place rapidly enough to permit the attainment of equilibrium in times of the order of hundredths of a second at 61°. This diffusion of segments is a process requiring activation energy, as is evidenced by its large dependence upon temperature. The electrocapillary properties of polyelectrolytes can be investigated usefully by the differential capacity method and the degree of coverage of the surface can be determined. Evidence is cited which shows that the adsorbed segments of un-ionized PMA act individually in their ability to exclude the solvent and the ions of the electrolyte.

Acknowledgment.—The support of the U. S. Office of Naval Research is gratefully acknowledged.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WASHINGTON]

Classification of π-Electron States[1]

BY WILLIAM T. SIMPSON

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A classification of π-electron states is proposed in which two types are distinguished. The first type is described as involving resonance among normal structures. Empirical justification may be found in the spectra of dyes, radicals and aromatic hydrocarbons. The second is described as involving resonance among excited structures. States of this type are reached in transitions in the carotenoid pigments. The spectra of benzene, azulene and naphthalene are examined and the various states classified as belonging to one or the other of the two types under consideration.

Introduction

In this paper it will be shown that 2p(π) valence shell states may profitably be classified into two types: states of the first type arise from resonance among valence bond structures, and include the ground state; states representing the second type arise from a migration of excitation energy considered localized initially in a double bond. This will be said to result from resonance among excited structures.

The importance of classification theory has been discussed by Platt[2]; and the classification of π-electron states and transitions has already been carried out in several different ways. These include classification into long and round field spectra,[3] differentiation of the α and *p* bands of Clar[4] (*e.g.*, involving transition to the B_{2u} and B_{1u} states of benzene) and recent emphasis on the importance of differing amounts of configuration interaction.[5] (The first and second π-electron excited states may often be classified as different from each other owing to the fact that the first excited state is chiefly a single configuration, while the second is in essence not a single configuration.)

The method of classification to be described here is on the surface different from the others, though on closer examination it proves to be related. The present approach is phenomenological, and designed to conform as closely as possible to the classical theory of valence in chemistry.

The plan of the paper is first to make clear what is meant by the two different kinds of states, involving resonance among normal and excited structures. Next some of the simple aromatic hydrocarbons are considered, as examples of molecules having both types of states. In the course of the consideration of these examples some principles such as estimation of intensities and polarizations are brought in.

Resonance among Normal Structures.—"Normal structures" are structures in the context of the classical theory of valence which have the greatest stability. This would for example exclude the Dewar structures for benzene, and structures like the following

$$\overset{\ominus\cdot\cdot}{O}-\overset{\oplus}{C}H-\overset{\cdot\cdot\ominus}{O}$$

for formate ion. The energy of a structure is determined by the number and strength of bonds, stability of non-bonding electron pairs, etc., appraised in the usual intuitive fashion. This use of the classical theory of valence results in a certain amount of ambiguity as, for example, with amides, having the structures

$$R_2\overset{\cdot\cdot}{N}-CH=O,\ R_2\overset{\oplus}{N}=CH-\overset{\cdot\cdot\ominus}{O}$$

Here the second structure might be classed as normal by analogy with the corresponding structure for formate ion

$$O=CH-\overset{\cdot\cdot\ominus}{O}$$

or, alternatively, as significantly less stable than the first. The difficulty with ambiguity has to be mentioned, but does not seem to be a serious problem in what follows.

Recent developments in molecular electronic state spectroscopy include the determination of the polarizations of bands for a number of key molecules. This now makes it possible to test the following *hypothesis:* Whenever, according to the classical theory of valence, there is more than one normal structure to represent a molecule there will be as many low-lying electronic states as there are structure, with symmetries appropriate to the wave functions from which the structures were derived. The formulation and testing of this *hypothesis* requires that a study be made of the prediction of symmetry species from structures or, equivalently, the polarizations of bands.[6]

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[1] This research was supported in part by the Air Research and Development Command under Contract AF 18(600)-375.

