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SEMIQUANTITATIVE THEORY OF RESONANCE USING PAULING BOND ORDERS*

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Abstract—It is shown how the widely used but purely qualitative theory of resonance in organic chemistry can be extended to a semiquantitative form. The extension is accomplished for ground states by relating π electron energies to Pauling bond orders, which are derivable by inspection from Kekulé-type resonance structures. For excited states ionic structures must also be considered. The model is applied mainly to hydrocarbon systems in calculations of resonance effects in electrophilic substitution, Diels-Alder reactions, radical stability, ionization potentials, and electronic spectra. Results are expressible in terms of a single parameter which plays a role essentially equivalent to that of β in simple molecular orbital theory. In a series of molecules the semiquantitative ordering of activation energies for attack at various sites, and the variations of radical stability, ionization potential, and spectroscopic red shifts are found to be in substantial agreement with results of molecular orbital calculations. For oxygen acids the approach provides a rough rationalization of Pauling's empirical rule for acid strength.

Advantages and weaknesses of the Pauling order scheme are discussed. The principal virtue of the scheme is its extreme simplicity. It can be handled by anyone who can write resonance forms. For this reason there is some hope that it may be developed into a useful tool, even for chemists unschooled in mathematical arts and uninitiated in orbital theory.

THE theory of resonance in organic chemistry has enjoyed a great popularity for many years. Its utility has been that chemists, however disinclined in mathematical arts they might be individually, could apply it to a wide variety of systems and get qualitative answers having a certain quantum mechanical basis. Irrespective of the absolute validity of interpretations derived with its aid, the theory has real merit. It provides a convenient correlation framework onto which an enormous array of empirical observations can be affixed systematically. In recent years the molecular orbital theory has played an increasing role in organic chemistry. Its strongest advantage over elementary resonance theory is that it yields semiquantitative rather than purely qualitative results. Nevertheless, the mathematical complexities of the molecular orbital theory act as a formidable barrier to its widespread use by practicing chemists. For this reason the discovery of a scheme for putting the conventional theory of resonance on a semiquantitative basis, and one which can be easily handled by anyone who can write resonance structures, may be of some practical interest.

A rationalization of the numerical resonance theory which we shall use in the following for systems with paired electrons was recently described in another paper,[1] where it was applied to resonance energies of polynuclear aromatic molecules. The purpose of the present paper is neither to defend the quantitative validity of the new

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[1] L. S. Bartell, *J. Phys. Chem.* 67, 1865 (1963).

approach nor to use it in entirely new applications. It is simply to illustrate to chemists who might be interested in experimenting with it, the range of applicability in several representative chemical systems. These systems include not only ground states of stable molecules and transition states, but also excited electronic states and ions.

MODEL FOR SINGLET GROUND STATES

It was shown (Ref. 1) how the assumption that bond energies depend smoothly on π electron bond order leads to a treatment of resonance energies of aromatic molecules. The form adopted for the dependency was a truncated series expansion

$$E_{ij} = c_0 + c_1 p_{ij} + c_2 p_{ij}^2 \tag{1}$$

where E_{ij} represents bond energy, p_{ij} represents bond order, and the c_n are constants characteristic of the bond type. The whole key to a quantitative treatment is the deduction of the p_{ij}. These quantities, in turn, depend upon a scheme for assessing the relative weights to be assigned to the various resonance forms which can be written. If proper weights were known, estimates could presumably be made not only of energies, but also of such quantities as bond lengths, dipole moments, etc. The derivation of the weights from first principles would be a valence bond problem more complex than the MO problem we are seeking to circumvent. A simple alternative which affords a satisfactory approximation for many purposes is the use of Pauling bond orders.[2] These bond orders are based on a weighting in which all resonance structures which are nominally equivalent energetically are given equal weight. All structures which are associated with higher energy by virtue of formal bonds, charge separation, etc., are rejected. Several authors[2] have shown that Pauling bond orders correlate experimental bond lengths at least as satisfactorily as the most elaborate alternative current theories, and Pauling orders were found, in Ref. 1, to work satisfactorily in calculations of aromatic resonance energies. Accordingly, we shall concentrate on their use in the remainder of this paper.

The sum over all bonds of the E_{ij} of Eq. (1) gives the total bond energy. Resonance energies (RE) are found by taking the difference between the total bond energy for a molecule and the bond energy calculated for a single reference structure. For ground states in which all electrons are paired it is easily shown that the terms involving c_0 and c_1 cancel, giving the simple result[3]

$$\mathrm{RE} = c_2\{N_d - \sum_{\text{bonds}} p_{ij}^2\} \tag{2}$$

where N_d is the number of double bonds in any individual resonance structure. Consequently, the RE can be calculated at once from the bond orders, p_{ij}, which are known by inspection from the array of relevant resonance forms. As in all semi-empirical theories there is an adjustable parameter which, in this case, is c_2. The

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[2] For a discussion of various kinds of bond order conventions and a comparison with Pauling bond orders see N. S. Ham and K. Ruedenberg, *J. Chem. Phys.* **29**, 1215 (1958); D. W. J. Cruickshank and R. A. Sparks, *Proc. Roy. Soc.* A, **258**, 270 (1960); D. W. J. Cruickshank, *Tetrahedron* **17**, 155 (1962).

[3] In this paper RE values are calculated assuming that all π electron frameworks are planar and unstrained. Exceptions of this are, of course, well-known for certain systems (e.g. cycloöctatetraene, triphenylmethyl) in configurations of lowest energy.

remarkable thing is that there is only one such parameter for hydrocarbon singlet ground states, and it can be assumed to be the same for all hydrocarbon molecules.

