole moment. This, however, is of only indirect concern to the problem of color, for we shall see that it is not the dipole moment but the polarizability that is of immediate importance.

Simple substances of the ethylenic type begin to absorb at 2000 Å., those containing the carbonyl group have a first absorption maximum at about 2800 Å., while azomethane, $H_3CN=NCH_3$, is yellow and has its first absorption maximum at 3500 Å. We have not found data for simple compounds containing the double bond between carbon and nitrogen or carbon and sulfur, but the former will presumably lie between the ethylene and the carbonyl, and the latter will be found to absorb at longer wave lengths than azomethane. We do not know what part the lone or non-bonding pairs of electrons on nitrogen, oxygen, and sulfur may take in the process of light absorption, but shall assume that it is not an important one.

What is it that determines the difference in the chromophoric character of these groups? If we assume that the double bond acts as a single oscillating unit, we may consider that the restoring force, for unit displacement of electrons in the line joining the atoms, diminishes in the above series from $C=C$ to $C=S$. In other words, if we plot the potential against the displacement we shall have a series of parabolas (figure 5), of which the height at a given value of the displacement is proportional to k , the constant of restoring force. Using the formula which will be developed in the next

section, we have obtained the relative values of k in the case of the three bonds for which we have just given the absorption maxima.

Even if we are justified in drawing such curves, we do not know whether they would remain parabolas for any large displacement. Nevertheless, it is evident that a continued displacement of this character would lead eventually to a condition corresponding to one of our formulas, which we have called the ionic contributors to resonance. Therefore we may expect that these polarized forms will contribute more to the actual state of resonance the lower the value of k .

Since the amount of the relative contribution to resonance of the major and minor forms depends upon the difference in energy, we may make the contribution of the minor forms greater by diminishing their energy or by

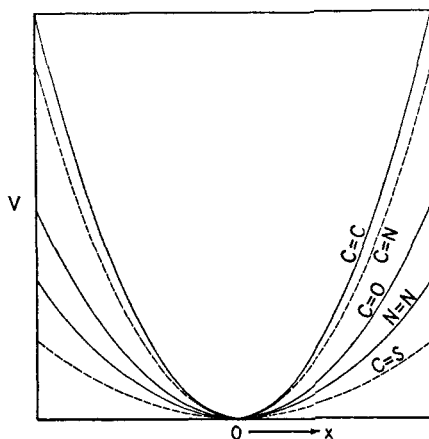


Fig. 5. Potential curves for different chromophores

increasing the energy of the major or classical form. We shall find it convenient in one of the following sections to ascribe the difference between the several double bonds to differences in double bond strain in the classical structure. In other words, we shall say that there is an increasing strain in the double bond as we pass in our series from $C=C$ to $C=S$.

We have not found it necessary in tracing the relationship between optical properties and resonance to assume the kind of resonance that Pauling (50) and others have employed, in which the two electrons of an electron pair are separated while their spins are kept anti-parallel. In the first place such a resonance would not be directly related to the absorption of light and in the second place we believe that, whenever there is a strong tendency for such a process to occur, the pair is likely to break, to form an electromeric odd molecule such as the biradicals, which have been very fully studied by Müller (48).

Conjugation

The great class of organic dyes chiefly comprises substances whose color is due, not to single chromophores of the type we have been discussing, but to several such groups in a state of mutual conjugation. Usually we find an unbroken succession of alternating single and double bonds, either in single order or branching (cross conjugation). Diltthey (18) made this statement more general by including any succession of atoms each of which is "coördinatively unsaturated." By this expression he meant to include

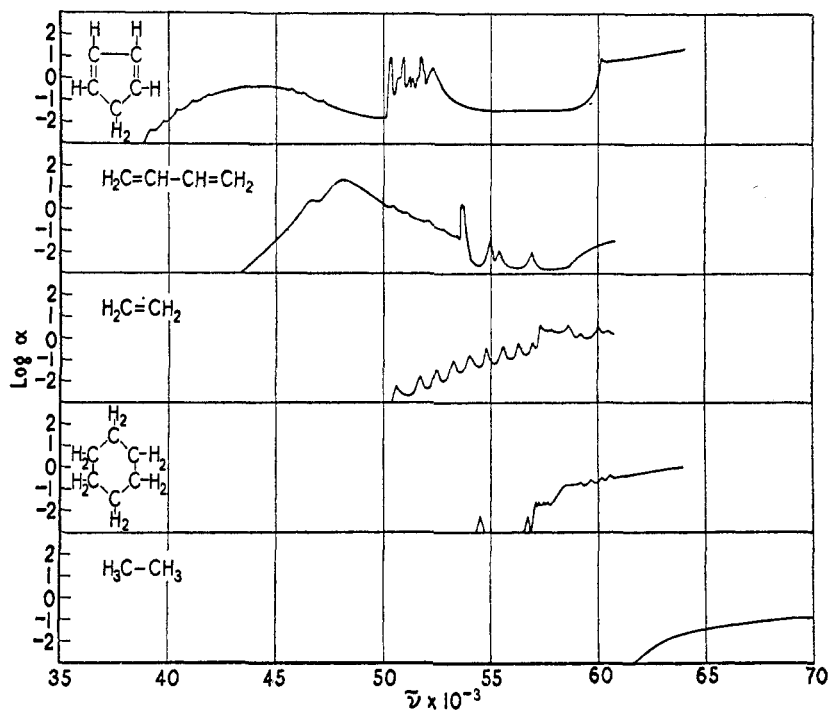


FIG. 6. Absorption curves of cyclopentadiene, 1,3-butadiene, ethylene, cyclohexane, and ethane

not only carbon atoms, each of which is attached to a double bond, but also atoms like nitrogen, oxygen, and sulfur, which are capable of forming "onium" compounds. There seems little doubt that in many of the important sulfur dyes there are chains of at least two sulfur atoms which join chromophoric groups into a single chromophoric unit. Even this definition is not quite broad enough, for it would not include the derivatives of cyclopropane, whose absorption spectra we have already discussed. Instead of attempting to complete such a formal definition, let us rather

investigate the nature of the effect produced by conjugation upon the absorption of light.

The simplest kind of conjugation is that between two double bonds in a symmetrical molecule such as butadiene or cyclopentadiene. The absorption curves of these substances, as well as those of ethylene, cyclohexane, and ethane are reproduced in figure 6 from the work of Scheibe and Grieneisen (61). The ordinate is $\log \alpha$, where α is a quantity proportional to the extinction coefficient, but expressed in arbitrary units. The two lowest

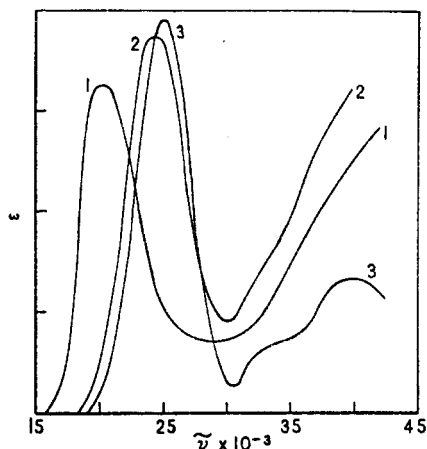
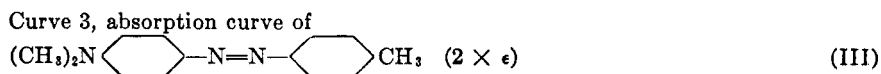
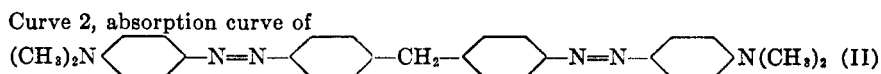
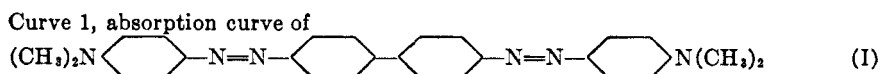


FIG. 7. Absorption curves of some azo dyes in ethanol



curves show the type of absorption in single-bonded systems. The third is characteristic of a simple double bond, which already has in a considerable degree the properties of resonance. The two upper curves typify the absorption of conjugated systems. In these, and especially in the curve for cyclopentadiene, we have, in addition to an absorption suggesting that of ethylene, a new wide curve which we shall now attribute to electronic oscillation throughout the conjugating system. It is what we shall call a fundamental band. If we have a molecule with two single bonds

between the two double bonds, according to the scheme $C=C-C-C=C$, as in 1,4-pentadiene, we no longer have this fundamental band and the absorption is now that of isolated double bonds acting individually.

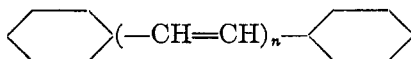
A CH_2 group placed between two parts of a conjugating system may be likened to an insulator introduced into an electrically conducting system, dividing it into two parts. Let us illustrate this in a more complicated case from one of the papers of Brode (53) on the azo dyes. In figure 7 the first curve is that for the fully conjugated structure (I), the second is for structure II, with a central "insulation," and the third shows double the molar extinction coefficient for substance III, which represents about one-half of one of the previous structures. It is evident that each half of substance II is absorbing nearly as though the other half were absent.

When a conjugated system is absorbing in its fundamental band it appears as though the individual oscillators have lost their individuality and have become subject to certain rules governing the whole molecule. We assume that these rules have to do with relationships in phase between the motions of the several oscillators. Before proceeding with a discussion of conjugation in general, we shall develop our concepts by dealing first with certain simple types of conjugated systems.

NEARLY LINEAR MOLECULES

As the simplest and best example of our ideas of conjugation let us consider in some detail the optical behavior of a long chain of alternating single and double carbon bonds, basing our discussion very largely upon the extremely important series of experiments carried out by Hausser, Kuhn and Smakula (23 to 29). The observations were made upon a series of diphenylpolyenes, upon polyenes with other end members, such as aldehyde, acid, and furyl groups, and upon various carotinoids. While all polyenic chains have a zigzag character, nevertheless they are non-branching chains which for our present purposes we may regard as linear.

Figure 8 shows the absorption in the visible and near ultraviolet of the compounds



Each curve represents a single electronic band, the structure being satisfactorily ascribed by the authors to the atomic vibrations characteristic of the olefins. This structure has been accentuated by the use of a solution in mixed ether and alcohol at -196°C . The same bands, but with the structure nearly eliminated, are obtained in solvents at room temperatures, as we have seen in figure 2. The steady increase in wave length with increasing length of the molecule is very striking. Moreover Hausser (23) has shown that, when the frequency of the first maximum is plotted against

the total number of conjugated double bonds for about seventy compounds of polyenic type, all of the points approximate to the same curve (figure 9).

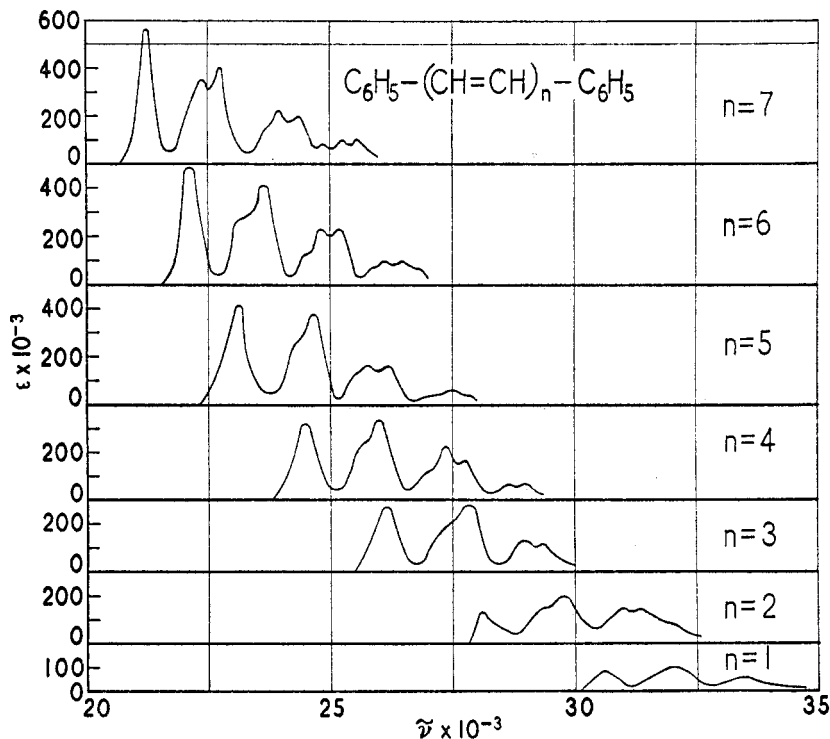


FIG. 8. Absorption curves in the visible and near ultraviolet of diphenylpolyenes in ether-alcohol mixtures at -196°C .