[2] J. R. Platt, *J. Opt. Soc. Am.*, **43**, 252 (1953).

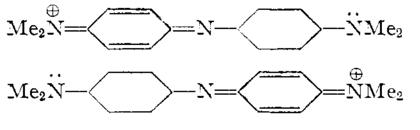
[3] J. R. Platt, *J. Chem. Phys.*, **18**, 1168 (1950).

[4] W. Moffitt, *ibid.*, **22**, 320 (1954).

[5] The importance of this interaction has been recognized by a number of workers including Parr and Pariser, Moffitt and Dewar and Longuet-Higgins; R. Pariser, *J. Chem. Phys.*, **24**, 250 (1956).

[6] W. T. Simpson, THIS JOURNAL, **75**, 597 (1953); W. T. Simpson and C. W. Looney, *ibid.*, **76**, 6285 (1954).

When there are just two equivalent normal structures, the prediction of the polarization of a transition between states involving these structures is particularly simple. It turns out that the direction of polarization of the transition moment vector is the difference in the moments of the structures. Thus, for example, for a dye having the following structures: (Kekulé structures are considered lumped together; detailed consideration of the Kekulé structures brings in transitions in the ultraviolet as discussed below for benzene)



the electric vector of the light interacts most strongly with the molecule when vibrating along the nitrogen–nitrogen line.

In working with the *hypothesis* it is also required that certain semantic difficulties connected with the use of classical valence theory in conjunction with quantum theory be recognized.[6] Moreover, the phrase "low-lying" must be interpreted in a flexible but not necessarily unrealistic manner.

An important test of the hypothesis is afforded by benzene, which has the two Kekulé structures, and has two states corresponding to these structures, the ground or A_{1g} state and the next or B_{2u} state.[7] There are many other confirmatory examples, afforded by dyes, radicals and aromatic hydrocarbons. Representative examples have been considered elsewhere,[6,8] though the aromatic hydrocarbon spectra have not as yet been intensively interpreted from the standpoint of the part played by the structures.

In fact, the *hypothesis* is, in the opinion of the writer, borne out with unexpected consistency in virtually all of the cases which occur. It is therefore suggested that the states related to normal structures be classified together. They are ground-state-like in character. The energy difference between them is often the smallest transition energy for the molecule, and, as pointed up by the example of the cyanine dyes, the energy difference in some cases actually approaches zero.[9]

Further, it is suggested these states be designated N, N′, N″, . . .[10] Only the N state without a prime is the normal or ground state. The A_{1g}, B_{2u} transition for benzene, which is a valence shell transition and is for most purposes classified as N,V_1, thus in the present instance becomes the N,N′ transition. The B_{2u} state would be thought of as "an N state." Not all π-electron transitions involve states falling in this class.

Resonance among Excited Structures.—Davydov treated the π-electron spectrum of biphenyl[11] by assuming as a first approximation that the molecule consisted of two benzene systems coupled together by an electrostatic potential, without electron exchange. Later polyenes were treated in a similar way, with ethylene as the basic unit[12]; and these ideas have been further developed.[13]

It has been shown, moreover, that for carotenes this approach is singularly appropriate.[14] Carotene spectra clearly show transitions from an N state to various upper states in which a single double bond is excited, but the excitation energy is delocalized (though the electrons are not).[15] There are different ways in which the excitation is distributed, corresponding to states having different energies. The source of the energy differences may be approximately understood from electrostatic considerations as involving momentary favorable and unfavorable mutual orientations of dipoles.[14] The excitation energy may be thought of as distributed by "resonance" in that all individual double bonds have the same excitation frequency. If the approach involving migration of localized excitation energy is singularly appropriate for carotenes, it follows that it must also be important in all analogous compounds, as, for example, butadiene and biacetyl.

