THE CORRELATION OF RESONANCE STRUCTURE WITH ULTRAVIOLET ABSORPTION IN NITRO-SUBSTITUTED ORGANIC MOLECULES[1]

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A semi-historical review is given of the work on the absorption spectra of organic molecules. The classical concepts of auxochromes and chromophores are related to present-day ideas on electronic structure. The ground and excited states of the common chromophores are shown to be similar in configuration. The relative importance of inductive and resonance effects is discussed. The nitroparaffins afford especially interesting examples of the effects of structure on resonance and absorption.

The interpretation of the ultraviolet absorption spectra of complex molecules may be approached from various angles. The calculation of the energies of the electronic levels by the methods of molecular orbitals, for example, is an interesting problem but the difficulties are so great that we cannot hope for much in the way of practical results in the near future.

Sklar (6), Sponer (7), and others have obtained very satisfactory results in the empirical interpretation of the spectral data for benzene and the substituted benzenes in which the substituent is a relatively inactive group. In this interpretation the identification of the vibrational progressions has proved very helpful in distinguishing between allowed and forbidden transitions. It is only in the case of symmetrical structures such as benzene, however, that the vibrational progressions can be recognized. As soon as the symmetry of the benzene molecule is destroyed by the substitution of active groups the vibrational structure disappears and with more complex molecules, particularly in solution, one obtains only continuous absorption and the only observable quantity is the extinction coefficient as a function of wave length. The observer may consider himself fortunate if one or more maxima exist.

With spectra of this sort the most that one can hope for is to identify the absorption with certain active groups in the molecule. There will usually be alternative electronic structures in resonance, including in the excited state at least polar structures in which a carbon atom may have only six electrons with a resulting positive charge or a free pair of electrons with a resulting negative charge. The rules which establish the orthodox structures permissible are quite easily formulated. One does not consider structures which involve the accumulation of excessive charge on one atom or adjacent atoms. A corollary of this is that

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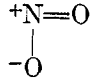
an electron pair may rotate around an atom as a center but always remains attached to one of the atoms with which it is originally associated.

In the absence of more quantitative or more exact theoretical approaches, therefore, it seems worth while to consider what may be accomplished in the way of correlation of absorption with active groups and resonance structures in purely empirical and qualitative fashion.

ACTIVE GROUPS: CHROMOPHORES AND AUXOCHROMES

All atoms show absorption in the far ultraviolet (Schumann region). In this region one obtains an absorption which has been characterized by Mulliken (2) as a Rydberg spectrum. The characteristic absorption of the quartz region is quite different and is to be attributed to electrons which may be regarded as "unsaturation" electrons. Those electrons which are fixed in single bonds are too firmly bound to be affected by wave lengths greater than $\lambda = 2000$ A. Any "active" electrons which produce absorption in the quartz region may, therefore, be assumed to be either electrons in π-type bond orbitals or electron pairs not in a bond. The most important chromophoric groups are

$$C{=}C \qquad C{=}O$$



$${}^{+}\underset{\underset{{}^{-}O}{|}}{N}{=}O$$

and are characterized by a double bond in which one bond may be considered to be of the π type, i.e., the electron orbitals are at right angles to the direction of the axis of the two atoms and the electrons are less strongly bound. The characteristic absorption process for these groups is, according to Mulliken, the transfer of both π electrons to one atom ($N \rightarrow V$ transition), a change which results in an ionic bond. In the case of the C=C bond either atom may receive the electrons and become negative, but by the same token the energy required for this process is so great that the absorption lies beyond the quartz region. The weak absorption shown by benzene at 2600 A. has been shown by Sklar to be due to an excitation from the lower symmetric state to the antisymmetric states resulting from the two Kekulé structures. Since the polar states do not enter into this transition appreciably, the dipole strength of the transition is small; in fact, the transition would be forbidden were it not combined with certain vibrations of restricted symmetry.