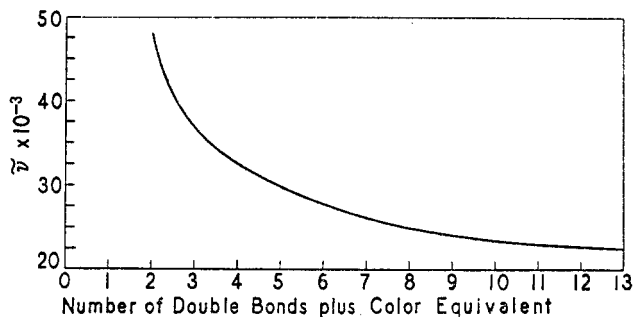
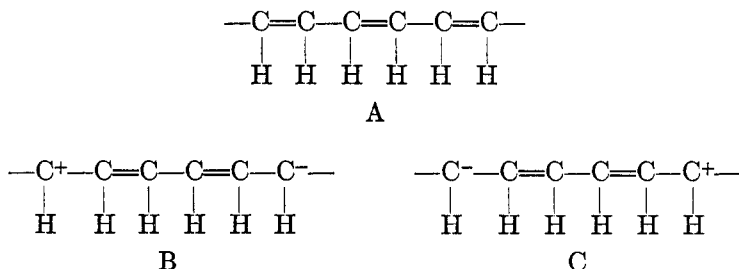


FIG. 9. Plot of frequency of first maximum against the total number of conjugated double bonds for seventy compounds of the polyenic type.

He includes all the double bonds in the end members except in the case of the phenyl group, to which he arbitrarily assigns a "color equivalent" of

one and one-half double bonds. His curve shows a simple functional relationship between the frequency of absorption and the length of the conjugated chain. What this relationship is we shall now attempt to ascertain.

Let us write for a polyene, omitting the end members, the major contributing structure A and the two symmetrical minor structures B and C:



We need not assume that the resonating molecule ever reaches the extreme forms B and C but rather that there may be concerted motions of the electrons from the major structure A, in the direction either of B or of C.

On account of its symmetry the normal state of the molecule has no dipole moment. If, however, it is placed in an electric field, for example, a positive plate at the right and a negative plate at the left, the electrons are shifted in the direction of structure B. The dipole moment produced per unit field strength is the polarizability. We may now consider this electronic displacement in either of two equivalent ways. We may consider the molecule as a whole and the total displacement from one end to the other, or we may consider the individual units (---C=C) and, ignoring



end effects, add the dipole moments produced in the several units. Let us choose the latter course. If μ is the moment produced in each unit in a field of strength E , then α , the polarizability, is given by the equation

$$\alpha = \mu/E \quad (1)$$

We do not need to decide how many electrons are involved in our process. If $-e$ is the effective charge which is displaced and x is the displacement from the normal position, then

$$\mu = ex \quad (2)$$

The electric force is $-eE$. When a displacement has taken place, this must be balanced by a restoring force which, assuming Hooke's law, may be written as $-kx$. Then

$$-eE = kx \quad (3)$$

Combining these equations we find for the coefficient of restoring force k the equation

$$k = e^2/\alpha \quad (4)$$

When our molecule is in an alternating electromagnetic field, such as that of radiation of wave length large compared with the dimensions of the molecule, we shall have an induced oscillation throughout the length of the molecule in which the displacement will be the same in magnitude and in direction for each unit. We are now going to assume that in the electronically excited states there are oscillations within the molecule that are of the same character as these induced oscillations. Let m be the mass of the effec-

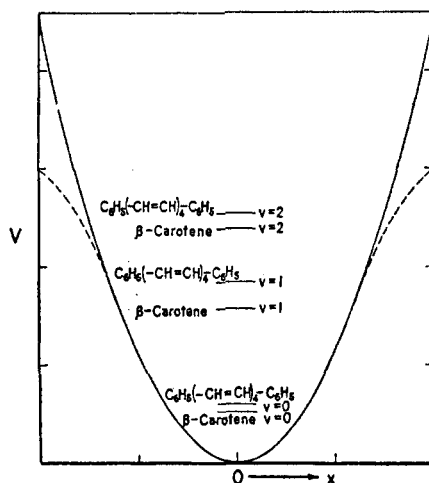


FIG. 10. Plot of potential against x , the electronic displacement

tive electrons in each unit, so that $-e/m$ is the familiar ratio of charge to mass for one electron; then in the molecule composed of n units the oscillations will be those corresponding to the constant k and to a mass equal to nm .

In other words, we have replaced our system of unit oscillators by a single oscillator with the same coefficient of restoring force, and with a mass proportional to the number of units. We may now use the ordinary methods applied to a simple linear oscillator. If we plot in figure 10 the potential against x , the electronic displacement, we obtain the parabola characteristic of simple harmonic motion, in which the potential is equal to kx^2 . We shall later consider a possible anharmonicity of the type represented by the dotted line.

The energy levels, W_v , of an oscillator of mass nm and restoring force constant k , are given by the expression

$$W_v = (v + \frac{1}{2})h\nu_0 \quad (5)$$

where $2\pi\nu_0 = \sqrt{k/nm}$ and v is the quantum number of the oscillation. Therefore the frequency of light which can change the oscillator from $v = 0$ to $v = 1$ is simply $\nu = \nu_0$. Changing to wave length λ , and using a new constant which includes the effective mass of one unit, we have the equation

$$\lambda^2 = k'n \quad (6)$$

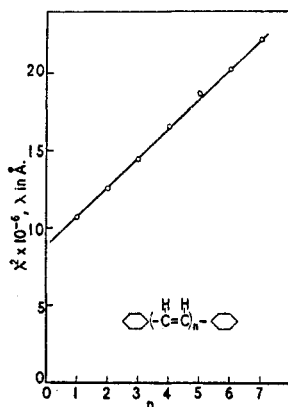


FIG. 11. Plot of the square of the wave length against the number of units of the polyenic chain

Let us test this equation by means of the most extensive and accurate single series of measurements that have so far been obtained in the study of the absorption spectra of organic molecules. These are the measurements of Hausser, R. Kuhn, and Seitz (25) on the diphenylpolyenes, which we have already reproduced in figure 8. Taking the frequencies of the first absorption maxima as given in their table, we have obtained the wave lengths whose squares are plotted in figure 11 against the number of units, n , of the polyenic chain. The very close approach of the individual points to a straight line is an excellent verification of equation 6. The intercept of this line on the n -axis shows that, if we wish to make λ^2 not merely linear with but proportional to n , we must add to the latter the equivalent of 2.35 units for each phenyl group, while Hausser assigned 1.5 units to this group. We attach, however, no importance to this. Our equation was derived for a number of equivalent units. What effect is produced by

ending the chain, or by using different end groups, cannot be predicted. The main thing is that we have linearity of λ^2 with n in the higher values of n . It may be accidental that the points for small n fall on the same line.

Insofar as the statement of Hausser is correct, that some seventy polyenic substances fall on a single curve, such as that of figure 9, we may say that the absorption frequencies may be calculated from a single value of k characteristic of a polyenic chain. Many of the data, however, are far from accurate, and in some of the simpler members of the series Hausser and also Smakula, who published a similar curve, apparently overlooked the faint bands of lowest frequency, such as we shall see in figure 15.

The measurements on the diphenylpolyenes also show an interesting relationship between the number of double bonds and the intensity of absorption. Whether the latter be measured by the maximum extinction coefficient, or by the area under the first absorption band, the authors found the intensity to be a linear function of n . It is tempting to look for general relationships among intensities similar to those found for frequencies, and we realize that in the study of color the intensities and the positions of absorption bands are of coördinate importance. We are obliged, however, in the present paper to neglect in most cases the problem of intensities, to which we hope to revert on another occasion.

The success of the idea of a single oscillator for a whole molecule leads to inquiry as to whether we ever have absorption to the next higher vibrational level than the first, i.e., $\Delta v = 2$. In the ordinary treatment of atomic oscillations, the probability of an absorption of light that carries the oscillator from the level $v = 0$ to level $v = 2$ is found to be zero for a harmonic oscillator, and to increase with increasing anharmonicity. If we carry over this idea to the electronic oscillator, we see that if the energy change from $v = 0$ to $v = 1$ is equal to the energy change in going from $v = 1$ to $v = 2$, or, in other words, if the potential curve is a true parabola, then we cannot expect to find the second-order bands corresponding to the transition from $v = 0$ to $v = 2$. On the other hand, if the potential curve is no longer a parabola, but something like the dotted curve of figure 10, and if the levels come closer together with increasing v , as indicated in that figure, these second-order bands should be observed, and with an intensity depending upon the anharmonicity.

Hausser, Kuhn and Seitz (25) found for the diphenylpolyenes a characteristic band of short wave length which they attributed to the phenyl groups. However, we find quite similar bands in many substances which contain no phenyl group. Thus in figure 12 are shown the absorption curves of various carotinoids given by Smakula (66a), all of which show, and most of which show uniquely, a band in the ultraviolet which would be difficult to account for except by our assumption. We give in table 1

Smakula's figures for the first band (band 1), which represents pure first-order electronic absorption, and for band 5 which we are now attributing to second-order absorption. It will be seen that the ratio of λ_1 to λ_5 lies in the narrow range 1.70 to 1.85.

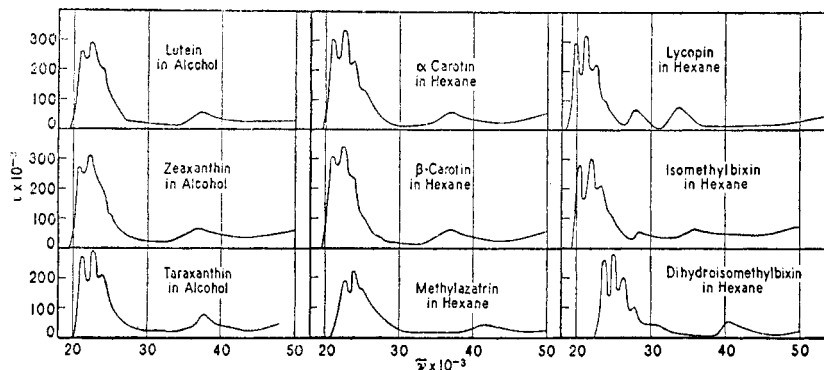


FIG. 12. Absorption curves of various carotinoids

TABLE 1

Values for band 1 and band 5 for some carotinoids

CAROTINOID	λ_1	λ_5	RATIO λ_1/λ_5
Methylazafrin*	442	240	1.85
Dihydroisomethylbixin	422	247	1.71
Isomethylbixin	490	277	1.77
β -Carotin	477	270	1.77
α -Carotin	475	270	1.76
Taraxanthin (in alcohol)	471	265	1.78
Lycopin	504	296	1.70
Zeaxanthin (in alcohol)	480	273	1.76
Lutein (in alcohol)	475	267	1.78
Crocetin	445	254	1.75
Violazanthin (in alcohol)	471	265	1.78

* All these substances were measured in hexane solution unless otherwise specified.