The upper states for polyene-like molecules may be considered as involving resonance among structures of an unorthodox type. Such structures are here called *excited structures* (though this term has been used differently in the past, mainly to describe long-bonded structures in the context of the valence bond method). There are as many excited structures as there are double bonds; and there are as many excited states as excited structures. Half these states lie below the value for the upper state reached in the strong N,V transition for isolated double bonds (absorption at *ca.* 1600 Å.), and half lie above the value. If the number of bonds is odd, the energy of one state coincides with the value for an isolated bond.[14]

Thus for hexatriene we have three states grouped around the ethylenic V state arising from resonance among the structures

$$\mathrm{C\overset{*}{=}C{-}C{=}C{-}C{=}C}$$
$$\mathrm{C{=}C{-}C\overset{*}{=}C{-}C{=}C}$$
$$\mathrm{C{=}C{-}C{=}C{-}C\overset{*}{=}C}$$

(an asterisk signifies localized excitation) and, of course, also a single N state corresponding to the structure

$$\mathrm{C{=}C{-}C{=}C{-}C{=}C}$$

It is proposed to classify these upper states together and to label them E, E′, E″, . . ., so that, for example, hexatriene has three E states. The long wave length transition at *ca.* 2600 Å. is thus labeled N,E. Except for the normal state, in the polyenes

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(7) A. C. Albrecht and W. T. Simpson, *J. Chem. Phys.*, **23**, 1480 (1955).

(8) A. C. Albrecht and W. T. Simpson, THIS JOURNAL, **77**, 4454 (1955); C. W. Looney and W. T. Simpson, *ibid.*, **76**, 6293 (1954).

(9) See, for example, L. G. S. Brooker, *Revs. Mod. Phys.*, **14**, 275 (1942).

(10) The conventional notation for all excited π-electron states is V_1, V_2, V_3, . . . corresponding to the fact that the excited electrons are still in π-molecular orbitals, or in the *valence* shell. The ground or normal state is N. The suggestions about notation in this paper involve taking liberties with the N,V notation, but this should not lead to difficulties if the modified notation is used exclusively in connection with the classification of states through the medium of structures.

(11) A. S. Davydov, *Zhur. Eksptl. Teoret. Fiz.*, **18**, 201 (1948).

(12) W. T. Simpson, THIS JOURNAL, **73**, 5363 (1951).

(13) Wm. Moffitt, Ohio State Spectroscopy Symposium, 1954; H. C. Longuet-Higgins and J. N. Murrell, *Proc. Phys. Soc.*, **A68**, 601 (1955); K. S. Pitzer, *J. Chem. Phys.*, **23**, 1735 (1955); and K. S. Pitzer and W. E Donath, Austin Conference on Molecular Quantum Mechanics, 1955.

(14) W. T. Simpson, THIS JOURNAL, **77**, 6164 (1955).

(15) The delocalization may be considered to occur through a process analogous to the emission of radiation by one double bond followed closely by the absorption of this radiation by an adjacent double bond.

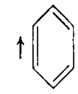
we are dealing just with E states.[16] In a compound like benzene we may expect to have to deal with more than one N state and also more than one E state, and this must be our next concern.

Classification of the States of Benzene.—With benzene it is inconvenient to try to connect up structures with electronic states using the simple rule about the polarization being given by the difference of the moments of the structures. Instead, the species of the states are determined by applying the character operator

$$\sum_{R} \chi(R)R$$

for the group of the molecule, D_{6h}, to representative structures, and noting the species which give non-vanishing linear combinations. When this is done for a Kekulé structure it is found that the plus and minus linear combinations belong to A_{1g} and B_{2u} in agreement with experiment. These are the N states.

For the E states the character operator is applied to a wave function for any one of the excited structures. If the excitation is patterned after the N,V transition for ethylene the transformation properties may be obtained starting with a diagram like the following to represent the wave function



(The arrow transforms like the polarization direction as governed by local symmetry.) The location of the arrow tells which double bond is excited and the orientation of the arrow gives the phase of the excited wave function, or, alternatively, the sense of the instantaneous dipole. The species for the non-vanishing functions generated, and hence for the E states, are B_{1u} and A_{2g} and also E_{1u} and E_{2g}. Before considering the benzene states in greater detail we shall now consider points having to do with the general validity of the classification scheme.