The constant c_2 is seen, then, to play a role similar to that of the resonance integral β in MO theory, and it is useful to relate c_2 to β for sake of comparison of results. This can be done by equating the resonance energy derived from Eq. (2) for some reference compound with that deduced by MO theory for the same compound. If we arbitrarily adopt benzene for the purpose[4] we get, from Eq. (2),

$$\begin{aligned} \mathrm{RE} &= c_2\{3 - [(\tfrac{1}{2})^2 + (\tfrac{1}{2})^2 + (\tfrac{1}{2})^2 + (\tfrac{1}{2})^2 + (\tfrac{1}{2})^2 + (\tfrac{1}{2})^2]\} \\ &= 3c_2/2. \end{aligned}$$

The simple LCAO MO result for benzene is RE $= 2\beta$, from which we find $c_2 = 4\beta/3$, whence[5]

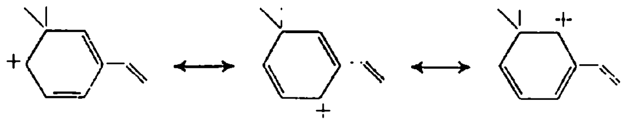
$$\mathrm{RE} = (4/3)\beta\{N_\alpha - \sum_{\text{bonds}} p_{ij}{}^2\}. \tag{3}$$

It should be noted that the use of Pauling bond orders in Eqs. (2) and (3) leads to a calculated resonance energy of zero for nonaromatic conjugated systems such as butadiene. This is a consequence of the Pauling bond order convention rather than a property of the underlying idea of the model. It is a consequence which is not seriously in disagreement with observations either of bond energy or bond length according to several recent interpretations.[6,7] A discussion of the possible role of hybridization changes or compression energies will not be given here as the problems raised are no different for the present model than for conventional MO theory.

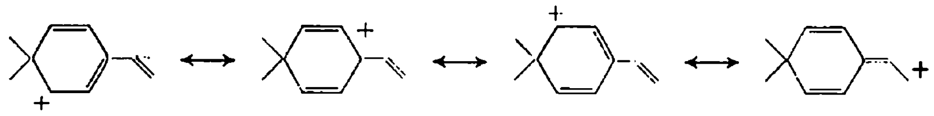
APPLICATIONS TO SINGLET HYDROCARBON SYSTEMS

The simplest application of the Pauling bond order model is the calculation of RE values of aromatic molecules for use in correlating heats of formation,(done in Ref. 1). The approach is also applicable to problems in chemical kinetics in calculating the loss of resonance energy suffered in the formation of transition states. Illustrations of this are given for the cases of electrophilic substitution and Diels-Alder reactions.

Electrophilic substitution. Let us first consider as a simple (if impratical) sample calculation the comparison of *meta* and *para* substitution in styrene. Conventional structures for transition states are, for *meta*



and for *para*



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[4] Results are not very sensitive to this choice. A better over-all fit might result if we adopted a value c_2 larger by 10 or 20%.

[5] The parameter c_2 is positive, as is RE by our convention. The customary definition of the MO parameter β makes it negative. For simplicity in presentation, however, we shall consider the symbol β to represent the (positive) absolute magnitude.

[6] M. J. S. Dewar and H. N. Schmeising, *Tetrahedron* **5**, 166 (1959); *ibid.* **11**, 96 (1960).

[7] L. S. Bartell, *J. Chem. Phys.* **32**, 827 (1960); *Tetrahedron* **17**, 177 (1962).

The corresponding Pauling orders, p_{ij}, are illustrated in Fig. 1. Insertion of the p_{ij} into equation (3) gives RE (*meta*) $= 1{\cdot}185\beta$ and RE (*para*) $= 1{\cdot}500\beta$, from which it is inferred that the activation energy is $0{\cdot}315\beta$ lower for *para* than *meta*. If β is given its customary thermochemical value of about 18 kcal, it is seen that the *para* directing tendency is quite appreciable, according to the model. Both *para* and *meta* attack entail a substantial loss in RE, for RE (benzene skeleton) $= 2\beta$.

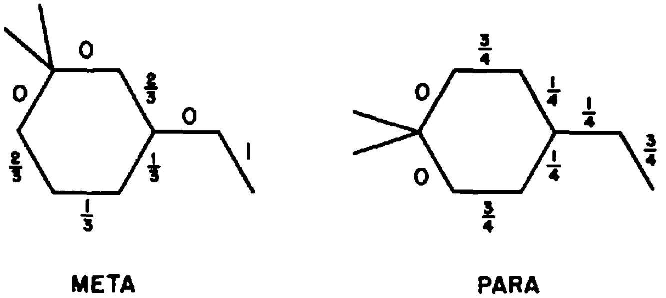

FIG. 1. Pauling bond orders for *meta* and *para* transition states in electrophilic substitution of styrene.

A more practical application is to electrophilic substitution in polyacenes where computed differences in localization energies can be compared with those derived by Dewar's MO approximation method.[8] Results are plotted in Fig. 2 for attack at various sites of a number of hydrocarbons. The Pauling order curve represents the

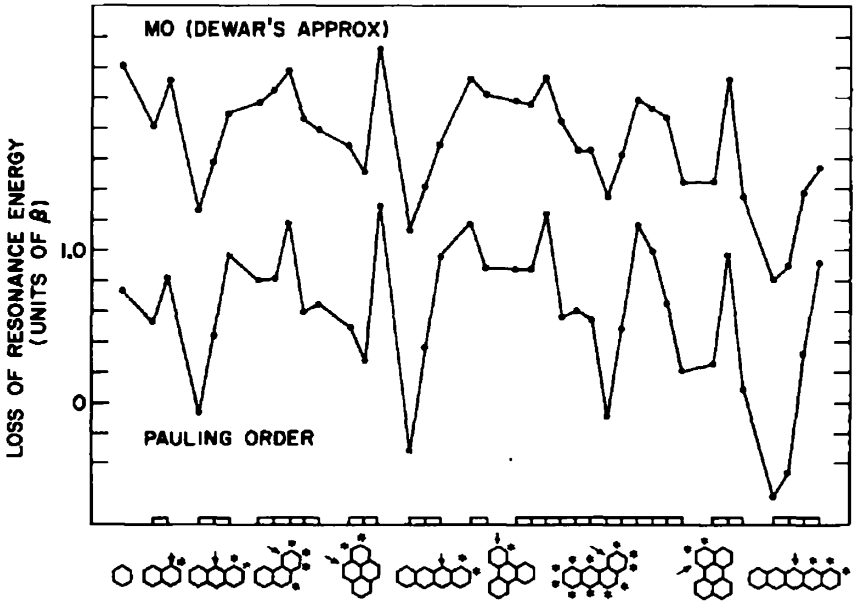

FIG. 2. Calculated variation of activation energy in electrophilic substitution for a series of aromatic hydrocarbons. For a given molecule the left-hand point corresponds to attack at the site identified by the arrow. Successive points to the right correspond to attack at the starred sites as ordered in clockwise sequence around the molecular diagrams.