In the case of groups such as NO_2 and C=O the difference in electronegativity of the two atoms determines the direction of the electron shift and favors this shift, so that the energy of the excited state is lower than for C=C and the absorption shifts into the quartz region. Actually, of course, the π-electron bond may be considered as of mixed covalent and ionic type. In the ground state the covalent type will prevail and the bond will be stabilized by resonance. In the excited state the bond will be approximately the ionic type and will be somewhat less stable because of resonance. The effect of resonance, therefore, is to increase the excitation energy, but the resonance effect will be small unless the covalent and ionic energies are nearly equal, which is not usually the case.

It is thus seen that there are two mechanisms of excitation in benzene that give rise to absorption in different regions. These two mechanisms are fused in the case of more polar groups such as C═O or NO_2 into a single process which combines the essential characteristics of both processes.

AUXOCHROMES

Certain groups when substituted in the benzene ring increase the ease of substitution in the ortho and para positions and also increase the extinction coefficient of the absorption in the quartz region, with usually some shift of the maximum to longer wave lengths. These groups are termed auxochromes, since they generally increase the depth of color when substituted in dye molecules. Typical auxochromes are CH_3, NH_2, OH, and Cl.

It is generally agreed that the effect of these groups is to contribute a negative charge to the benzene ring. This may be pictured as taking place in either of two ways. There may be a slight displacement of charge along the axis of the bond between the auxochrome and the carbon of the ring. This is called the inductive effect. There may actually be a shift of an additional pair of electrons on the auxochrome to form a double bond with the ring carbon and a resultant shift of the π electrons in the benzene ring to give a highly polar quinoid structure. This is termed a resonance effect.

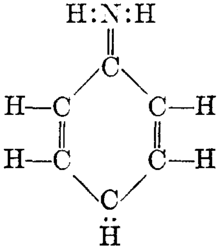
One frequently has difficulty in distinguishing between these two effects, and some writers (4) have sought to explain everything in terms of one effect or the other. It appears that some clarification of these ideas is given by the following considerations:

1. It is always necessary to assume resonance with a polar quinoid structure to account for ortho-para substitution.
2. In the case of the methyl group, no orthodox resonance structure can be written, so that the inductive effect must be assumed.
3. In the case of a group such as NH_2 or OH definite evidence exists for the double-bonded structure, so that the resonance effect must predominate.

It is an interesting fact that two groups as unlike as CH_3 and Cl should behave as auxochromes to about the same degree. Each produces only a slight increase in the extinction coefficient of the benzene absorption at 2600 A. Mulliken has explained the auxochromic effect of the methyl group as being due to hyperconjugation. This appears to be a technical term for what G. N. Lewis was wont to describe as "residual affinity." It appears as a maximum in diborane, where it is difficult to account for the bond between the two halves of the molecule. With chlorine, on the other hand, the inductive effect would presumably oppose the contribution of negative charge to the ring; at least this is the effect observed in the case of chloroacetic acid, where a marked increase in acid strength is to be attributed to the inductive effect. On the other hand, the chlorine atom has electron pairs available to form a double bond, so it must be assumed that the resonance predominates to a slight degree to produce a net auxochromic effect.

In the case of bromine and iodine the auxochromic effect is greatly reduced. The inductive effect will be less certainly reduced, but the predominating resonance effect is likewise decreased since the atoms in the lower rows of the periodic table do not as a rule form double bonds.

In the case of aniline the resonance effect is clearly demonstrated.

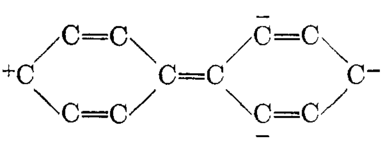


The existence of a double bond is substantiated by experimental evidence for the coplanarity of the NH_2 group with the benzene ring. The great increase in the extinction coefficient of aniline indicates the presence of the polar quinoid form, as is shown in the formula. On the other hand, if one forms the salt such as the hydrochloride the pair of electrons is no longer available to form a double bond and the absorption differs but little from that of benzene itself. The NH_3^+ group, because of the positive charge, has an inductive effect less than that of methyl and in the opposite direction.