In the present approach there are predicted to be as many relevant states as normal and excited structures. It is therefore at least required that all the wave functions corresponding to the normal and excited structures be linearly independent. It is fundamentally difficult to prove the independence because the normal structures are, according to hypothesis, related to the classical theory of valence. Explicit expressions for what might be called "true" wave functions corresponding to these structures are as a practical matter lacking (though conceptually they exist as linear combinations of actual stationary state wave functions).[6]

The study of the structures and states of benzene is a special case in which it becomes possible to demonstrate the full linear independence. This example, therefore, may be used as the cornerstone of the classification scheme presented in this paper. With benzene there is no ambiguity about what normal structures to consider; furthermore, the transformation properties of a representative single excited structure are unambiguously determined by a diagram such as the one given directly above. The high symmetry of benzene then permits the state species to be generated by the application of the character operator. No use of explicit forms for wave functions is required. There are three excited structures for each of the normal Kekulé structures, eight structures all together, and eight independent relevant states generated: A_{1g}, B_{2u}, B_{1u}, A_{2g}, $E_{1u}(2)$ and $E_{2g}(2)$. There can be no linear dependency among the structure functions.

It is possible to make an argument which covers the general case and which is at least plausible. Consider first that there is just one normal structure. The example of butadiene will now be used to illustrate the linear independence of the functions involved. The wave function for the normal structure is considered to be represented in its essentials by a product referring to the left and right double bonds, say $\psi_L\psi_R$. The functions for the two excited structures are then $\psi_L\dagger\psi_R$ and $\psi_L\psi_R\dagger$ where a dagger means localized excitation. The three functions are mutually orthogonal, because of the local orthogonality relation $\int\psi\psi\dagger d\tau = 0$. For example, $\int\psi_L\psi_R\psi_L\dagger\psi_R d\tau_L d\tau_R = 0$ because of $\int\psi_L\psi_L\dagger d\tau_L = 0$.

We turn now to the case of more than one normal structure. If the true structure functions are ψ^i, ψ^i, . . . let us assume that there exist functions according to the conventional valence bond method called φ^i, φ^j, . . . which are, respectively, embraced by the true ψ^i, ψ^j, . . . That this is reasonable follows from the accuracy of the φ's for exploded molecules having the same topology as the actual molecules. The linear independence of the ψ's may then be inferred from the well known linear independence of the φ's.

Alternatively, we may look at the diagrams of the structures: the $(\psi^i)^2$, $(\psi^j)^2$, . . ., and here we see always the implication of essential changes in electron distribution from one structure to the other. An example is afforded by the two normal structures of allyl anion

$$^{\ominus}\ddot{\mathrm{C}}\text{—}\mathrm{C}\text{=}\mathrm{C} \qquad \mathrm{C}\text{=}\mathrm{C}\text{—}\ddot{\mathrm{C}}^{\ominus}$$

In order that the plausibility argument be complete it still has to be shown that wave functions corresponding to the excited structures based on one normal structure are linearly independent of the functions for other normal structures. To illustrate the contrary possibility, it could happen that the function for the excited structure

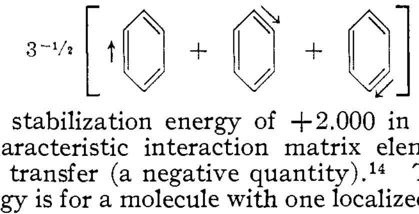
$$^{\ominus}\ddot{\mathrm{C}}\text{—}\mathrm{C}\overset{*}{=}\mathrm{C}$$

depends on the function for

$$\mathrm{C}\text{=}\mathrm{C}\text{—}\ddot{\mathrm{C}}^{\ominus} \text{ and } \mathrm{C}\overset{*}{=}\mathrm{C}\text{—}\ddot{\mathrm{C}}^{\ominus}$$

In order to prove the desired linear independence here it is probably best to rely on essential changes in electron distribution between the normal structures. For example, in the case of allyl anion the functions differ in whether or not there is a chance of finding two electrons simultaneously on, say, the carbon atom on the left. This difference leads to the required linear independence.