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[8] M. J. S. Dewar, *J. Amer. Chem. Soc.* 74, 3357 (1952).

quantity [RE (*trans* state)—RE (reactant)] in terms of β. Both the MO and Pauling order values differ from activation energies by disposable constants. The significant comparison is of the relative stabilities of the various transition states. It can be seen that the agreement in ordering reactivities of sites is quite good. The principal difference is that the present model emphasizes differences between sites more than the MO approximation. Insufficient experimental data exist to indicate which method gives the more reasonable results.

Diels-Alder reaction. According to Brown,[9] the activation energy for the reaction of a dienophile with a polynuclear aromatic hydrocarbon is related to the loss of energy involved when two of the π electrons from the aromatic molecule form *para* σ bonds. Figure 3 illustrates the case in which naphthalene is the diene. The Pauling orders shown in Fig. 3 imply, according to Eq (3), a substantial loss of resonance energy in the course of the reaction.

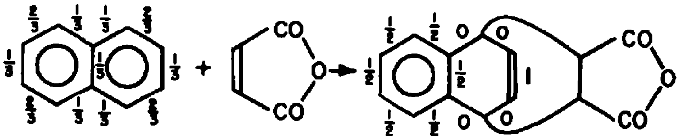

FIG. 3. Pauling bond orders for Diels-Alder reaction illustrated with naphthalene as the diene.

In Fig. 4 are shown, for a variety of polyacenes and sites of attack, the resonance energy losses calculated with the use of Eq. (3). These are compared with Brown's simple LCAO MO calculation,[9] with his MO calculations including overlap,[9] and with Wheland's suggested empirical RE losses.[10] As before, the scale factor allowing a direct comparison of the Pauling order and MO results is set by equating the calculated RE values for benzene. The empirical values are compared assuming Wheland's recommended RE value for benzene of 36 kcal/mole.[10]

The qualitative agreement between the profiles of all of the curves is reasonably good. It is apparent that the features of the simple MO curve oscillate more gently than those of the Pauling order curve. Inclusion of the overlap integral in the secular equations of the MO calculations has the interesting effect of enhancing the features and making them agree better with those of the empirical and Pauling order curves. Curiously, Dewar's approximate MO method[8] applied to the problem gives features of greater amplitude than exhibited by any of the curves plotted in Fig. 4. This is contrary to the case of electrophilic substitution where Dewar's results were more washed out than those of the Pauling order model (Fig. 2).

EXCITED STATES

The results (ref. 1) and the preceding section indicate that there is a useful area of application of the Pauling order resonance scheme in ground state energy calculations. Having established this, it is natural to investigate whether the scheme lends itself to calculations on excited electronic states, also. A virtue of the MO method is that it provides a straightforward basis for treating excited states as well as ground states. Expectations for easy success of the Pauling order model, on the other hand,

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[9] R. D. Brown, *J. Chem. Soc.* 691 (1950).

[10] G. W. Wheland, *Resonance in Organic Chemistry* p. 379. John Wiley, New York (1955).

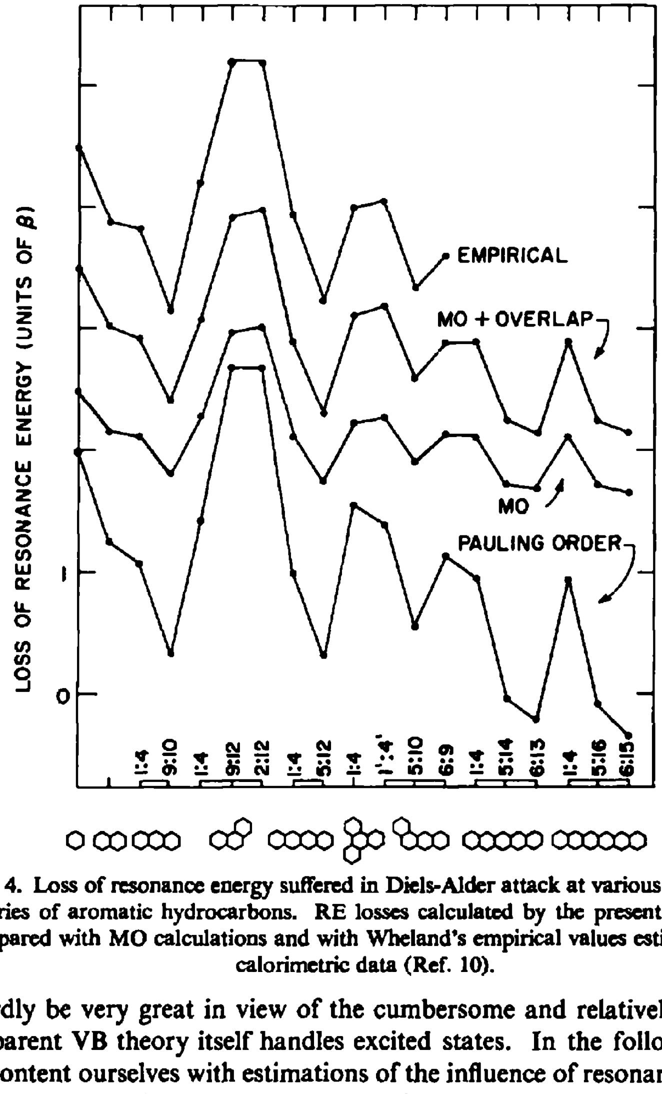

Fig. 4. Loss of resonance energy suffered in Diels-Alder attack at various positions in a series of aromatic hydrocarbons. RE losses calculated by the present scheme are compared with MO calculations and with Wheland's empirical values estimated from calorimetric data (Ref. 10).

could hardly be very great in view of the cumbersome and relatively unsatisfactory way the parent VB theory itself handles excited states. In the following, therefore, we shall content ourselves with estimations of the influence of resonance on excitation energies, and neglect the treatment of the excitation energy itself.