It has been shown by Sklar that the electric vector that is active in absorption in the molecules discussed above lies in the plane of the ring and at right angles to the axis of substitution. The dipole strength for this transition cannot be large, and a small value for the extinction coefficient results. If, however, a strongly active (i.e., chromophoric) group is substituted, it may be assumed that the electric vector parallel to the axis of substitution becomes active in absorption and a 100-fold increase in the extinction coefficient may result. In such cases it is not surprising that all trace of vibrational structure disappears. It is with absorption of this type that we are concerned in this discussion.

THE PHENYL GROUP AS AN AUXOCHROME: BIPHENYL

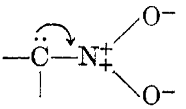
As will be shown in the discussion later, most chromophoric groups behave in a manner exactly opposite to that of an auxochrome, i.e., they behave as if unsaturated and remove negative charge from the ring. In the case of biphenyl, however, the phenyl groups must behave both as chromophores and as auxochromes. This behavior is confirmed by the characteristic ortho–para substitution observed in biphenyl. It was shown by O'Shaughnessy and Rodebush (3) that the strong absorption in biphenyl is only obtained when the rings are coplanar, which means that ionic structures are the important ones, at least in the excited states, since the only structures that can involve both rings in resonance are highly polar. Thus:



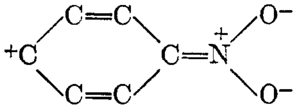
There are, of course, two ortho structures and one para structure for each ring, nine in all, and any attempt to distinguish between different parts of the molecule as auxochrome or chromophore is meaningless, since the electric vector that produces the absorption is the resultant for the whole molecule. The fact that the extinction coefficient for biphenyl is 100 times that for benzene is not surprising when one considers the great polarity of the excited structure. The fact that the maximum absorption is at about the same wave length must be regarded as a coincidence, since there is little resemblance between the excited states in the two molecules.

THE NITRO GROUP AS CHROMOPHORE

Chromophores are typically unsaturated, since they contain π-type bonds. The reason for the unsaturated behavior is that there is always a relatively stable resonance structure possible, in which the π-type covalent bond is converted to an ionic bond. In order for this to happen, however, it is necessary that an additional pair of electrons be supplied to the nitrogen atom. Thus:



If the pair of electrons is drawn from the benzene ring as in nitrobenzene, we have a typical polar quinoid structure:



This structure accounts for the greatly increased absorption of nitrobenzene over that of nitromethane or benzene itself.

NITRO-SUBSTITUTED BIPHENYLS

The symmetrically nitro-substituted biphenyls have been investigated by Williamson and Rodebush (9).[2] Sherwood and Calvin (5) have studied the absorption of some unsymmetrically substituted biphenyls. The results are in agreement with the postulated behavior. Because of the steric interference, the 2,2′-substituted biphenyls depart from the coplanar position and the resonance is destroyed. The absorption is approximately that of two nitrobenzene molecules. 4,4′-Dinitrobiphenyl shows an increased extinction coefficient and shift of the maximum to longer wave lengths, which is to be attributed to the increased polarity of the excited state and the lowering of the energy that is required to produce this state. This effect is still more pronounced in the case of the 4-

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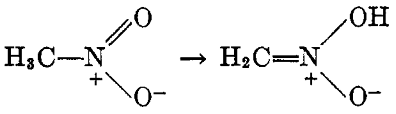
[2] The results reported on 4,4′-dinitrobiphenyl are in error. The compound studied had evidently undergone rearrangement. The absorption of this molecule has recently been studied in this Laboratory, and results will be published. The absorption is very similar to that of 4,4′-dicarboxybiphenyl.

amino-4′-nitrobiphenyl studied by Calvin, where we have a combined auxochromic and chromophoric effect acting in the same direction to stabilize a polar structure.