Returning to the consideration of the E states in benzene, we seek insight into their nature by looking at the E states for a single Kekulé structure. These are three in number, one doubly degenerate. For the non-degenerate level the state function is



with a stabilization energy of +2.000 in units of the characteristic interaction matrix element for energy transfer (a negative quantity).[14] The zero of energy is for a molecule with one localized double bond excited. The calculated transition energy from a normal structure to this state is formally

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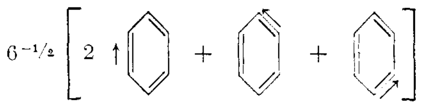
[16] The excited structure concept can be generalized. For example in the *p*-polyphenyls the localized excitation of a benzene ring rather than of a double bond migrates (see ref. 11). We may consider excited structures as providing a scheme for dealing with the unmanageably large number of ionic structures which it is usually possible to write.

the same as for the lowest energy N,E transition for an infinitely long chain polyene, because having the arrows lined up head to tail turns out to mean the most favorable disposition of instantaneous dipoles, and having the dipoles in a circle is equivalent to having them in an infinite chain. One of the functions for the degenerate level, again based on just one Kekulé structure, is



The state is destabilized now, with an energy of -1.000.

We may interpret the B_{1u} and A_{2g} states in benzene itself as related to the non-degenerate state depicted above, though split owing to the fact that actually both Kekulé structures are involved; and we interpret the E_{1u} and E_{2g} states in a similar fashion (see Fig. 1).

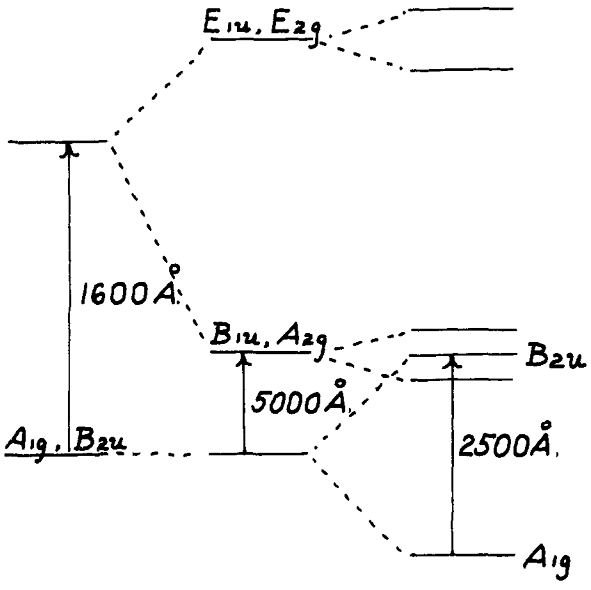


Fig. 1.—Schematic energy level diagram for benzene: on the left, no interaction; in the middle, resonance among excited structures splits the E states; on the right, resonance among normal structures splits the N states and further splits the E states.

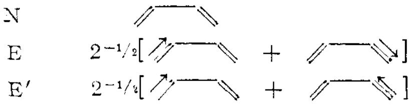
Referring to the figure, the empirical N,E split giving absorption at *ca.* 5000 Å. is an estimate for an infinitely long chain polyene taken from a consideration of the carotenoids. The A_{1g}, B_{2u} split is from observation; corresponding to it is an empirical stabilization of the N state by one-half the transition energy. The A_{1g} (B_{1u}, A_{2g}) transition is thus predicted to come at about 2500 Å. The degenerate transitions come out too high, which is also a shortcoming of some elaborate quantal calculations (though for different reasons). It is not possible using only the simple considerations above to say which of the levels, B_{1u} or A_{2g} should lie lower, but the general picture is satisfactory both as regards agreement with experiment as things now stand and with various theories.