Let us begin by considering the ground and first excited states of polyenes. Heretofore we have completely ignored "ionic" valence-bond structures. We can now no longer neglect them, for excited states are liberally weighted with "ionic" resonance-forms.[11] For ethylene, both the ground and first excited singlet states can be satisfactorily represented by appropriate linear combinations of the VB wave functions corresponding to

$$\underset{\text{I}}{\mathrm{C{=}C}}, \qquad \underset{\text{II}_a}{\overset{+}{\mathrm{C}}\text{—}\overset{-}{\mathrm{C}}}, \qquad \underset{\text{II}_b}{\overset{-}{\mathrm{C}}\text{—}\overset{+}{\mathrm{C}}}$$

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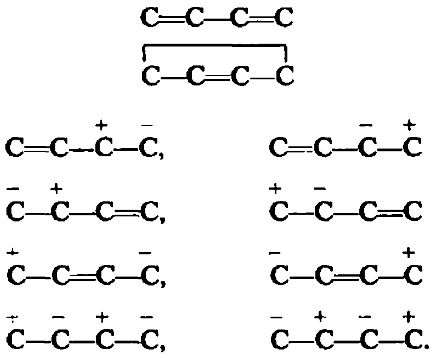
[11] To use an intuitive argument, this charge separation is revealed by the vigorously oscillating charge distribution during an electronic transition. The time-dependent wave function may be regarded as a linear combination of ground and excited ψ's with time-dependent coefficients.

Furthermore, we may have some confidence that the ground state is predominantly I, and the excited state is a superposition principally of $\mathrm{II_a}$ and $\mathrm{II_b}$.[12] Similarly, for butadiene, the appropriate structures are



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

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

$\mathrm{V_{a,b,c,d}}$ $\mathrm{C{=}C{-}\overset{+}{C}{-}\overset{-}{C}}$, $\mathrm{C{=}C{-}\overset{-}{C}{-}\overset{+}{C}}$

$\mathrm{\overset{-}{C}{-}\overset{+}{C}{-}C{=}C}$, $\mathrm{\overset{+}{C}{-}\overset{-}{C}{-}C{=}C}$

$\mathrm{VI_{a,b}}$ $\mathrm{\overset{+}{C}{-}C{=}C{-}\overset{-}{C}}$, $\mathrm{\overset{-}{C}{-}C{=}C{-}\overset{+}{C}}$

$\mathrm{VII_{a,b}}$ $\mathrm{\overset{+}{C}{-}\overset{-}{C}{-}\overset{+}{C}{-}\overset{-}{C}}$, $\mathrm{\overset{-}{C}{-}\overset{+}{C}{-}\overset{-}{C}{-}\overset{+}{C}}$.

Of these we consider III to represent the ground state and reject IV, as before, because of its formal bond. We consider the first excited state to be described by V–VII, but neglect VI and VII because of their more extensive charge separation. For uncertain reasons it is popular in written discussions of butadiene to invoke VI and neglect V. We do the opposite (1) because it is plausible,[13] and (2) because the convention it sets for polyenes gives us the simplest systematic means possible for assessing the bond orders, p_{ij}, needed to calculate effects of resonance.

For higher polyenes we shall describe the ground state by structures analogous to I and III and excited states by ionic structures analogous to II and V. It may be seen by inspection that this has the effect of making the bond orders alternate between 1 and 0 in the ground state and between $(N_d - 1)/N_d$ and 0 in the excited state, where N_d is the number of double bonds in the ground state structure. Applying Eq. (1) and summing over bond energies, we find

$$E(\text{ground}) = (2N_d - 1)c_0 + N_d c_1 + N_d c_2$$

and

$$E(\text{excited}) = d + (2N_d - 1)c_0 + (N_d - 1)c_1 + N_d c_2[(N_d - 1)/N_d]^2$$

in which d is a parameter to account for the energy of charge separation. This result implies that we can express all excitation energies, $\Delta E = h\nu$, simply in terms of ΔE for a reference molecule. If we choose butadiene, for sake of argument, with

$$\Delta E_B = d - c_1 - 1{\cdot}5c_2 \qquad (4)$$

it is easily seen that ΔE for any polyene becomes

$$\begin{aligned}\Delta E &= \Delta E_B - [(N_d - 2)/2N_d]c_2 \\ &= \Delta E_B - [(2N_d - 4)/3N_d]\beta. \qquad (5)\end{aligned}$$

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[12] The antisymmetrized MO wave function for the first excited singlet state reduces, indeed, to $(\psi_{\mathrm{II_a}} - \psi_{\mathrm{II_b}})$.

[13] There is both experimental and theoretical evidence, however, that the π bond order of the central bond in the excited state is appreciably greater than in the ground state. The rejection of IV, VI, and VII is obviously crude and somewhat arbitrary, but it is the only simple scheme which circumvents adding another adjustable parameter.

The second term on the right corresponds, then, to the red shift to be expected with increasing N_d.

It is possible to determine empirically a value for β which fits experimental data reasonably well. As might be expected, the value of β required is essentially the MO value to fit spectral data rather than the much lower MO value to fit calorimetric ground state RE data. It is more interesting, however, to see how well the model works if we dispose of β altogether by giving ΔE_B its MO value of 1·236 β. When substituted into Eq. (5), this gives

$$\Delta E/\Delta E_B = 1 - 0{\cdot}540\,(N_d - 2)/N_d. \tag{6}$$

A comparison of the red shift implied by equation (6) with red shifts observed,[14] and calculated by MO theory[15] is shown in Fig. 5. Once again the crude Pauling order model is found to provide a significant degree of correlation.