Let us now return to the simpler diphenylpolyenes with one, two, three, and four double bonds between the phenyl groups. Here, according to the authors' data, the ratios between corresponding λ 's are respectively 1.39, 1.44, 1.51, and 1.58. Inspection of these figures, together with the average ratio 1.76 for the long-chain carotinoids, indicates that we are really dealing with second-order absorption. For as we go to larger values of n , where the energy levels sink toward the bottom of the potential curve where it is

nearly parabolic, the ratio of the first-order to the second-order wave lengths is approaching 2.

Independent evidence that these are second-order bands of the diphenylpolyenes is furnished by their intensities. It was found that the ratio of intensity of the second-order to the first-order bands diminishes with increasing n . This is to be expected from our hypothesis, for with increasing n we are approaching the purely harmonic region, where the relative intensity of the second-order bands should approach zero. If instead of the parabola we use a curve given by the equation $V = \frac{1}{2} kx^2 + bx^4$ for which the corresponding quantum levels have been evaluated, we find, taking a negative value of b , that the above ratios increase with n , but not so rapidly as the experimental values. It will be interesting to try other functions in which the curve departs even more rapidly from the parabolic form, with increasing displacement.

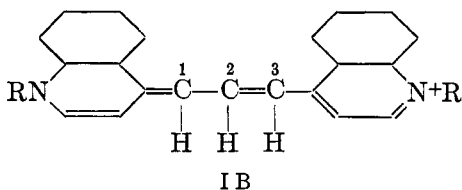
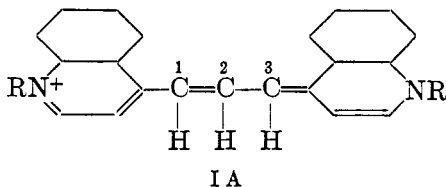
The second-order bands which, like the first-order bands, belong to the fundamental oscillation of the molecule as a whole, and which are to be expected in a great variety of substances, are ordinarily obscured by another type of band, which is due to only a part of the molecule, and which we shall discuss presently under the name of bands of partial oscillation.

Linear oscillators of another type

In discussing the polyenes we have assumed that in the actual resonating molecule, even in the electronically excited states, the electrons never get far from the positions indicated in the classical formula. While we have assumed that the electrons are capable of concerted movements as to phase, we have not supposed the restoring force within a single unit to be appreciably affected by the electrons of the next unit. We might go to the other extreme and assume in certain other kinds of molecules that the electronic cloud is diffuse and more or less uniformly distributed throughout the length of the chain, and that the restoring force is now chiefly dependent upon the position of other neighboring electrons. We should then have an analogy to the longitudinal vibrations in an elastic string, where the frequency is inversely proportional to the length of the string. It is therefore interesting to see whether there are series of nearly linear molecules in which the wave length of maximum absorption is linear with the length of the chain, and whether the constitution of such molecules is such as to suggest a more or less uniform and continuous distribution of the electronic cloud.

In the polyenes we saw that the main contributor to the resonance state was represented by the classical formula (A). Turning now to the carbocyanines and similar dyes, which have been much investigated, the conditions are quite different. For the ion of a cyanine such as is represented

below, we have no one main contributing structure, but two symmetrical structures contributing equally to the resonance state, namely,

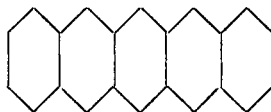


Whatever the electronic distribution may be, it will be the same between atoms 1 and 2 and between atoms 2 and 3. The properties of such a system will be further discussed in the following section.

The best absorption data for substances of this class are those obtained by Fisher and Hamer (19) and Beilenson, Fisher, and Hamer (3) upon a series of carbocyanines which differ only in the number of ethylene groups added to the connecting chain. Again we use the data from the table given by the authors. These data are reproduced in figure 13, where λ is plotted against the number of double bonds lying between the two nitrogens. It is evident that the relation is linear. Similar data have been obtained by these authors and by Brooker and coworkers (7, 8) for other series of similar substances. Apparently within the limits of error the same relationship holds.

Another series of substances in which this linear relationship appears to be valid, although the experimental error is large, was obtained by Hausser (23) by dissolving the diphenylpolyenes in concentrated sulfuric acid. Here the absorption maxima have moved far toward the red. The resonance in this type of molecule will be compared with that in the cyanine type, in the following section.

Finally we may mention an entirely different class of substances, the linear condensed ring systems (13), from benzene to pentacene,



Here we are dealing again with neutral molecules, but with a high degree of conjugation. As far as we can gather from the existing experimental data,

λ seems to be roughly linear with the number of rings, indicating that here also the electronic cloud is diffuse and not much localized.

Between the two types of linear molecules represented by the polyenes and the cyanines we may expect to find many intermediate substances, especially such compounds as have, in the part of the molecule in which oscillation occurs, a charge which is less than unit charge. Sufficiently exact data for testing this supposition are at present lacking. Still another type of nearly linear molecules, the *p*-polyphenyls, will be discussed in the next section.

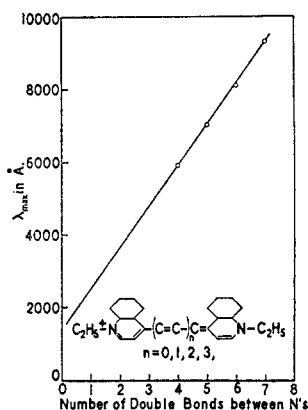
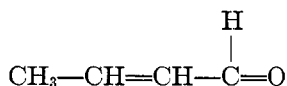


Fig. 13. Plot of wave length against the number of double bonds between the two nitrogen atoms for a series of carbocyanines

FURTHER REMARKS ON CONJUGATION

The important effect of conjugation on absorption has already been illustrated in figures 6 and 7. The latter figure shows that, when a molecule has two double bonds which are insulated from each other, each will show its own absorption; so also in figure 14 (57) we see the effect of such insulation between two carbonyl groups. Curve 2, for dipropionylethane, is almost identical with the dotted curve 3, which shows twice the absorption coefficient of acetone. On the other hand, curve 1, for the conjugated diacetyl, shows a powerful fundamental absorption at lower frequencies, as well as a "partial" band not far from the other curves.

These fundamental bands of the whole conjugated system, which are so pronounced in dyes, may in simpler molecules be of such low intensity as to be frequently overlooked. Thus in the case of crotonaldehyde (figure 15),



which has been studied by Lüthy (45), the weak fundamental band, which is less than one-thousandth as intense as the next band at higher frequency and would not be seen except on a logarithmic plot, was missed completely by Smakula in the tabulation to which we have referred.

Similar conditions are found in the case of benzene, whose absorption spectrum has been more thoroughly studied than that of any other substance, chiefly in the range between 2300 and 2800 Å. The absorption in

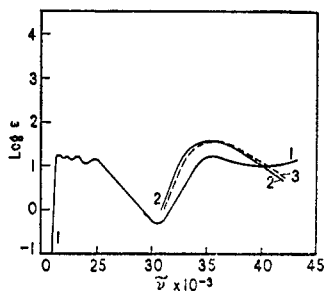


Fig. 14. Effect of insulation of carbonyl groups on the absorption. Curve 1, $\text{CH}_3\text{COCOCH}_3$ in hexane; curve 2, $\text{C}_2\text{H}_5\text{COCH}_2\text{CH}_2\text{COC}_2\text{H}_5$ in hexane; curve 3, CH_3COCH_3 in hexane ($2 \times \epsilon$).

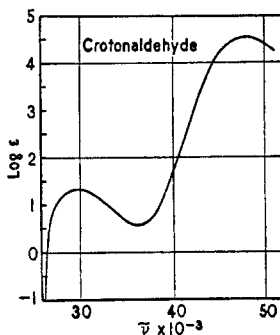


Fig. 15. Absorption curve of crotonaldehyde.

this region, however, is very small compared with that at higher frequencies. The bands of ethylbenzene (which are almost identical with those of benzene) and of styrene are shown in the two diagrams given by Smakula (66b), which we reproduce in figure 16. In the dotted curve the extinction coefficients have been multiplied fivefold, in order to show how weak is the fundamental absorption band of ethylbenzene compared with that of styrene, the latter being one of the first members of the highly conjugated series that we have already discussed.

The weak absorption of benzene, in its conjugation band, shows that the phenomena of color and of resonance, although they are closely related, are not related in such a way that high resonance energy implies large absorption of light. The chief resonance of benzene is the sort in which there are two major contributing structures of equal importance, the two Kekulé structures; but this resonance does not directly contribute to light absorption. It is only the minor contributing structures, such as may be represented by the formulas



that are involved in the absorption. Insofar as these ionic structures become important, they diminish the Kekulé resonance and, conversely, the great strength of the Kekulé resonance diminishes the contribution of the ionic forms.

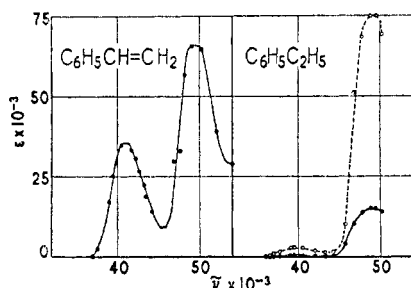


FIG. 16. Absorption curves of styrene (left) and ethylbenzene (right)

The same principle applies to the polyphenyls. The only two structures which are concerned with light absorption are expressed by the formulas



but these formulas require a completely quinoid condition and therefore can exist only at the expense of the numerous types of Kekulé resonance.

When the number of phenyl groups in the chain is small, the large percentage increase in length produced by one additional phenyl group, will produce so large a change in the polarizability as to offset the counteracting tendency of the Kekulé resonance and we should expect a considerable increase in the wave length of the absorption maximum. On the other hand, when the chain is already long, each new phenyl group will produce only a relatively small increase in length; but the electronic oscillation, if it is to run through the whole molecule, must do so at the expense of two new Kekulé resonances for each group added.

Gillam and Hey (20a), in a very recent article, have determined the wave length of maximum absorption of five *p*-polyphenyls in chloroform. Their results are as follows: diphenyl 2515 Å; terphenyl 2800 Å; quaterphenyl 3000 Å; quinquiphenyl 3100 Å; sexiphenyl 3175 Å. Presumably further increase in the length of the chain will produce little change in the *position* of the absorption band. The essential difference between the conjugation in the polyphenyls and in the polyenes may be brought out by considering the effect of inducing a positive charge on one end of the chains. What we may call the center of gravity of the residual negative charge will, in the polyenes, move away indefinitely as the length of the chain increases. In the polyphenyls it will move out through a few groups only, and then be nearly stationary as the chain is indefinitely increased.

Bands of partial oscillation

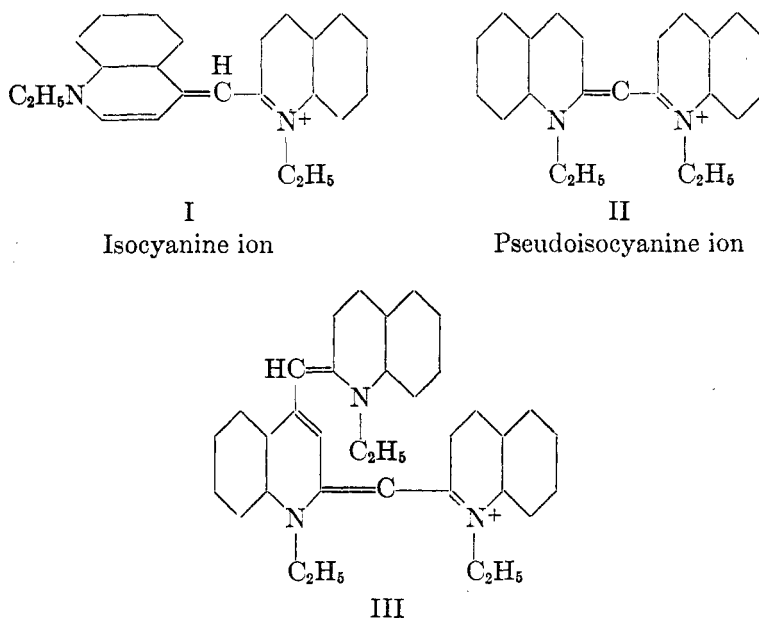
In such figures as we have presented, showing the fundamental band due to the whole conjugated system, and another band of higher frequency, we can conceive the latter to be due to a localized oscillation in some part of the molecule, involving in some cases only a single chromophore. These bands of partial oscillation are not our primary concern, but since we shall mention them occasionally they may briefly be discussed here. When there is insulation between two chromophoric groups,—for example, when they are separated by one or more saturated carbon atoms as in figures 7 and 14,—their oscillations are independent. However, when we have two conjugated double bonds, even if we are able to stimulate an oscillation in one of them alone, we need not expect to obtain the absorption which that double bond shows when isolated, for the process of conjugation or resonance has changed the energy of the whole molecule. Nevertheless by its form and position we are usually able to identify approximately these bands of partial oscillation with the bands of the individual chromophores, as we see in figure 15.