In the next two sections the classification scheme is illustrated further, with azulene and naphthalene used as examples.

Azulene.—First the transition moment connecting the N states is considered. The normal structures together with hypothetical electric moments are

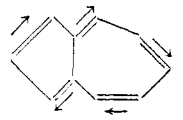
The transition moment is then the difference of the moments of the structures (as noted in the section Resonance among Normal Structures). The individual structures indicate no charge separation so the moments would be expected to be extremely small. The directions of the vectors are related by symmetry, so that even without knowing the direction for a single structure we may use our rule to predict the polarization direction of the N,N′ transition: it is along the short axis.

We digress briefly now, to consider polarizations for N,E transitions: when there is only one N state there is a simple rule. The excited structure wave functions are examined and the vectors added to give the transition moment vector. Thus for *s-cis*-butadiene, with states



the N,E transition is long axis polarized while the N,E′ transition is short axis polarized. Incidentally, the E′ state has higher energy than the E state because it has instantaneous dipoles lined up head to head.

The first E state for azulene based on a single normal structure probably has the vectors phased as in the diagram. This figure is a composite of diagrams representing wave functions for individual excited structures.

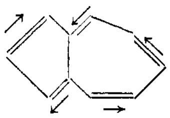


Note that there is a repulsive orientation of instantaneous dipoles across the permanent single bond (vectors tail-to-tail). If the vectors were all of equal length the transition moment vector would be small, and lie along the long axis. The vectors are not required by symmetry to be all of equal length, so that there would be a small resultant vector of undetermined direction. The splitting up of the first E state resulting from the resonance among normal structures should then give a pair of weak transitions polarized along the long and short axis.

The situation involving N states as well as E states is summarized in Fig. 2. Because of the circular topology the N (E,E′) transition would have roughly the same energy as for an infinitely long polyene, if it were not for the N,N′ interaction. This interaction gives a lowering of the N state by half the observed transition energy (*i.e.*, half of about 15 kks. (kilokaysers)) and thus a predicted wave length of absorption of *ca.* 3700 Å. for the center of the first two N,E transitions.

The predictions summarized in the figure resemble results of a recent calculation[17] by Pariser which seems to be itself in excellent agreement with experiment. In Pariser's work there are two transitions calculated to appear centered around 3400 Å., each having a low intensity, and polarized short axis and long axis, and there is a weak short axis polarized transition predicted to come at 7100 Å. The azulene spectrum permits of analysis as above because the first transition is extremely weak and short axis polarized, and the second transition is long axis polarized, coming at 3400 Å.[18]

Other E levels have not yet been characterized experimentally. The higher E level shown in Fig. 2 could conceivably be above E levels with phase reversals (referring to a single normal structure) such as in the following composite diagram.



Here there is no repulsive orientation of instantaneous dipoles across the permanent single bond.

The interpretation of the azulene spectrum is not a strong factor to support the system of classification described in this paper. What needs to be, and is demonstrated here, is compatibility with the *hypothesis* about states derived from interaction among normal structures. It would be difficult to sharpen the argument at this point. A possibility would be to select a wave function computed for the first singlet excited state of azulene according to what is judged to be the most satisfactory quantal method, and compute the overlap of this function with the difference of two functions selected to correspond to the normal structures. However there does not seem to be a uniquely satisfactory way at present to select these functions, particularly the ones corresponding to the structures.

The argument from a phenomenological standpoint is, however, reasonably convincing; the first transition for azulene is related to the 2600 Å. band of benzene through the 3100 Å. of naphthalene.[19] The benzene band, as shown above, should be classified as N,N'.

With the analysis of benzene and azulene we can now profitably consider naphthalene.