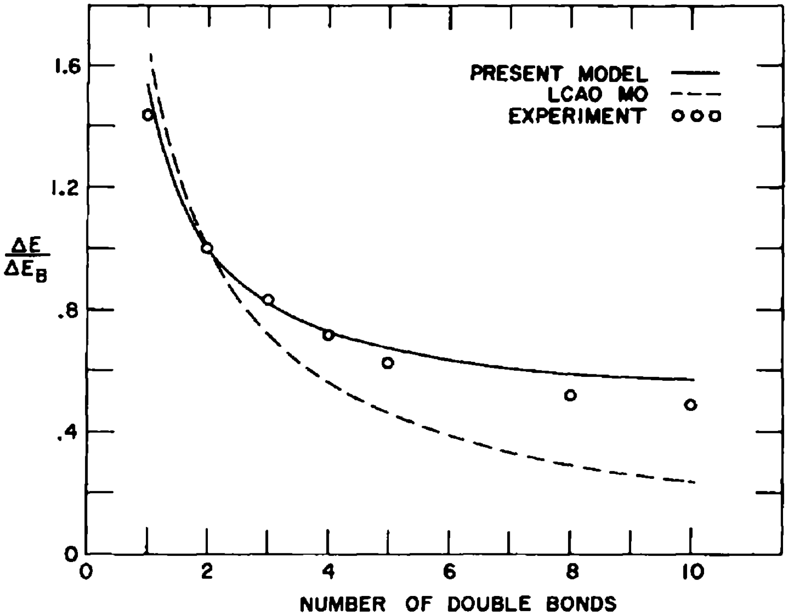

Fig. 5. Red shift in lowest $\pi \rightarrow \pi^*$ electronic excitation of polyenes as a function of length of conjugated chain. The ordinate represents the ratio of excitation energy to the reference excitation energy of butadiene.

It would be of interest to apply an analogous model to polyacenes where the foregoing arbitrary procedure of ignoring the π character of nominally pure σ bonds is obviated. Unfortunately, in contrast to the polyene case where only one excited state had to be considered, the situation with the aromatics is greatly complicated by the existence of numerous excited states of comparable energy.[16] There is no difficulty in applying, mechanically, the Pauling order model to deduce a value for the red shift

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[14] K. S. Pitzer, *Quantum Chemistry* p. 272. Prentice-Hall, New York (1953).

[15] A. Streitwieser, *Molecular Orbital Theory for Organic Chemists* p. 207. John Wiley, New York (1961).

[16] R. L. Hummel and Klaus Ruedenberg, *J. Phys. Chem.* **66**, 2334 (1962).

of, say, linear polyacenes with increasing numbers of rings. The difficulty lies in determining which, if any, of the excited states the red shift should apply to. As a matter of fact, the red shift calculated by the present model is in appreciable disagreement with many of the individual transitions plotted for linear polyacenes by Hummel and Ruedenberg.[16] It is pleasing to note, however, that the calculated red shift agrees quite well with the average for all transitions to low lying excited singlet states.

RADICALS

Another problem treated qualitatively by the theory of resonance concerns the stability of resonance stabilized free radicals. It is immediately apparent that the Pauling order scheme, which takes into account only electron pair bonds, is completely incapable of copying with even the simplest resonance stabilized one-electron case, the ethylene cation

$$\overset{+}{\mathrm{C}}-\overset{\bullet}{\mathrm{C}} \leftrightarrow \overset{\bullet}{\mathrm{C}}-\overset{+}{\mathrm{C}}$$

which is analogous to the hydrogen molecule-ion. Both the VB and MO approaches, on the other hand, show that the π electron energy is lower than that in $\gt\!\!-\mathrm{C}\cdot$ by β, the MO resonance integral. If radical stability is to be included in our simple scheme, it is necessary to graft on an extension. The simplest extension in keeping with the spirit of the Pauling order model is to consider the energy of interaction of an unpaired electron with an atom, i, to be smoothly related to the fraction, u_i, of the resonance structures in which the electron is on i or

$$E_i = w(c_0' + c_1'u_i + c_2'u_i^2) \tag{7}$$

where w is a weighting factor independent of i. Rough considerations of the variation of bonding character as the total number of π electrons per carbon atom increases, suggest that w has the form

$$w \simeq \{1 + [(n - n_e)/(n - 1)]^2\}/2$$

where n_e is the total number of π electrons and n is the number of carbons in the π electron framework. It is to be noted that w varies between 1 and 1/2, and is always unity for a one-electron system.

The conservation rule applying to the p_{ij}, also works for the u_i, reducing the expression for the RE to a parameter c_2' which can be calibrated in terms of β. If the ethylene cation is chosen for the calibration the expression for the resonance energy of unpaired electrons becomes

$$\begin{aligned}\mathrm{RE\,(unp.\ el.)} &= w(1 - \Sigma u_i^2)c_2' \\ &= \beta\left(1 + \left[\frac{n - n_e}{n - 1}\right]^2\right)(1 - \Sigma u_i^2)\end{aligned} \tag{8}$$

It is fair to observe before going on that this device for accommodating radicals, while having a certain plausibility, is introduced more artificially than the original Eq. (1). The need for some explicit accounting of unpaired electrons is plainly evident, and the form chosen parallels the original equation. Nevertheless it is

TABLE 1. RESONANCE STABILIZATION OF CERTAIN RADICALS AND RADICAL IONS (UNITS OF β)