The question now arises as to the relative intensity of the bands of total and of partial oscillation. In the process of conjugation a certain amount of energy is set free which is known as the resonance energy. If we divide Planck's constant h by this resonance energy, we have a number which has the dimensions of time, and it is occasionally useful to consider that this number gives the order of magnitude of the time required to establish in the molecule the normal conditions of the resonance state.

The resonance energy of a conjugated diene amounts to several kilocalories, which gives for the resonance time a value between 10^{-13} and 10^{-14} sec. Now the period of the light which is absorbed by butadiene is of the order of 10^{-15} sec. The fact that the period of light is short compared with the period of resonance may explain the observation that, as we

proceed farther into the ultraviolet, all absorption spectra appear to an increasing degree to be characteristic of individual chromophores. On the other hand, in the case of dyes which absorb in the visible, where the period of the light is greater and the time of resonance, because of large resonance energies, is shorter, the absorptions are characteristic of well-conjugated systems acting as single units.

These bands of partial vibration are almost invariably to be found in the ultraviolet, where they are usually to be ascribed to simple chromophoric groups, such as the phenyl or vinyl groups, but they are also to be found in the visible, where they belong to large parts of an extensive conjugation. We shall illustrate this by means of the absorption curves obtained by Brooker and Smith (8) for a number of cyanines. In the accompanying set of formulas, I and II represent isocyanine and pseudoisocyanine, while III is a more complex structure containing, in a sense, both I and II.



In each case only one of the resonance forms is given. The main contributors to resonance may be obtained by assigning the positive charge to any one of the nitrogen atoms. The absorption curves are shown in figure 17. The two isocyanines give the entirely similar curves 1 and 2. We shall reserve our comments upon the double peaks until we discuss later an important paper by Scheibe. In curve 3 we see the important new band in the red, which we ascribe to the electronic vibration in the molecule

as a whole. It seems very reasonable to ascribe the right-hand portion of this curve to a partial oscillation, belonging to that part of the molecule which is similar to structure I, or to that part which is similar to structure II, or to a merging of the two. The fact that this part of the curve appears at higher frequency than in curves 1 and 2 is an illustration of a very general principle, which will be treated later under the head of cross conjugation.

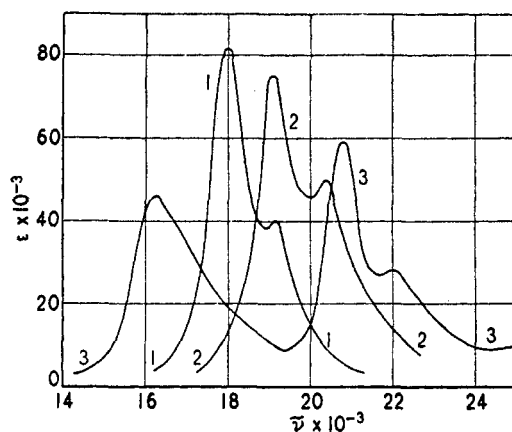
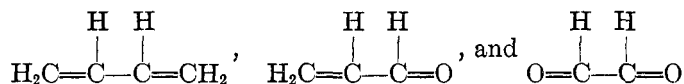


FIG. 17. Absorption curves of a number of cyanines. Curve 1, isocyanine ion in ethanol; curve 2, pseudoisocyanine ion in ethanol; curve 3, 2,4-di[(1-ethyl-2(1)quinolyldine)methyl]-1-ethyl quinolinium ion in ethanol.

Relations between the absorption of a conjugated system and of its component parts

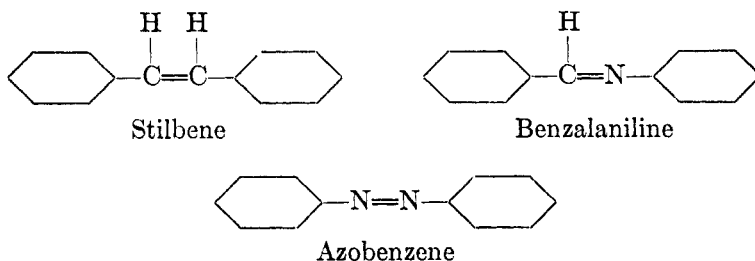
We have not succeeded in finding any way of calculating quantitatively the absorption frequencies of conjugated molecules from those found for the individual component double bonds, nor are there any data sufficiently accurate to test such a calculation. Qualitatively, however, we may predict, from our idea of strain, the absorption of numerous types of conjugation.

The frequency of absorption will be lower when the electronic displacements are such as to diminish the double-bond character in bonds of high strain, and higher when the displacements increase the double-bond character in such bonds. Thus the double bonds C=C, C=N, C=O, N=N, and C=S will lower the absorption frequency in this order. In the three molecules



the absorption maxima are approximately at 2200, 3500, and 4600 Å.

The three substances, stilbene, benzalaniline, and azobenzene have



progressively lower absorption frequencies. The first absorption maxima are, respectively, about 3100, 3300, and 4500 Å.

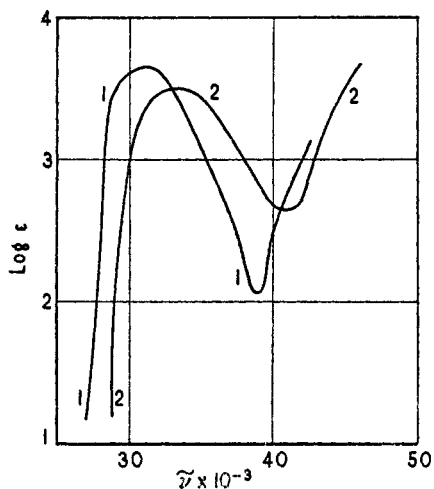
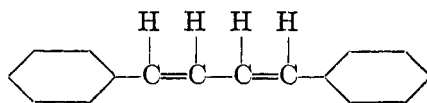


FIG. 18. Absorption curves of diphenylbutadiene (curve 1) and benzalazine (curve 2)

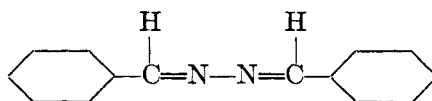
The strongest of these chromophoric groups, or, in other words, the one that we consider to be in the state of greatest strain, is $C=S$. It gives colored compounds even of such simple type as thioacetophenone and thiobenzophenone. The latter has an absorption maximum at 6200 Å. (9).

An interesting corollary follows from our statement that $N=N$ is more chromophoric than $C=C$, because of the strain which favors the ionic contributors to resonance. We should find, in a conjugated system which in its ordinary form is written with a single bond between two nitrogen atoms, that the absorption frequency is higher than in the corresponding compound with carbon atoms, for in this case the ionic forms can only occur when the highly strained double bond is produced between the two nitrogen atoms. This is true, as shown, for example, by figure 18, which

reproduces the results of Rădulescu (55) on the two compounds



and



The first, purely ethylenic, substance gives curve 1, whereas the second substance, with the N—N bond, absorbs at higher frequency (curve 2).

Steric effects on conjugation

The degree of conjugation, and therefore the mobility of electrons, in a system may depend not only upon the nature of the double bonds but also upon certain steric relations.

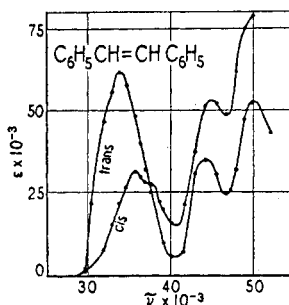


FIG. 19. Absorption curves of the *cis*- and *trans*-forms of stilbene

If we construct in space a model of the molecules of *trans*- and *cis*-stilbene we see in the latter case that, if we use the proper bond distances and angles, two of the ortho hydrogens of the benzene rings are presumably brought sufficiently close to exert upon one another a considerable repulsive force. This will tend to force the system out of a plane, with the effect of reducing resonance.

The optical effects are shown in figure 19 (67), which shows the absorption curves of these two substances. The effect of the powerful conjugation of *trans*-stilbene is shown both in the position and in the intensity of its fundamental band.

Even in *trans*-stilbene, when the hydrogen atoms are replaced by one or two methyl groups, these methyl hydrogens come close enough to the benzene ring to produce a similar effect, as shown in figure 20 (43), in which

the first curve is that of stilbene, and the second and third are those of the mono- and dimethylstilbenes.

Finally, when we come to some of the ortho-substituted biphenyls, the bands of conjugation disappear when there are four methyls or four chlo-

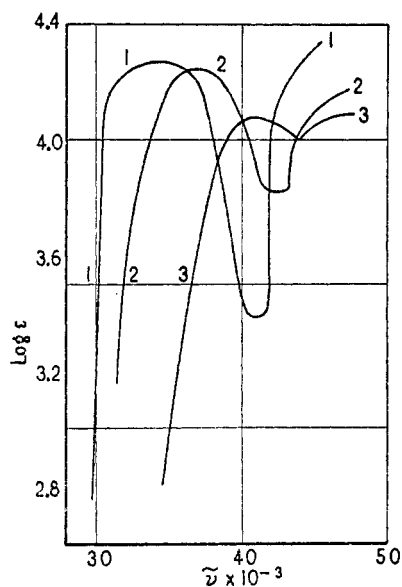
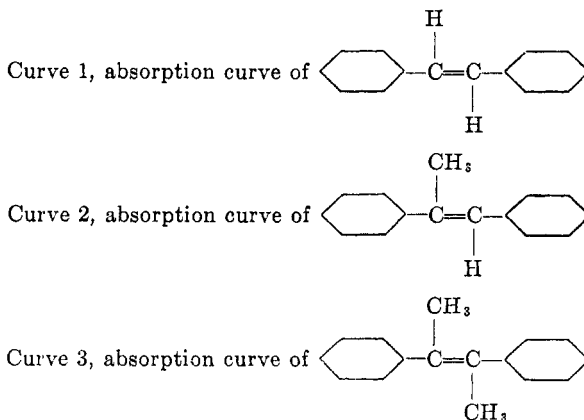


FIG. 20. Absorption curves of stilbene and methyl stilbenes



rines in the ortho-positions, as shown by Pickett, Walter, and France (52). Here no approach to the planar structure is possible, and the authors themselves remark, following a suggestion of Kistiakowsky, that the

differences in the spectra "may be dependent on the planar form of the molecule."

Evidence of the diminution in resonance by steric influences which prevent coplanarity has been drawn from chemical behavior by Calvin (11) and from dipole moments by Birtles and Hampson (5) and by Ingham and Hampson (34).