Naphthalene.—With dyes the intense absorption bands involve N states, so there is a close connection between the study of spectroscopy and ground state phenomena.[20] With the aromatic hydrocarbons the intense transitions are to E states so there have been fewer opportunities either to use spectroscopy to understand ground state phenomena, or the reverse. However weak in intensity N,N' transitions may be, or however hard to assign, they are probably the key to understanding ground state effects for the aromatic hydrocarbons. With the assignment of the N,N' transitions in the spectra of benzene and azulene it should be possible to make predictions about the N states for naphthalene (and for other compounds as well).

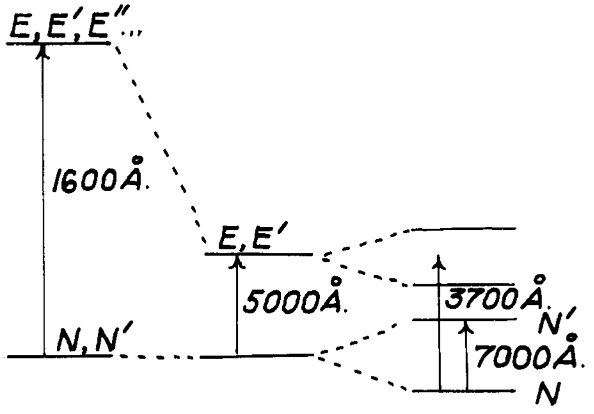
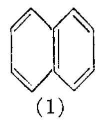
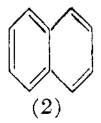
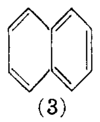


Fig. 2.—Schematic energy level diagram for azulene showing N states and first two E states. First step shows splitting of levels owing to interaction of excited structures. Second step shows effect of interaction of normal structures.

To begin, the three normal structures are


(1)

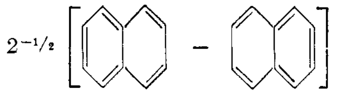

(2)


(3)

It can be seen that the interaction between wave functions corresponding to structure (1) and either (2) or (3) is analogous to the Kekulé interaction in benzene. The interaction involving (2) and (3) is analogous to the interaction splitting the N and N' states in azulene. We therefore take as values for the interaction matrix elements half the observed first transition energies for benzene and azulene, though the benzene value may be a little high owing to the fact that the bond lengths in naphthalene are different. We also assume that all the diagonal elements are equal, and thus may be taken as zero. This gives for the naphthalene energy matrix in the structure representation[6] in units of kks.

$$\begin{pmatrix} 0 & -20 & -20 \\ -20 & 0 & -7 \\ -20 & -7 & 0 \end{pmatrix}$$

The eigenvalues come at −32, 7 and 25, so that the energy of the ground state is −32 kks., or 88 kcal./mole below the energy for a single structure (vertical resonance energy). (The values for benzene are ±20 kks., so the resonance energy is 55 kcal./mole.) The N,N' transition energy is predicted to be 39 kks. (2600 Å.) and the transition would be expected to be very weak, polarized along the long axis. The polarization direction follows from a closer examination of the solution of the matrix diagonalization problem. The function corresponding to the middle root (7 kks.) is the one represented by



Now by ignoring the presence of structure (1) in the ground state one can apply the simple rule mentioned in the section on resonance among normal structures: the transition moment direction is given by forming the difference of the electric moments

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(17) R. Pariser, Austin Conference on Molecular Quantum Mechanics, 1955.

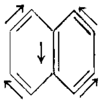
(18) D. S. McClure, *J. Chem. Phys.*, **22**, 1256 (1954).

(19) D. E. Mann, J. R. Platt and H. B. Klevens, *ibid.*, **17**, 481 (1949).