Radical	Double bond contrib. Eq. (3)	Unpaired el. contrib. Eq. (8)	Total	MO result
$\overset{+}{\mathrm{C}}\text{—}\dot{\mathrm{C}}$[a]	0	1·00	1·00	1·00
$\bar{\mathrm{C}}\text{—}\dot{\mathrm{C}}$[a]	0	1·00	1·00	1·00
$\mathrm{C{=}C\text{—}\dot{C}}$[b]	0·67	0·50	1·17	0·83
$\phi\text{—}\dot{\mathrm{C}}\mathrm{H}_2$[c]	0·03	0·72	0·75	0·72[d]
$\phi_2\dot{\mathrm{C}}\mathrm{H}$[c]	0·40	0·84	1·24	1·30[d]
$\phi_3\dot{\mathrm{C}}$[c]	0·61	0·89	1·50	1·80[d]
One electron in polyene frame:[a]				
$n = 1$	0	0	0	0
$n = 2$	0	1·00	1·00	1·00
$n = 4$	0	1·50	1·50	1·62
$n = \infty$	0	2·00	2·00	2·00

[a] Reference: separated C atoms.

[b] Reference: C=C and $\dot{\mathrm{C}}$.

[c] Excess over benzene rings. π electron frameworks assumed coplanar even for $\phi_2\dot{\mathrm{C}}\mathrm{H}$ and $\phi_3\dot{\mathrm{C}}$ where coplanarity is sterically improbable.

[d] G. W. Wheland, *J. Amer. Chem. Soc.* 63, 2025 (1941).

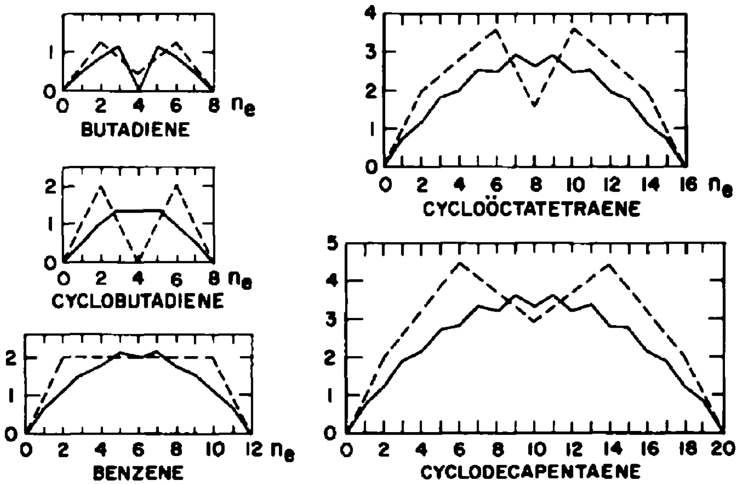

FIG. 6. Dependency of resonance energy (units of β) on the number of π electrons occupying the conjugated network. Solid lines represent values calculated by the present scheme; dashed lines represent MO values. References adopted for computing resonance energies of the n-carbon networks are n/2 ethylene sigma skeletons.

aesthetically offensive that a new parameter c_2' had to be invoked and calibrated in our resonance theory scheme whereas the MO theory handles radicals as readily as it handles systems of paired electrons.

In Table 1 and in Fig. 6 the results of the present scheme are compared with those of simple MO theory. It may be observed that the dependency on chain length and on the number of electrons occupying the π electron framework is fairly good. One result deserves comment. The Pauling order contribution, Eq. (3), for the benzyl radical or, similarly, the benzyl cation or anion, is only $0{\cdot}03\beta$ greater than that in benzene itself. This is unexpectedly low in view of the fact that the benzyl system has five resonance forms as compared with only two for benzene itself. It was noted and explained in reference 1 that the Pauling order RE usually correlates very strongly with the number of resonance forms, as expected from the theory of resonance. The benzyl system shows that the RE of the present model, however, depends on the details of the electronic structure (rightly or wrongly) and is not equivalent to a simple counting of resonance forms.

IONIZATION POTENTIALS

The resonance stabilization of a π electron system tends to increase as the π electron network increases in size. According to the present model the RE of singly charged cations tends to increase more rapidly with network size than the RE of neutral molecules. Since large cations are preferentially stabilized it should require less energy to ionize a large aromatic molecule than a small one. If we assume that the energy to ionize is the same for all aromatics except for resonance effects, we predict, using benzene (ϕ) for a reference, that

$$\begin{aligned} I &= I_\phi - (I_\phi - I) \\ &= I_\phi - \{[\mathrm{RE}(n_e = n - 1) - \mathrm{RE}(n_e = n)] \\ &\qquad - [\mathrm{RE}(n_e = 5) - \mathrm{RE}(n_e = 6)]_\phi\} \\ &= I_\phi - \Delta\Delta\mathrm{RE} \end{aligned} \tag{9}$$

where I represents the ionization potential and RE values are calculated with the use of Eqs. (3) and (8). The above assumption is exactly analogous to the one made earlier for electronic spectra. Further, it is precisely equivalent to the assumption made in simple MO treatments of ionization potentials.[17]

The results of this simple treatment for various compounds are compared in Fig. 7 with experimental ionization potentials[18] and with MO calculations.[17] It is found in aromatic systems that the influence on $\Delta\Delta$RE of the unpaired electron (Eq. 8) in cations is minor in comparison with the effect of double bond resonance (Eq. 3). The experimental values in Fig. 7 are themselves subject to appreciable uncertainty. Nevertheless, it can be seen in the limited number of cases studied that (a) both the present and the MO methods are more or less in accord with experiment for aromatic molecules, and (b) the empirical values of β implied for the present and MO methods are roughly the same. Also plotted, in addition to the aromatic molecules, is ethylene. The present model evidently works reasonably well for ethylene even though the MO approach fails. Not plotted is butadiene for which both calculational schemes fail, the present method failing more dismally than the MO method.

For molecules of the type treated above it is easy to show that both calculational methods predict that $\Delta\Delta$RE values are the same for the formation of anions as for the formation of cations. No gaseous electron affinity results are available but experimental polarographic reduction potentials afford a similar comparison, as

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[17] A. Streitwieser, *Molecular Orbital Theory for Organic Chemists* p. 188. John Wiley, New York (1961).