GENERAL RULES OF COLOR

Since the original chromophore and auxochrome theory of Witt, there have been very few theories of color that have proved applicable to more than a limited group of dyes. A theory of Dilthey (18), which has been strongly emphasized by Wizinger (71), deserves our attention. According to this theory, while other types of substances show weak absorption, running well into the visible region, by far the most powerful absorbers of visible light are "ionoid." There is no doubt that this is a very important observation, but it can at best be only a partial statement of a more general principle, even with the most liberal interpretation of the word "ionoid." Wizinger implies that the strongly colored substance must be an ion or an inner salt, but this must be incorrect, as may be seen immediately when we consider the so-called halochromic phenomenon. A vast number of neutral organic substances become brilliantly colored upon the addition of hydrogen ion (51), but these same substances absorb with approximately the same intensity and at almost the same frequency when neutral substances such as boron trichloride or stannic chloride are added in place of hydrogen ion; yet in these cases the resulting molecules are not ions. Also, it should be pointed out that neutral substances such as *p*-nitroaniline or 4-nitro-4'-aminostilbene, both of which are yellow to orange-red, lose their color or become only a pale yellow upon the addition of hydrogen ion.

Let us see whether it is possible to establish the general principles underlying the phenomenon of color, from our theory of electronic oscillations. We may visualize a sort of "ideal" molecule in which every electron-pair is situated in so deep a potential trough that it can be excited to a higher energy state only by the addition of a large amount of energy. The nearest approach to such an ideal molecule is furnished by the aliphatic hydrocarbons. Even in these cases we have seen that there is a diminution in the energy required for excitation when a ring is formed (see figure 6), and this effect doubtless increases in accordance with the Baeyer strain theory until we reach the three-membered system of cyclopropane, and indeed until we reach the two-membered system of ethylene. We may conceive that, even in these simple cases, that which we call a state of strain has moved some of the electron pairs into positions where excitation is more easily effected.

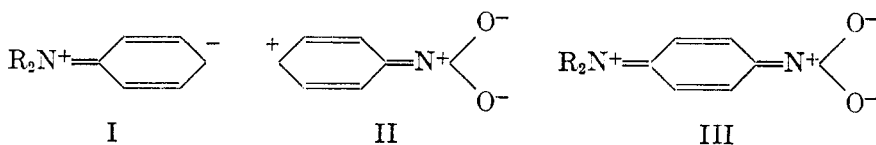
The fact that cyclopentadiene absorbs at a lower frequency than butadiene, as illustrated in figure 6, may be attributed to the increased strain and therefore the increased energy of the classical structure. So we have found it convenient to assume an increasing strain in the series of double bonds from C=C to C=S. The effect of these strains is to move the normal state of the molecule away from the more ideal condition represented by the classical formula.

We are assuming that *every displacement from the ideal state makes further displacement easier*, or, in other words, increases the mobility of electrons. We have already given one example of this in studying the polyenes, where we were led to the conclusion that increasing the displacement caused a diminution in the coefficient of restoring force.

One way of viewing this phenomenon is to think that the electronic clouds are highly localized at the places where electron-pairs appear in the classical structure, but that they become diffuse, and more uniformly distributed, when there is any displacement from that structure. We then associate this increased diffusion with a higher mobility and with a lower value of the restoring force constant.

Thus if we wish to produce a bathochromic effect in a molecule (a) we may increase the masses of the oscillating system by increasing the number of participating electrons, which may be accomplished by increasing the extent of the conjugating system, as in the polyenes or the phthalocyanines, or (b) we may increase the mobility of the electrons. We may now see how this mobility may be increased in the several important classes of substances.

The first case we must deal with is the one in which we start with a resonating molecule, in which the main contributor is a classical structure such that no atom has a formal electric charge. Here one of the most important methods of producing a bathochromic effect is by the use of an auxochrome. Benzene is such a molecule. If we substitute for one of the benzene hydrogens a basic auxochrome, such as NR_2 , or an acid auxochrome, such as NO_2 , we have new resonating states in which there is a shift toward the resonating forms I and II.



If the benzene ring has both these auxochromes para to each other as in formula III, we have a much greater contribution from the polarized form, and the electronic center has been moved much farther to the right. The

fact that the dipole moment of *p*-nitroaniline is considerably greater than the sum of the moments of nitrobenzene and aniline may be regarded as an illustration of the principle that a displacement from the "ideal" molecule renders further displacement easier. Even in *p*-nitroaniline the equilibrium center of the electrons is still far removed from that which would be found if the molecule actually had structure III, as shown by the fact that the dipole moment is only about one-fifth of that which would be calculated for the complete inner salt. All of these substitutions increase the mobility, especially in *p*-nitroaniline whose absorption band reaches into the visible region.

There has been a widespread belief that the dielectric constant of the medium has a large influence upon absorption curves. We do not see that

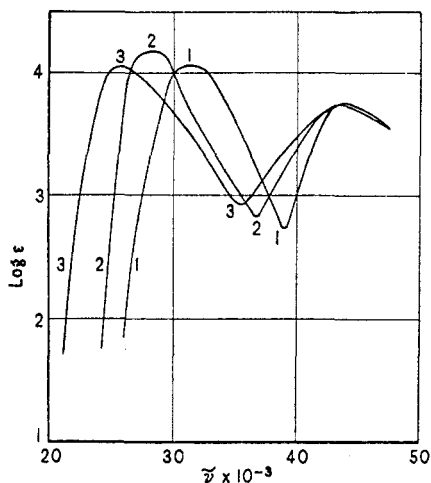
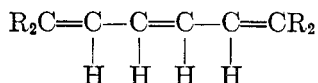


FIG. 21. Absorption curves of *p*-nitroaniline in hexane (curve 1), dioxane (curve 2), and water (curve 3)

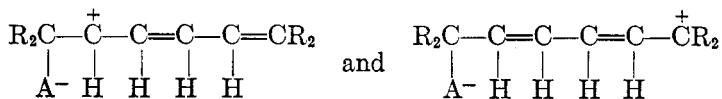
this should be so, nor in general do the experiments seem to indicate that it is so. However, in such cases as the three that we have just considered, we not only expect and find such an influence, but these examples provide an excellent further illustration of our principle that electron mobility increases with increasing departure from the ideal state of the classical structure. In these substituted benzenes the contribution of the ionic forms becomes greater if the energy required for the separation of charges becomes less, as happens in a solvent of high dielectric constant. This further displacement from the ideal molecule has the effect of increasing the mobility according to our principle. This is illustrated in the absorption curves of *p*-nitroaniline in (1) hexane, (2) dioxane, and (3) water, as shown in figure 21 (16). It is to be emphasized, however, that the ionic

forms in such substances as the polyenes are not much favored by a solvent of high dipole moment; since the resonance state has no average moment, and the motions of the electrons are too rapid to be followed by the dipoles of the solvent.

Starting again with a molecule in which the chief resonance contributor is a classical structure, we can produce a greater bathochromic effect than is caused by any ordinary auxochrome, by adding an acid, or in rare cases a base, to one end of a double bond that is part of a conjugating structure. The effects upon absorption are the same qualitatively and usually quantitatively, whether the added acid is hydrogen ion or one of the generalized acids (37) such as boron trichloride or stannic chloride. We have seen in the preceding section the enormous bathochromic effect when the polyenes are dissolved in concentrated sulfuric acid. Identical colors are obtained by treating them with boron trichloride (39). Let us examine what happens to the resonance within the molecule in this case, which is one of the simplest examples of the important halochromic phenomenon. Take the polyene



In the resonating molecule by far the most important contributing structure is the one written. Supposing now that the neutral acid A is added at the first carbon atom; then we have a series of resonance structures such as

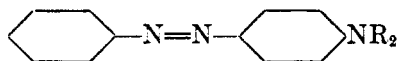


in which the positive charge is placed on the second, fourth, or sixth carbon atom. Perhaps the last structure contributes most, but they are all important, and no one of them even approximates to an ideal molecule. The result is that a molecule in which electron-pairs were capable of only small motions about definite positions has now been converted into a molecule in which the electron cloud has become diffuse and which approaches, but does not reach, the state about to be described.

We now come to the class of substances which includes the great majority of powerful dyes, and which presumably Dilthey had chiefly in mind when he proposed the "ionoid" theory. It is the class we have already had exemplified by the cyanines, in all of which the intense color is due to an ion in which the charge may equally well be placed at either end of a chain, and practically all the resonance may be regarded as between the two opposite forms. If we were able to plot the density of electronic cloud in

the molecule, it would presumably be very diffuse and certainly would show no distinction between those places where we arbitrarily place double or single bonds. The condition is not very different from that in the polyenes dissolved in sulfuric acid, except that there the density of electrons more or less uniformly diminishes from one end of the molecule to the other, whereas here we have a uniform condition along the chain, especially if the two end groups are identical. Even if the end groups are not the same but yet are of the same general character, the same conditions prevail. This is shown by the fact that Beilenson, Fisher and Hamer (3) were able to calculate with moderate accuracy the absorption of hybrid cyanines with a group A at one end and B at the other, from the spectrum of the A, A and the B, B dyes.

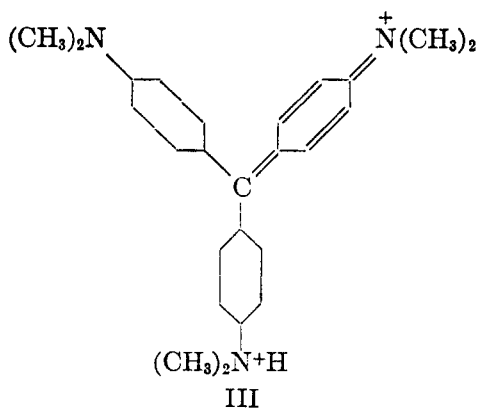
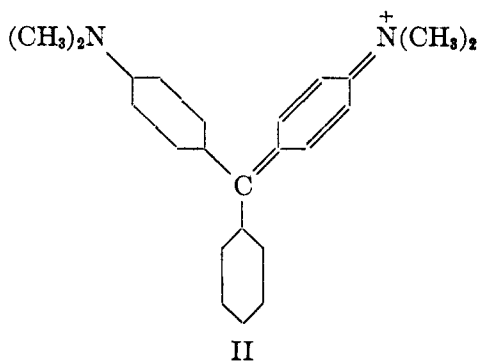
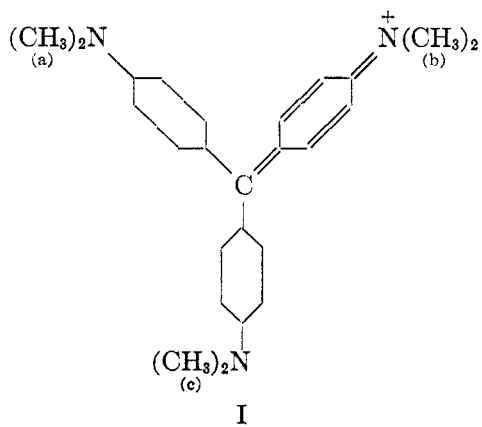
Most of our common acid-base indicators are substances which, when they are in their more strongly colored form, have acquired a charge which is not confined to one place in the molecule but rather appears, in different phases of resonance, in distant parts of the molecule. Thus the indicators of the type

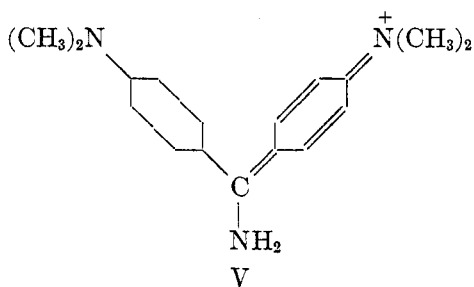
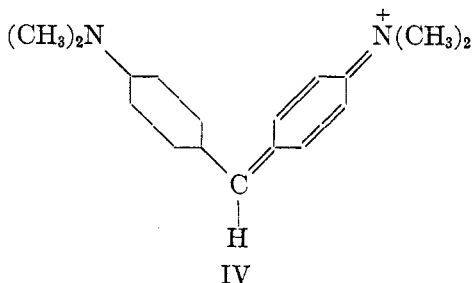


are well-conjugated molecules, as shown by their yellow color in the neutral state. This resonance, however, is one in which a single classical structure is the main contributor. When hydrogen ion is added to the nitrogen atom farthest to the left, an intense red color appears. The chief resonance is now between two structures, one of which has the positive charge on that nitrogen, while the other has it on the amino nitrogen.