The case of 3,3′-dinitrobiphenyl is interesting. The absorption observed is about the same as for 3,3′-dicarboxybiphenyl; at the longest wave length the absorption is about the same as that of biphenyl itself, but instead of a maximum at 2600 A. one observes a shoulder with a great increase in extinction coefficient as one goes toward shorter wave lengths. The explanation of this behavior is to be found in the fact that it is not possible to write an orthodox resonance structure involving the chromophoric groups in the 3,3′-position, so that one obtains the absorption of an unsubstituted biphenyl at the wave length 2600 A. There do exist excited structures of much higher energy involving the chromophoric groups, and this gives rise to absorption with a maximum beyond the quartz region which overlaps the biphenyl absorption.

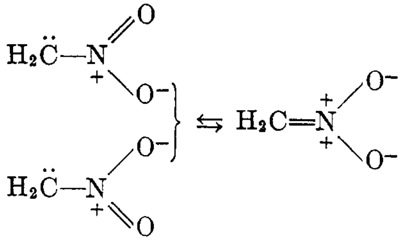
THE NITROPARAFFINS

If there is a hydrogen on the carbon atom to which the nitrogen is attached, as in nitromethane, there is a possibility of a shift of the hydrogen to the aci form



$$\mathrm{H_3C{-}\overset{+}{N}(=O)O^-} \rightarrow \mathrm{H_2C{=}\overset{+}{N}(OH)O^-} \qquad (1)$$

and in alkaline solution one obtains the negative ion, which has these resonance forms:



Because of the tendency of this anion to polymerize or decompose, the experimental results on its absorption cannot be regarded as established with certainty, but the absorption maximum occurs at somewhat shorter wave lengths than that of nitromethane itself but with an extinction coefficient of the same order of magnitude as that of nitrobenzene. Any correspondence in the absorption of the aci form of the nitroparaffins to that of the nitro forms must be regarded as purely coincidental. On the other hand, the differences in the absorption of nitromethane and nitrobenzene may be attributed to differences in the auxochromic action of methyl and phenyl. Always, of course, one must keep in mind that the absorption is a property of the molecule as a whole and not of a particular group.

The nitro derivatives were the subject of Hantzsch's classic work on the pseudo acids. Hantzsch (1) was able to demonstrate that for phenylnitromethane two crystal forms exist, which he identified with the two forms shown above in equation 1. Recently Turnbull and Maron (8) have attempted to estimate the ionization constants for the two forms in solution.

It was pointed out above that only one form should exist for the ion, which should be a resonance hybrid. This conclusion was in doubt for some years because of the reported persistence of optical activity, but this doubt has now been resolved. As soon as the ion is neutralized, however, one structure or the other must be established and the resonance energy, at least so far as the carbon–nitrogen bond is concerned, must disappear.

Since the nitro form is a very weak acid, the conversion to the aci form in solution of moderate alkalinity is a slow reaction, and the establishment of equilibrium between the two forms may not take place readily. Thus, it may be possible to produce one form or the other in solution by changing the pH regardless of the relative stability of the two forms. It is clear that the aci form would be relatively more stable in aqueous solution than in hexane, for example, but it is not possible to say which is the more stable form. One might expect phenylnitromethane to be more acidic than nitromethane, and it is possible that the stability relations may be reversed for the two derivatives.

The absorption curves for the two forms should be different from each other and from that for the ion. Since the curves for any two forms will probably cross at some wave length, we may expect an isobestic point, and since it is unlikely that the curves for three different forms will cross at the same point we should expect three isobestic points. It should be possible by the study of the ultraviolet absorption in solution to locate these points and to determine the relative amounts of the different forms present in solution and from these calculate the relative stabilities.

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