(20) See, for example, the work on dipole moments of L. M. Kushner and C. P. Smyth, THIS JOURNAL, **71**, 1401 (1949).

of the individual structures (2) and (3). It is believed this transition corresponds to the weak long axis polarized 3100 Å. transition actually found.[18,21]

It is difficult to make energy predictions involving the E states, because of the resonance among normal structures. The lowest energy E state, based on just the first normal structure,[22] has the vectors phased as



The transition energy before resonance among normal structures as considered would be expected to be not far from the value for an infinitely long polyene. The transition moment vector is directed along the short axis. The three vectors on the left cancel approximately, as they do exactly with the B$_{1u}$ state of benzene, so that the intensity should be of the order of that expected for *s-cis*-butadiene (which in turn is the same as for ethylene, according to the expected trigonometry). This predicted polarization and intensity corresponds quite well to that observed for the second singlet transition for naphthalene at 2700 Å. which is accordingly assigned as N,E.

The observed transition energies to this first E state change over a series of cata-condensed hydrocarbons in a regular fashion.[23] They approach a limit at *ca.* 5500 Å. which is not far from the limiting absorption for polyenes. If we accept the classification scheme given above, it then appears that resonance among normal structures lowers the ground state much more than the first E state in benzene (2000 Å.) and naphthalene (2700 Å.) but as the molecules become bigger the effects become more nearly equal so that in the limit the N,E transition energy is about the same as would be expected if there were no resonance among normal structures.

Comparison with the Orbital Approach.—When a molecule has only a single normal structure the implication is that there is a high degree of localization of electrons in the bonds. Resonance among normal structures, as is well known, is the way the classical theory of valence accommodates itself to delocalization. The molecular orbital approach stands in a complementary position regarding localization effects. Thus with extreme delocalization (as with dyes) the molecular orbital approach is particularly natural, while with considerable localization (as found in the carotenes) the orbital theory also needs to accommodate, which it does through configurational interaction. Just as we "understand" resonance among valence bond structures by adopting an orbital point of view, so we can hope to understand many of the effects of configurational interaction by qualitative interpretations using structures.

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Reactivities of Twisted or Stretched C=C Double Bonds[1]

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The reactivities of aromatic and olefinic compounds toward methyl radicals, measured by their methyl affinities, are related to the corresponding localization energies. This relation is demonstrated for a series of aromatic hydrocarbons. It is pointed out that localization energies are proportional to β, the exchange integral. Bending of an aromatic hydrocarbon out of planar configuration or twisting or stretching a C=C double bond decreases the overlap of p orbitals and, hence, decreases β. Consequently, the localization energies of such molecules decrease, and the reactivities and the methyl affinities of the respective compounds increase. These conclusions are tested on a series of suitable compounds and their validities are fully demonstrated.

The reaction $CH_3 + A \rightarrow A{\cdot}CH_3$, where A represents an aromatic or an olefinic molecule, is well suited for studies of relations between the reactivity and the chemical constitution of molecules. The values of the relative rate constants of such bimolecular reactions, further referred to as methyl affinities, can be determined easily by a special experimental technique devised for this purpose and already described in earlier communications.[2,3] The results, obtained from studies of several classes of compounds,[2-6] indicate that simple relations exist between methyl affinities and other structural properties of the respective molecules. One such a relation recently has been discussed by Coulson[7] who has shown that logs of methyl affinities of aromatic hydrocarbons are related linearly to the corresponding localization energies. This relation illustrated by Fig. 1, has been extended now, and its validity has been demonstrated for a few more hydrocarbons not considered in Coulson's paper (see also Table I).

Localization energies are calculated by solving the appropriate secular equations, and the results appear in the form $C_i{\cdot}\beta$, where C_i's are numerical coefficients determined entirely by the form of the secular equations, while β is the so-called exchange integral. We notice, therefore, that the localization energies decrease whenever the coefficients C_i's or the exchange integral β decrease in their

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(1) This paper reports the continuation of studies communicated previously to THIS JOURNAL (M. Levy, M. S. Newman and M. Szwarc, THIS JOURNAL, **77**, 4225 (1955). The latter investigation was supported by a grant from the National Science Foundation.

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