Schwarzenbach (63) has made a careful study of a number of indicators which exhibit several successive color changes, and has shown that the highly colored forms are always the ones in which the charge may equally well be placed at one extremity or the other of a symmetrical molecule. He has also pointed out that these highly colored forms are also the more stable, but this is not always the case. This point has been brought out in our discussion of benzene, and will now be further illustrated, as we offer an explanation of what has seemed a striking anomaly in the theory of color (71).

The ion of crystal violet (I), p. 309, is a highly resonating molecule. The three chief contributing forms, all alike, are obtained by assigning the positive charge in turn to the three nitrogen atoms. As evidenced by its chemical behavior, it has far more resonance energy than malachite green (II), but while the absorption band of crystal violet has a maximum at 5900 Å., that of malachite green lies at 6230 Å. This is not an isolated phenomenon, but many cases could be cited; for example, as acid is gradually added





to crystal violet, its chief absorption moves first toward the red and then toward the violet, as we have seen in figure 2. In substance III, produced by adding one hydrogen ion to the ion of crystal violet, the absorption maximum lies at 6300 Å. Also we have studied (73) the absorption of the ion of Michler's hydrol (IV). Its absorption maximum is at 6200 Å. In these three substances—II, III, and IV—the resonance energy of crystal violet has been reduced by varying amounts, but they show nearly identical absorptions, all at higher wave length than that of crystal violet (I). We may also compare compounds IV and V (auramine). In the latter, although hydrogen has been replaced by the amino group and thus the possibilities of resonance have been increased, the absorption is nevertheless at a far lower wave length, namely, 4200 Å. (36).

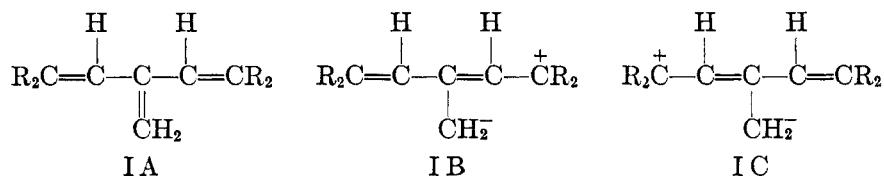
The explanation of these facts from our present point of view is an extremely simple one. If we add the auxochrome NR_2 to malachite green or to Michler's hydrol, to form crystal violet or auramine, we have increased the resonance by increasing the number of important resonance forms. The positive charge in the former pair can be considered as belonging to either one nitrogen or the other. In the latter pair it may be shared by all three nitrogens. While this increases the resonance, it does not favor the resonance that is responsible for color.

Consider in formulas I to V a horizontal axis which represents the direction of an electronic oscillation. In form I we have a positive charge which

belongs collectively to the three auxochromes. Those phases, however, in which this charge is on auxochrome *c* do not contribute to the horizontal oscillations between auxochromes *a* and *b*. We may say roughly that only two-thirds of a charge is capable of this *ab* oscillation. In formulas II, III, and IV, on the other hand, we have a full charge capable of oscillating horizontally. When we come to formula V, it is presumable that the nitrogen on the central carbon atom can be assigned more than one-third of the positive charge. All of these statements are in complete accord with the observed colors. We have referred to a similar case in discussing figure 17. Regarding electronic oscillations in the vertical direction we shall have something to say in a later section.

The ideas just illustrated may be formulated in a general principle. When the color of a substance is associated with an oscillation along a certain path in the molecule, and when it is due to an excess charge (positive or negative) which may move toward one or the other ends of this path, then the frequency of absorption will be increased by any influence that diminishes the amount of that charge, and decreased by any influence that makes this charge larger.

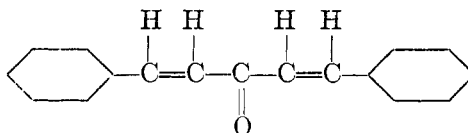
We may apply this principle to explain the remarkable effect of cross conjugation upon color. Let us examine the substance represented by formula IA.



At first sight it would appear that the oscillations should be extremely limited, namely, through the central double bond to the right or through the central double bond to the left, yet this substance absorbs at much lower frequency than a straight-chain triene. We must, however, remember that two of the contributing structures are those in which the central double bond is broken, leaving the lower carbon atom negative or positive, and therefore forcing an excess positive or negative charge into the rest of the molecule. To illustrate the first case we write the formulas IB and IC which, because of their symmetry, contribute equally to resonance, and also because of their symmetry increase the tendency to break the central double bond. Now since the forms IB and IC are analogous to the structures of the cyanine ions, we see that, insofar as they contribute to the actual resonance state, they will have a strong bathochromic effect.

Similarly we might consider substances of the type of phorone, in which the central double bond goes to oxygen instead of to CH₂. In such com-

pounds the oxygen, because of its strong tendency to become negative, contributes a considerable positive charge to the main axis of oscillation. The absorption bands extend into the visible. An interesting group of similar substances is found in dibenzalacetone and its derivatives.



Dibenzalacetone

These substances are colored, usually yellow, and it is evident that the transfer of excess positive charge into the horizontal, well-conjugated chain represents a very important contribution to the actual state of resonance. We can form an idea of the amount of this contribution when we forcibly destroy the central double bond by the addition of an acid to the oxygen. We get the same colors (39) whether this acid is hydrogen ion or boron trichloride. However the change of color is not great; we estimate roughly that the absorption maximum is carried about 1000 Å. toward the red when acid is added to dibenzalacetone, dipiperonalacetone, and dianisalacetone. In other words, even before the addition of acid the resonance form in which the carbonyl double bond is broken is a major contributor to the resonance state.

This strong tendency to break the double bond, which we here observe in the case of C=O, we should expect, from our earlier considerations, to be even more marked with C=S. This has been found by Burawoy (9), who obtained the absorption spectra of the compounds $((\text{CH}_3)_2\text{NC}_6\text{H}_4)_2\text{C}=\text{X}$, where X is CH₂, NH, O, or S. The bathochromic effect increases in this order, and is very large in the case of sulfur.

The most important dyes, except those ions in which the charge may oscillate from one part of the molecule to another, belong to the anthraquinone and indigo types. These all contain carbonyl groups, and it seems reasonable to suppose that the general marked chromophoric character of the carbonyl groups is closely analogous to the effect that we have been discussing.

Summary

Let us summarize the theory of color that we have been developing. Light absorption is due to the excitation of electronic oscillations. In a molecule of the "ideal" type such as a paraffin the energy of excitation is high, but diminishes as the molecule is strained. A great strain is produced by double bonds, which differ from each other in this regard.

Color ordinarily appears in conjugated systems, where the two deter-

mining factors are (a) numbers of electrons involved, and (b) electron mobility. The mobility is small in a molecule whose properties correspond to a formula in which all electrons are paired and there is no "formal" charge on any atom. When such a structure is the major contributing form of a resonating molecule the mobility is still small. When, however, the actual state of a molecule differs considerably from a classical or ideal structure the mobility is greatly increased. In other words, displacement from the ideal structure makes further displacement easier. Strong color is obtained when two important resonance forms are such that the change from one to the other involves the movement of an electric charge. This is a unit charge in many dyes of the ionic type; but there are many neutral dyes in which that part of the molecule in which an oscillation can occur acquires some positive or negative charge from the rest of the molecule. In such cases any change in the molecule which increases that charge enhances the color of the molecule.

ORIENTATION OF ELECTRONIC OSCILLATIONS WITHIN THE MOLECULE

It has long been known that an intimate relation exists between the orientation of a molecule and that direction of polarized light which shows the maximum absorption. This relation has been studied most unambiguously in crystals for which x-ray data show the relative positions of the atoms. We may quote from Hartshorne and Stuart (22): "The study of colored crystals by x-ray methods has revealed how this pleochroism is related to their structure. In organic crystals, the absorption is greatest when light is vibrating along the direction of the bonds in the chromophore groups. . . . Thus in *p*-azoxyanisole, when the vibrations are parallel to the length of the molecule, i.e., to the N=N double bond, the light is yellow, and when the vibrations are transverse, it is colorless." Such work as that of Bernal and Crowfoot (4) on *p*-azoxyanisole, upon which this statement was based, is of an arduous type, and few examples of a complete analysis are available. For this reason more rapid, although less definite, observations have frequently been made by orienting dyes in or on an anisotropic film, such as cellophane (35).

In our previous discussion of long molecules we did not specify the precise direction of the electronic oscillation. In the longer cyanines there is no distinction in the actual molecule between single and double bonds, since the two main resonating structures are entirely similar. There can hardly be any question therefore that the direction of oscillation coincides with the molecular axis. This is by no means so evident in the case of the polyenes, for there the major contributing structure consists of definitely alternating double bonds in a zigzag, in which all the double bonds are parallel. Now since we have assumed that, even in the excited state,

the displacements of the electrons are not large, it might be concluded that the axis of oscillation would lie between the axis of the molecule and the line which is parallel to the double bonds in the classical structure. Using the x-ray data of Hengstenberg and R. Kuhn (30), Calvin (73) has made preliminary observations on diphenyloctatetraene and diphenyldodecahexaene, which show that the maximum absorption is observed when the electric vector of polarized light is approximately along the axis of the molecule. On the other hand, we are informed by Professor Bernal that W. H. Taylor has examined the entirely similar substance β -carotin, and finds that the vector of maximum absorption is in a direction more nearly corresponding to the line parallel to the double bonds in the classical formula.

When we come to molecules that have considerable extension in more than one direction, our theory of electronic oscillations leads to very definite conclusions regarding the relative orientations of the molecule and of the vector of the exciting light. We have distinguished between the

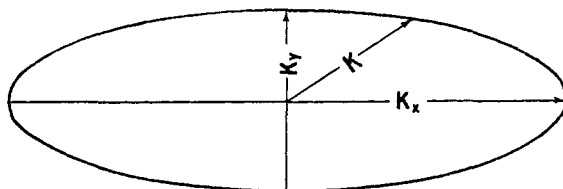


FIG. 22

fundamental bands of the molecule as a whole and the bands of partial oscillation, which concern only a part of the molecule or an individual chromophore. Regarding the latter type of bands we have little information as to the direction of oscillations. A large and important field of investigation with polarized ultraviolet light is almost entirely unexplored. We may predict that when a substance has a series of bands, of which one is a fundamental and the others represent partial oscillations, which may be roughly ascribed to individual groups, the directions of polarization for maximum absorption of two partials will be determined only by the relative orientation of the two groups.

With the fundamental bands the conditions are quite different. Here we have assumed that the oscillations within the molecule may be regarded as the equivalent of a single oscillator in quasi-harmonic motion. In such a case, if we have a planar molecule, the restoring force constant may be different in different directions, as shown in figure 22. Plotting it as a vector, it determines an ellipse, so that by choosing suitable coordinate axes, k is at a maximum in the x direction and at a minimum in the per-

pendicular y direction. The oscillations resolve themselves into independent oscillations of frequency ν_x and ν_y such that $\nu_x/\nu_y^2 = k_x/k_y$. (The figure has inadvertently been drawn so as to make k greater in the x direction, but our normal procedure will be to call the band of lowest frequency the x band.)

We may therefore expect to find for a planar molecule, with no center of symmetry, two fundamental electronic bands at different frequencies, one of which will disappear when the electric vector of polarized light is in the y direction, the other when it is in the x direction.

Some observations with crystals may be pertinent. Taylor (68) has found with crystals of methylene blue a maximum blue color with one direction of polarized light and a maximum brown color in a perpendicular direction. Calvin (73) has likewise found, with crystals of cyanine, green and red colors with maxima in directions also at 90° to one another. The interpretation of these facts is, however, not quite certain and may involve the z bands, which we shall mention presently.