[18] M. E. Wacks and V. H. Dibeler, *J. Chem. Phys.* **31**, 1557 (1959); K. Watanabe, *Ibid.* **26**, 542 (1957).

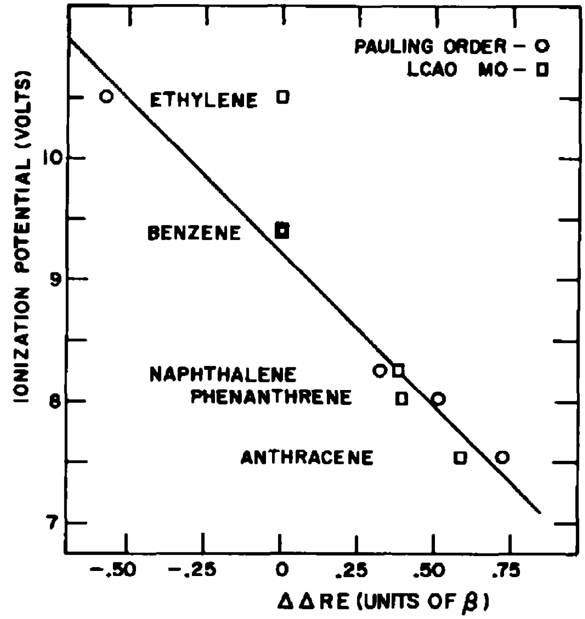

Fig. 7. Experimental ionization potentials compared with calculated values of ΔΔ RE.

discussed by Streitwieser.[17] Results resemble those of Fig. 7 with the exception that a smaller empirical value of β is required to fit the data, owing to solvation and other effects.

NON-HYDROCARBON SYSTEMS

It is characteristic of any semiempirical method such as conventional VB theory or MO theory that at least one new parameter must be invoked for each different kind of atom considered. Since the reader may feel that enough parameters have been unleashed in this paper already, no attempt will be made to extend the scheme quantitatively to embrace heteroatoms. There is no obvious reason why such an extension could not be made, however, in view of the qualitative success of resonance theory with general systems, and it is certainly true that an extension is needed if the scheme is to be of general utility to organic chemists.

We shall comment on only two non-hydrocarbon applications, each of them related to effects of resonance on acid strength. As noted by Pauling,[19] the strengths of oxygen acids, $XO_n(OH)_m$, which dissociate to form the resonance stabilized anions

$$[XO_{n+1}(OH)_{m-1}]^{-1}$$

depend orderly on the number of equivalent oxygens, $n + 1$ in number, of the anion. If it is assumed that individual resonance structures have Pauling bond orders, p_{XO}, of unity for n of these oxygens and zero for the oxygen bearing the formal charge of -1, Eq. (3) is easily seen to give

$$RE = 4(n/n + 1)\beta/3 \qquad (10)$$

or

$$RE(n) - RE(n - 1) = 4\beta/[3(n^2 + n)] \qquad (11)$$

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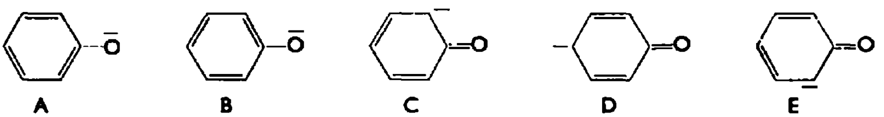
[19] L. Pauling, *Nature of the Chemical Bond* p. 325. Cornell University Press, Ithaca, New York (1960); *General Chemistry*, W. H. Freeman, San Fransisco (1947).

This implies a greater anion stability as n increases and, hence, a greater acidity. Pauling observes that $\Delta G^\circ(n) - \Delta G^\circ(n-1)$ for the dissociation is of the magnitude of 7 kcal/mole, which is very roughly in agreement with Eq. (11) if β is given its usual hydrocarbon thermochemical value of about 18 kcal/mole.

The other illustration concerns the phenoxide ion with structures



These are exactly analogous to the benzyl structures mentioned earlier, except that we would expect the quinoid structures C–E to be relatively less stable than the structures A and B by virtue of the electronegativity difference between carbon and oxygen. It will be recalled that the RE excess (over benzene) for the benzyl anion is only 0·03β if all structures are given equal weight in Eq. (3). If, however, we arbitrarily give structures C–E only 1/3 the weight of A and B, it is interesting to note that the RE excess increases to 0·205β.[20] Such an increase would materially enhance the calculated acidity of phenol.

DISCUSSION

All in all it is quite remarkable how faithfully such a simple extension of qualitative resonance theory tends to follow the results of more elaborate theoretical approaches in a wide variety of applications. This fact should not be allowed to obscure certain imperfections.

First, there is nothing in the present scheme to suggest the Hückel $4n + 2$ rule for aromaticity. In this respect the resonance model resembles the simple VB approach which suffers the same deficiency. In fairness, however, it must be admitted that the actual resonance energies of the simple MO method are scarcely more suggestive of the $4n + 2$ rule than the resonance energies of our present scheme, as Fig. 6 reveals. It is the auxiliary idea of filled orbitals implicit in the MO method which leads to the Hückel rule.[21]

Also, as mentioned earlier, the treatment of ground singlet states, excited states, and radicals requires the calibration of three parameters in the resonance scheme, namely c_2 (Eq. 2), d-c_1 (Eq. 4), and c_2' (Eq. 8). The MO theory accomplishes the same job with but one parameter, β.

As noted by Ham and Ruedenberg,[2] Pauling bond orders are regularly related to other kinds of bond orders in alternate hydrocarbons but the regularity is partly lost with nonalternates. One manifestation of this appears in the case of the nonalternate, azulene. The resonance energy calculated by the MO method for azulene is less than that calculated for its alternate isomer, naphthalene, by about 9 %. Eq. (3), however, gives a resonance energy for azulene which is greater than that of naphthalene

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[20] Assuming the E_{CO} of Equation (1) is the same as that of E_{CC}, for sake of argument.