When we have spoken of the independence of the x and y oscillations we have not meant to imply that the y oscillations of higher energy may not go over into the x oscillations by a process of dissipation, in which atomic vibrations which are along neither of these axes participate. Such dissipation will be the subject of the next section. It is a common observation that, if any fluorescent substance is excited by light of far higher frequency than its fundamental absorption band, it emits the same light as if activated in this band itself.

A remarkable phenomenon has been found when fluorescence is produced by polarized light. Ordinarily under these circumstances it has been found, as we should expect, that the reëmitted light is polarized to some extent in the same direction as the exciting light. However, Wawilow (69) found that in the four substances rhodamin B, magdala red, aesculin, and fluorescein, the degree of polarization of the fluorescent light diminished with increasing frequency of the exciting light and actually became negative in a certain region, increasing again to positive values at still higher frequencies. In the case of fluorescein the greatest negative polarization occurred at about $32,000 \text{ cm}^{-1}$. Now the absorption spectrum of fluorescein in alkaline solution, according to Wrzesińska (72), is given in figure 23. It will be noted that there is an important band with a maximum at about $31,000 \text{ cm}^{-1}$ and we have no doubt that this is the y band corresponding to the same fundamental oscillator as the x band at about $20,000 \text{ cm}^{-1}$. Let us consider a molecule of fluorescein oriented as in figure 23, that is, with the x direction in the line through the three rings. A beam of light normal to the plane of the molecule and polarized in the y direction can excite only the y oscillation. If, before the molecule has had

opportunity to turn, the energy of the y oscillation is partly dissipated and partly converted into an x oscillation, and the energy of this oscillation is now emitted as light, the polarization observed in the line of sight will be mainly in the x direction, which is the phenomenon observed. Similarly if the light beam is in the x direction and the polarization of the absorbed light in the y direction, the emitted light will be polarized in the z direction, i.e., once more normal to y .

Whenever a planar molecule has no center of symmetry, and it appears from the formula that the value of k should not differ very greatly in the two normal directions, we may expect to find these x and y bands. Let us compare the absorption spectrum of the symmetrical crystal violet with that of malachite green, which has an amino group on only two of the benzene rings. Without discussing at the moment the possible resolution of the bands, crystal violet has only one broad band in the visible.

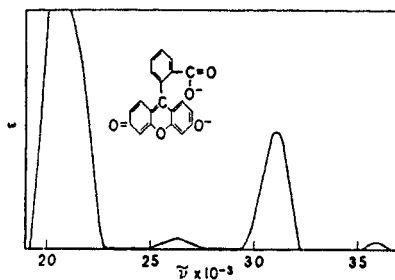


FIG. 23. Absorption spectrum of fluorescein

Malachite green has a broad band with a maximum at $\lambda = 6230 \text{ \AA}$. and a weaker band at $\lambda = 4300 \text{ \AA}$. An attempt to find the orientation of these bands by the method of fluorescence polarization is in progress.

When we come to molecules which have a high degree of polarizability in three directions, that is, ones for which the ellipse representing k is replaced by an ellipsoid, we have only two examples to offer, both given by Scheibe (59, 62) in a paper which has interested us greatly, not only because of the importance of the experimental results, but also because Scheibe's interpretation largely coincides with the ideas that we are here developing.

Scheibe studied crystals of naphthacene (2,3-benzanthracene) and found the familiar bands 4750, 4450, 4200 \AA ., which represent the structure of the fundamental electronic band. Absorption in this region is at a maximum when the beam of light is normal to the plane of the molecule. When the electric vector of polarized light was made normal to the plane of the molecule, a new band was found at $\lambda = 5250 \text{ \AA}$. This can only be interpreted on the assumption that there is a conjugation between the

molecules, which are face to face in the crystal (32), and that the absorption is a result of this conjugation in the z direction.

Far more extensive and instructive are Scheibe's studies of pseudoisocyanine. This substance, in very dilute aqueous solution, shows two bands similar to those which in the case of cyanine crystals we have previously attributed to the x and y directions (the y absorption being apparently intensified in the dimeric form of the substance). When the solutions are made more concentrated, a new intense and narrow band appears at a longer wave length, as shown in figure 24. The appearance of this band, which has no counterpart in the whole field of color chemistry, accompanies the formation of giant molecules. These Scheibe considers as

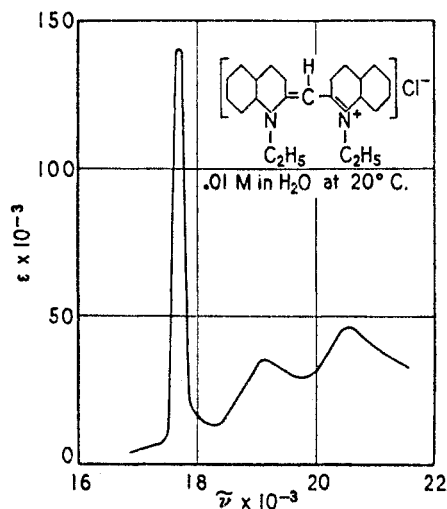


FIG. 24. Fluorescence band of pseudoisocyanine

long threads whose length is normal to the plane of the individual molecules. By various methods of orientation of these threads, together with a study of the fluorescence, he shows that the absorption and reëmission of the narrow band are characterized by an electric vector along the thread, or, as we should say, it is a z band. As Scheibe says "in the process of polymerization the molecules lie flat one to another and there occurs a fusion of certain electrons into a new system, causing the new band. These electrons absorb only light with an electric vector normal to the aromatic plane."

It is also interesting to note that this is the only type of substance, as far as we know, whose fluorescent band coincides in position and half-width with the absorption band.

We believe that the extraordinary narrowness of this z band is to be explained by considerations entirely similar to those that we have used in connection with the polyphenyls. The resonance normal to the planes of the individual molecules must be at the expense of the ordinary resonances of those molecules. Let us assume that polymers containing only a few molecules have an absorption in the z direction that is too weak to be observed, while the higher polymers all have about the same position of the absorption maximum. Then increasing the length of the thread will change only the intensity of absorption, and the phenomenon is readily understood.

INTERACTION BETWEEN ELECTRONIC AND ATOMIC VIBRATIONS

When a molecule that is at low temperature, and is therefore in the zero state of atomic as well as electronic vibration, absorbs light by passing to a higher electronic state, it may also reach one of the states of higher atomic vibration, the probability of each such transition being roughly determined by the familiar Franck-Condon principle. This gives rise to the structure of an electronic band such as has been illustrated in figure 1. This structure usually shows several bands with a separation of the order of 1000 cm.^{-1} However, in complicated molecules there are many types of vibration of much smaller energy, depending upon the mass and the degree of constraint of the various groups.

Even if these minor vibrations are not excited in the very process of light absorption but are excited almost immediately thereafter, thus making the life of the initial excited state very short, this alone, as we have already seen, will broaden the absorption bands. This broadening will tend to make the structure of bands disappear. We are going to think of the disappearance of structure and the quenching of fluorescence as closely related phenomena.

Every molecule that is excited by light has a finite probability of reëmitting the same kind of light. Every substance therefore must be to a certain extent fluorescent. Nevertheless, under ordinary circumstances this fluorescent light is too faint to observe, except in relatively few substances, and the cases are very rare in which the number of emitted photons is approximately equal to the number absorbed. The reason is that there are usually processes for removing the energy of the excited state which are far more probable, that is, which occur on the average in a much shorter time than the reëmission of light.

We have already pointed out the only case (59) known to us (pseudo-isocyanine) in which the band of reëmission is identical with the band of absorption. Ordinarily the bands of emission have a lowered frequency, owing to the loss of energy of electronic oscillation to the more prominent

atomic vibrations, and sometimes it has been found possible to predict the structure of the fluorescence from that of the absorption band (24). An idea of the very extensive work that is now being done in the field of fluorescence is given by the papers in two symposia, one held in Warsaw in 1936 (35) and one in Oxford in 1938 (44).

In atoms and simple molecules the quenching of fluorescence in the gaseous state usually results from collision with walls or with other gaseous molecules. A similar phenomenon is found occasionally in complex molecules; thus the quenching of the fluorescence of fluorescein ion in solution by various substances has been frequently studied. A similar exchange of energy between two molecules but in the opposite direction has been observed with indigo vapor (54), which fluoresces, but not when exposed to light of 2400–2800 Å. On the addition of aniline vapor, which absorbs in this region, the fluorescence of indigo appears.

However interesting these examples may be, as an extension of phenomena previously found in very simple molecules, we must recognize that the main processes that are responsible for quenching or preventing the fluorescence of substances like the organic dyes are within the molecule itself, and we must inquire how and when an electronic oscillation can transfer its energy to the various possible atomic vibrations in the molecule, which in turn, by contact with other molecules or by emission in the infrared, further dissipate their energy. To such a rapid (10^{-13} to 10^{-14} sec.) transfer of energy we may ascribe both the prevention of fluorescence and the disappearance of structure.

It should be possible from our theory of electronic oscillations, localized along definite axes of the molecule, to obtain an idea of the possibility or probability of these dissipative processes. In fact two rules, which we may subject to a variety of experimental tests, are immediately suggested: (1) A group is more likely to take part in the dissipative processes, which tend to eliminate both fluorescence and structure, if it is of large mass or is held by weak constraints, and thus is capable of vibrations of low energy. (2) However, such a group will not be effective unless it takes part in the resonance which is associated with the particular oscillation that is being excited. It seems probable, moreover, that the group will not be effective unless the extreme resonance formulas, toward which the oscillation tends, would favor a different atomic arrangement, with respect to distance or angle, than exists in the normal state of the molecule.

In any molecule the introduction of fluorine, chlorine, bromine, and iodine atoms has long been known to diminish fluorescence and in the order named. Fluorine has the smallest mass and is most tightly bound, while iodine has the largest mass and is least tightly bound. All four resonate with the benzene ring. Benzene itself has a higher efficiency of

fluorescence than the four phenyl halides and the fluorescence diminishes through the series (41).

Let us now compare the absorption spectra of these substances as shown in figure 25 (42). When we examine the structure of the bands, we see the same effect that we have noted with respect to fluorescence. The structure is nearly gone in chlorobenzene and has disappeared entirely in bromobenzene and iodobenzene.

The nitro group, which is one of the strongest acid chromophores, also is capable of vibrations of low energy. It destroys structure and in nearly all known cases completely eliminates fluorescence.

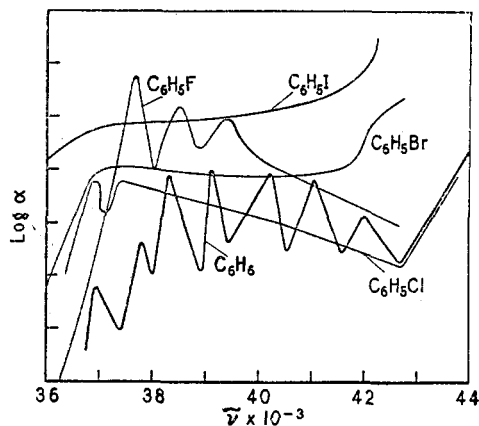


FIG. 25. Absorption curves of benzene and halogenobenzenes

Triphenylmethyl.....
p-Tritolylmethyl.....
p-Trichlorotriphenylmethyl..
p-Triiodotriphenylmethyl....
 Triphenylmethylcarbonic
 acid chloride.....
 Diphenylphoxymethyl.....
 Biphenylenebiphenylmethyl..

All of these groups that cause a rapid dissipation of the energy of electronic excitation, whether this is manifested by diminution of fluorescence or by diminution of structure, may be likened to loose bolts in some moving part of a machine. They provide a process by which the energy of the system is lost or degraded.

The phenyl group is another example of a radical of large mass held by low constraints, and is a powerful dissipative agent when it becomes a part of the conjugated structure, and is so situated that the resonance in which it participates is associated with that electronic oscillation belonging to

the particular frequency that is being absorbed. These conditions are met in biphenyl. It must, however, be noted that the effect is to be found when such a group as phenyl conjugates with the rest of the system but does not conjugate too strongly. If the conjugation is sufficient to give to the connecting link a large "double-bond character," the constraints of this link become too great to permit vibrations of low energy.