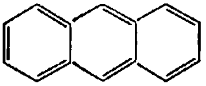
[21] Cyclobutadiene is the one case shown in Fig. 6 where the vanishing MO resonance energy at $n_s = n$ supports the Hückel rule. Even this is illusory as discussed by many authors. Craig [*Proc. Roy. Soc.* **A200**, 272, 340 (1950)] for example, has shown that inclusion of configuration interaction in the MO calculation leads to a stabilization of cyclobutadiene even greater than that given by the simple VB treatment, and further, implies a singlet ground state in contrast with the triplet expected from simple Hückel theory.

by about 2%. Such minor discrepancies in RE values are often not considered as serious but they may be indicative of imperfect handling of nonalternates by the present method.

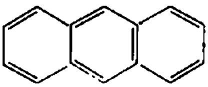
Another point which should not be overlooked is that the extreme simplicity of the present method begins to vanish as the complexity of the molecule increases, because of the tedium involved in writing all of the appropriate resonance forms. For example, ovalene ($C_{32}H_{14}$) in its ground state has 50 Kekulé-type resonance forms. The treatment of excited states or transition states in electrophilic substitution would require many-fold more. On the other hand, there is no great art in writing resonance forms, and if a small fraction are inadvertently missed it makes little difference in the p_{ij} and the calculated RE values.

One of the least satisfactory aspects of the Pauling order model is the lack of a bonafide derivation of it from quantum mechanical principles in terms of an explicit set of assumptions. To be sure, it may be argued that the assumptions in simple MO or VB theory are so severe that their justification is not fundamentally much greater. Nevertheless, it would be desirable to have a formal bridge in addition to the empirical bridges connecting the methods.

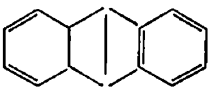
It would seem most natural to relate the Pauling order model to valence bond theory since the resonance forms used represent VB wave functions. Even if it is assumed that our basic relation, equation (1), can be rationalized in terms of VB theory, it is difficult to justify the equal weighting of resonance forms implicit in the Pauling bond orders and the total neglect of structures with formal bonds. In anthracene, for example, VB calculations[22] not only give the structure



a substantially lower weight than that of



but give it a lower weight, even, than that of



which is ignored altogether in determining Pauling bond orders. The problem of weighting is important because the RE of Eq. (3) is sensitive to it. It is not impossible that the very neglect of the non-Kekulé types of structures in determining Pauling bond orders has the effect of compensating for the weights, but this vague possibility can hardly be used to justify the present scheme.

We turn, then, to the simple MO method. The surprising finding by Ham and Ruedenberg[2] that Pauling bond orders can be derived directly from MO theory provides a clue of a possible link between the present model and the MO method. This clue has not yet been explored in detail, but it promises to offer the best justification of the otherwise flagrantly arbitrary weighting procedure used in defining Pauling bond orders.

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[22] M. B. Oakley and G. E. Kimball, *J. Chem. Phys.* 17, 706 (1949).

Finally, the unanswered questions of formal legitimacy notwithstanding, the fact remains that the present scheme correlates a wide variety of observables successfully. Somehow, it captures so large an element of truth so simply that it merits wider study, and it seems fitting to present it for general scrutiny at this time.

SUMMARY OF PROCEDURE FOR STABLEST STATES OF LOWEST MULTIPLICITY

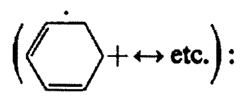
The scheme outlined here applies to a planar π electron hydrocarbon system with $n_e\pi$ electrons moving in a single conjugated network of n carbon atoms. Given such a system, all nominally equivalent Kekulé-type resonance forms are drawn. If n is even there will be $N_d = n_e/2$ double bonds. If n is odd there will be $N_d = (n_e - 1)/2$ double bonds and one unpaired electron. The Pauling order, p_{ij}, of bond ij is defined as the number of times bond ij appears as a double bond in the resonance forms divided by the total number of the forms. The quantity u_i of atom i is the number of forms in which the unpaired electron is on atom i divided by the total number of forms.

The resonance energy RE can be calculated, then, from

$$\mathrm{RE} = (4\beta/3)(N_d - \sum_{\text{bonds}} p_{ij}^2) + \beta\left(1 + \left[\frac{n - n_e}{n - 1}\right]^2\right)([1/n_r] - \sum_{\text{atoms}} u_i^2) \qquad (12)$$

where n_r is the number of atoms on which the unpaired electron is assumed to move *in the reference structure*. For example, in calculating RE values for the cyclic systems in Fig. 6, RE is considered to be the energy difference between n_e electrons in $n/2$ ethylene sigma skeletons and the same number of electrons in the n-membered carbon rings. It is readily seen that Eq. (7) requires n_r to be 2. On the other hand, it is conventional in the case of a radical like the benzyl radical to look at the excess stability compared with the benzene molecule and an isolated —$CH_2\cdot$ radical. In this example n_r must be taken as 1, and the benzene RE must be subtracted from the RE of Eq. (12) to give the excess RE.

Illustrative calculation. Given the benzene network with five π electrons



The two double bonds are shared equally, so that $p_{ij} = 2/6$ for all bonds ij. The unpaired electron is also shared equally, making all $u_i = 1/6$. If our RE reference is three ethylene sigma skeletons, Eq. (12) with $N_d = 2$, $n = 6$, $n_e = 5$, $n_r = 2$, gives

$$\begin{aligned}\mathrm{RE} &= (4\beta/3)(2 - 6[2/6]^2) + \beta(1 + [1/5]^2)(1/2 - 6[1/6]^2)\\ &= (1{\cdot}7778 + 0{\cdot}3467)\beta\\ &= 2{\cdot}124\beta.\end{aligned}$$

Acknowledgement—I wish to thank Mr. N. Magnani and Miss K. Wirth for their assistance with calculations.