We may illustrate by considering biphenyl and the diphenylpolyenes. In biphenyl the conjugation is not very great; indeed we have seen that even in the long chain of sexiphenyl the absorption band has not reached the visible region, yet the connecting links must have considerable double-bond character, i.e., the distance between the 1 and 1' carbon atoms is 1.48 Å. as against 1.53 Å. for the single carbon-carbon bond (17). In consequence the pronounced structure found for benzene is largely, but not entirely, obliterated, and also biphenyl shows some fluorescence.

When we pass to the diphenylpolyenes there is increased fluorescence (24), and we have seen that they show marked structure. Here we have substances the ordinary formulas of which contain single bonds with heavy groups on either side. Nevertheless, owing to the conjugation, all these bonds acquire a good deal of the character of double bonds. Moreover, it is to be noted that in these molecules of a linear or nearly linear character the interaction between the electronic oscillations and atomic displacements must have only a small component in a transverse direction, in which the vibrations of smallest energy would lie.

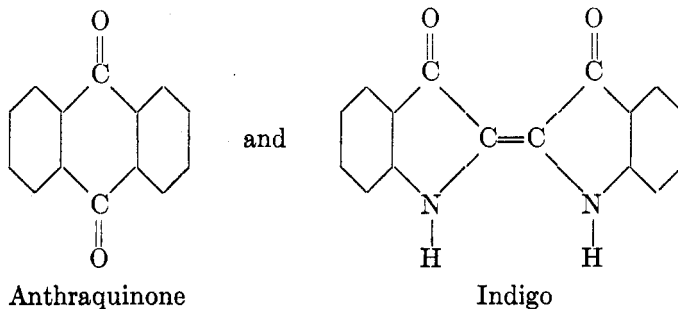
In condensed ring structures, such as perylene,



the planar structure is so rigid that there are no vibrations except of high energy, namely, those which determine the main structure of the electronic bands. If, however, side groups of the kind we have been discussing are substituted in perylene, the structure is not entirely obliterated, but the half-width of each band is greatly increased (15). This effect is greatest for the nitro group, and in 3,10-dinitroperylene the half-width has changed from 125 to 425 Å. If the broadening of the bands is due to the short life of the excited state, it means that the average excited molecule exists for hardly more than 10^{-14} sec. before the electronic energy is partly transferred to the vibration of the nitro group.

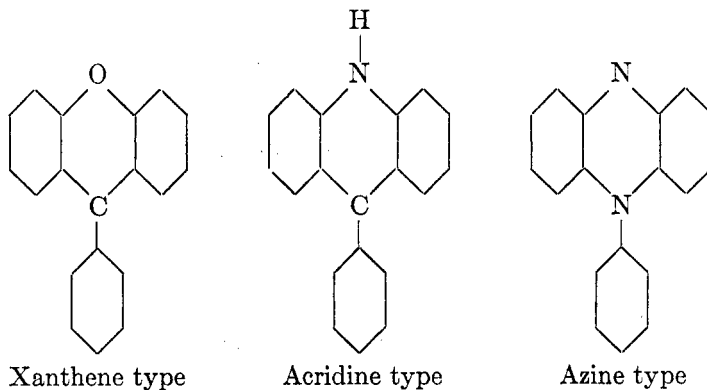
The unsubstituted condensed ring molecules are noted for their powerful fluorescence. Perylene is the only substance that we have found whose vapor fluoresces in ordinary light. The fluorescence of the substituted compounds should be far less pronounced.

Turning now to common dyes, fluorescence is highly restricted. In the *Colour Index* (14), which apparently states the existence of fluorescence whenever it was mentioned in the literature, out of some thirteen hundred substances only about eighty or ninety are listed as fluorescent, and over seventy of these belong to the five following classes: anthraquinone, indigo, azine, xanthene, and acridine dyes. The first two are represented by the structures



The first group resembles the condensed rings we have just discussed. There are no "loose bolts." In the indigos and thioindigos the two halves are separated by a double bond which produces large constraints.

The most remarkable fluorescence is found in the xanthene, acridine, and azine groups, which may be represented, omitting the ionic charge, by the skeleton structures,



Here we have striking confirmation of our rules. While each of them has a rigid structure in the upper part, each has a heavy group not very strongly held,—namely, the lower phenyl group. Furthermore, no matter what substituents we place in this group, they seem to have no effect in diminishing the fluorescence.

We must assume that in xanthene, acridine, and azine dyes the main absorption, and the one corresponding to the observed reëmission as fluorescence, is due to a horizontal oscillation in the upper part of the molecule, as drawn. It is easy to predict that when the γ bands of these substances are examined there will be little corresponding fluorescence, although we have seen one case in which the γ absorption presumably leads to x fluorescence.

Substituents such as OH, $N(\text{CH}_3)_2$, $\text{NH}(\text{C}_2\text{H}_5)$, and $N(\text{C}_2\text{H}_5)_2$ may be introduced into either of the side rings without destroying fluorescence, but not the group $\text{NH}(\text{C}_6\text{H}_5)$, for this introduces a phenyl group in a place where it becomes a part of the oscillating system. Thus rhoduline violet and methyl heliotrope O differ only in that the $N(\text{CH}_3)_2$ group in the former has been replaced by the $\text{NH}(\text{C}_6\text{H}_5)$ group in the latter. The former fluoresces, the latter does not.

Heretofore we have considered the phenomenon of fluorescence only as it appears under ordinary conditions and in ordinary solvents. As a rule fluorescence is far more frequently observed in the ultraviolet than in the visible region. This is probably attributable to increased probability of light emission with increase in the energy of excitation. Even if we confine ourselves to the visible range, the number of fluorescent substances may be greatly increased, and possibly may eventually be extended to include all colored substances, by proper choice of solvent and temperature. We have observed (73) that even such dyes as crystal violet and malachite green show brilliant fluorescence when they are dissolved in glycerol and slightly cooled. The effect in this and similar cases is caused, not primarily by the change of temperature, but by change in the physical nature of the solvent.

Glycerol has often been used as a solvent in experiments on fluorescence, and it has commonly been assumed that the enhanced fluorescence is to be attributed to the high viscosity of the solvent, which would tend to prevent other quenching molecules from reaching the excited molecule. This may be the case when this kind of quenching is responsible for the disappearance of fluorescence. If, however, as we suppose, the most important process in the dissipation of the energy of an electronically excited state is the transfer of energy to atomic vibrations of low energy, within the molecule, a mere change of viscosity cannot be supposed to be effective. However, increasing viscosity usually accompanies an increasing rigidity. Thus glycerol, when it is taken to -50°C . without crystallization, has become a brittle glass, and it would seem that, in such a medium, many of the vibrations of low energy would no longer be possible, because of the constraints imposed by the rigidly held molecules of the solvent. Even in a very fluid solvent similar constraints sometimes are found, if

the molecules of solvent are attached to the solute molecule in such a way as to diminish the freedom of certain vibrations.

ODD MOLECULES

In the paper by Lewis (38) entitled "The Atom and the Molecule," the last section on "The Color of Chemical Compounds" suggests, in old-fashioned phraseology, several of the ideas that we have developed in the present paper. In that paper, odd molecules, that is, molecules with an odd, or unpaired electron, were defined; and it was pointed out that, except for nitric oxide, every known odd molecule was colored. In the twenty-three years that have since elapsed many new molecules of this class have been prepared, and all of them are colored.

The remarkable absorption spectra of the free radicals were obtained in 1911 by Meyer and Wieland (47) and are reproduced in figure 26. We

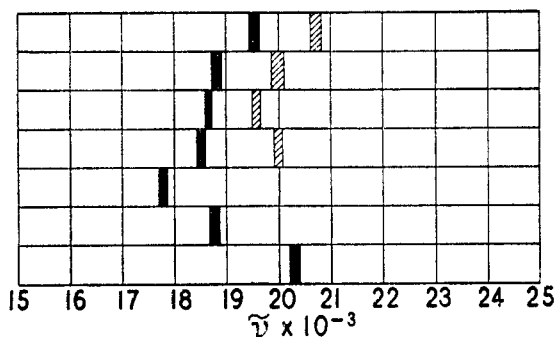


FIG. 26. Absorption spectra of the free radicals

shall comment presently upon the extreme narrowness of the absorption bands.

Examining these spectra, and noting the frequent presence of neighboring pairs of bands in molecules that have been regarded as possessing complete central symmetry in a plane, Lewis (73) concluded that the pair of bands is due to isomers of a new type.

If, using suitable bond distances and angles, the molecule of triphenylmethyl is represented in a plane, the distance between neighboring hydrogen atoms of two benzene rings is only about 0.5 Å. Now we have seen, in reviewing steric effects upon resonance, that the repulsion between two hydrogen atoms as close as this is sufficient to destroy the planarity. If, then, the three benzene rings cannot lie in one plane, but are nevertheless forced to lie near the plane, as a consequence of resonance, there are two possible structures, one symmetrical and the other unsymmetrical.

This would account for the two bands observed in the first four spectra. As a matter of fact Anderson (2) has found, and we have verified, that the right-hand band of triphenylmethyl is double; this may perhaps be due to x and y bands of the unsymmetrical isomer.

When we examine the last three spectra, which are single, we see that, at least in the last two, the molecules are such that the steric influence that would keep the molecule out of a plane is no longer present.

Experiments have been begun, and absorption measurements (73) have been made by Dr. G. T. Seaborg and Mr. O. Goldschmidt, in order to test this isomeric hypothesis. The odd molecule α -naphthylidiphenylmethyl should give four different isomers. Its absorption spectrum shows four very pronounced bands, the first three approximately at 6500, 5900, 5200 Å., and the last still rising near the violet.

If the two bands of triphenylmethyl are due to two substances in tautomeric equilibrium it should be possible to find a change in their relative intensity with the temperature. This effect has not yet been found.

Aside from this phenomenon of multiple bands the most striking characteristic of the spectra of free radicals is the narrowness of the individual bands. The chief band of triphenylmethyl at 5130 Å. has a half-width of hardly more than 100 Å. Such half-widths, however, we have met before in the narrow band of Scheibe (59) and in the individual resolved bands of unsubstituted perylene (15) and of the higher diphenyl polyenes (figure 8). We have attempted to interpret the broadening of the resolved bands of perylene by substituents, but such a small half-width as 100 to 150 Å. can be due to such a variety of causes that we shall not attempt their explanation. It is not due to a short life of the excited molecule, since this life can be measured when the substance is fluorescent and proves to be too long to cause any appreciable broadening.

The characteristic feature of these bands of the free radicals is that they stand alone and are not accompanied by neighboring bands corresponding to excitation of several of the prominent atomic vibrations of which the molecule is capable. This must mean that there is little interaction between the electronic oscillator and any of the atomic oscillators.

When we examine the conditions of resonance in a free radical we find them to be unique. When chlorine is removed from triphenylmethyl chloride, so as to leave an odd electron on the central carbon atom, this electron may pass into the general resonating system and there are nine contributing structures of nearly equal importance: namely, those in which the odd electron is given to the several ortho and para carbon atoms of the three rings. In spite of the fact that the presence of the odd electrons is sufficient to insure wide departure from what we have called an "ideal" molecule, it is to be noted that in each of the contributing structures that

we have just mentioned every atom has zero formal charge. There is therefore no direct relation between the various phases of resonance and the electronic oscillations that we have held responsible for the absorption of light.

The best that we can do at present is to suggest that the presence of an odd electron produces in such molecules a displacement of all electrons from the deep potential troughs of the "ideal" state, that there is thus produced a very mobile electronic cloud located near to, and with its center at, the central carbon atom, and that the oscillations in this cloud have no marked tendency to change the relative distances and angles between the several atoms of the molecule.

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