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A Topological Definition of Resonance Energy

C. F. Wilcox, Jr.*

Institute »Ruđer Bošković«, P. O. B. 1016, 41001 Zagreb, Croatia, Yugoslavia

A topological definition of resonance energy is proposed that is linearly correlated with the Hess and Schaad definition of resonance energy. It is shown that the derived topological parameters can be correlated with the results of a SCF π-electron model.

The Hückel model[1] for calculating π-electron enrgies begins with the adjacency matrix defined by the connectivity of the π-network. Manipulation of this matrix yields the one-electron energies and summation over the occupied levels gives the total Hückel π-energy. This process, by its numerical nature, provides only information about individual molecules so that extensive calculations are required to gain insight into the properties of classes of molecules. Even with vigorous effort such insights may be obscured by the wealth of numerical detail. An alternative approach is to seek semi-empirical relationships between the total π-energy and the topological parameters that characterize the adjacency matrices[2]. The trade-off is numerical precision for generality.

One such parametric relationship, given below as aquation (1), was developed recently for alternant hydrocarbons[3].

$$E_\pi = C_1 N + C_2 \nu + C_3 (4n_4 + \Sigma d_i^2) + Cy \ln (ASC) \tag{1}$$

where N is the number of π-centers, ν is the number of π-bonds, n_4 is the number of 4-membered rings, Σd_i^2 is a measure of branching (the sum of the squares of the degree of each vertex) and ASC is the algebraic structure count (the sum of the Kekulé structures taking into account their parity).

In this equation the functional form of the topological parameters (N, ν, etc.) was deduced from graph theory and the coefficients were evaluated by fitting a random, but representative, selection of polyolefinic, benzenoid and non-benzenoid hydrocarbons. The precision of this simple four-parameter expression for total π-energy was impressively good with an average error of about 2% in E_π. This seemingly small error looms large, however, when differences in π-energy are considered as in approximating activation energies of chemical reactions. Calculating relative reactivities, which necessitate taking a double difference, places an ever more extreme burden on such topological expressions and with equation 1, at least, the merits of each application must be scrutinized carefully[4].

* Permanent address: Cornell University, Ithaca, New York, 14850, U.S.A.

Hess and Schaad[5] have introduced a purely empirical eight-parameter scheme** for calculating the π-energies of *acyclic* polynes. The scheme reproduces the Hückel energies of a set of 40 branched and unbranched polyenes with an amazing precision of better than $\pm\, 0.1^{0}/_{0}$ (*i. e.*, $\pm\, 0.013\, \beta$). They defined a new resonance energy, RE, in which the energy of a reference Kekulé structure was calculated by their parametric scheme rather than by the traditional method of $E_{ref} = 8\, n\beta$, where n is the number of double bonds. The new definition was a major improvement over the old one in that acyclic polyolefins had essentially zero RE values, benzenoids all gave positive RE's and non-benzenoids to be unstable gave either negative RE's or very small positive values. The new resonance energies were well correlated with a number of chemical and physical properties[7].

The success of the Hess-Schaad scheme for reproducing polyolefinic π-energies draws attention to the question of whether the residual error in the topological approach lies more with the olefins or with the benzenoids and non-benzenoids. Put another way the question is whether the error of the topological approach is associated more with the cyclic delocalization portion of E_π or the larger contribution from the acyclic aspects of the network. In order to separate a resonance energy contribution from equation (1) it seems logical to define RE as in equation (2):
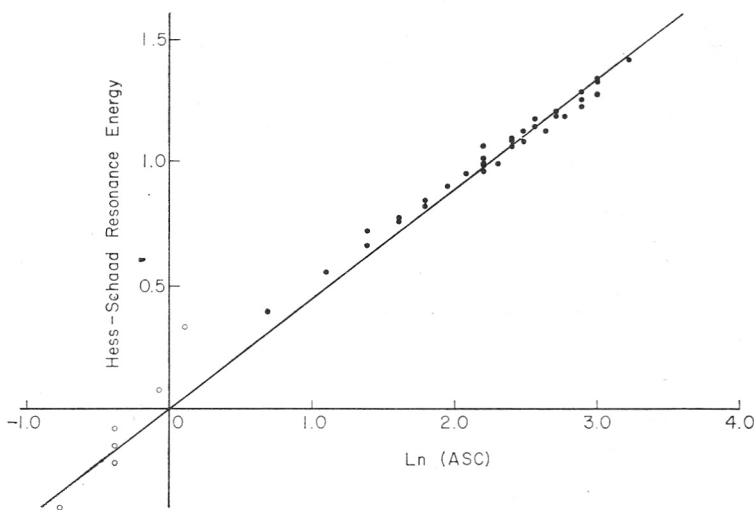
$$RE' = a_1 \ln(\text{ASC}) + a_2 n_4 \qquad (2)$$

Fig. 1

In Figure 1 are plotted (filled circles) the Hess-Schaad[7] RE values for 40 benzenoid hydrocarbons ($n_4 \equiv 0$) *vs* the corresponding $\ln(\text{ASC})$ values of

** As pointed out by Hess and Schaad two inherent redundancy relations make this actually a six parameter scheme. As given the energy of the reference structure depends slightly on the choice of Kekulé structure. Removed of this dependence introduced one additional constraint.

equation (2). It is immediately apparent that these two measures of resonance energy are closely correlated. The regression line confined to pass through the origin gives a slope $= a_1 = 0.445\,\beta$ with a standard deviation in RE of $0.04\,\beta$[8]. From this value of a_1 and RE values of the seven cyclobutadienoids included in Table II of Hess and Schaad[5] a value of $a_2 = -0.17\,\beta$ can be obtained. These seven points, were included in Figure 1 (cicles) by assigning each four-membered ring a value of $-0.38\,\beta = -0.17\,\beta/0.45$. They showed a least-squares error in RE of $\pm\,0.058\,\beta$.

For all 47 compounds the standard deviation in RE calculated via equation (2) is $0.03\,\beta$. The practical significance of this fit is that if the Hess and Schaad scheme for allicyclic polyolefins is merged with equation (2), the total E_π of all of the non-alternants can be reproduced with an average error of less than $0.04\,\beta$. This error represents a six-fold improvement over the purely topological equation (1) and suggests that the residual errors of (1) lie largely with the acyclic contribution to E_π. The source of this error is probably the limited treatment of branching implicit in the derivation of (1).

The value of graph theoretical equation like (2) lies, of course, not in their ability to approximate Hückel energies but rather in their use as a guide to the chemist in planning and interpreting experiments. One application of equation (2) is described in the next section.

FUSED CYCLOBUTADIENES

Dewar and Gleicher[9] have calculated relative thermodynamic stabilities of a large number of polycyclic hydrocarbons containing one and two aromatic hydrocarbon units fused to a cyclobutadiene ring. They employed two models, both of which are varients of the Pariser, Parr, Pople[1] approach but differ in that the one-electron resonance integrals, core repulsions and electron repulsion integrals were modified to reproduce ground state properties rather than spectral properties. The details of the model are not of concern here except to note that by including specific electron repulsion terms they are considerably more sophisticated than the simple Hückel model. It seemed of interest to determine the degree to which the results of these sophisticated calculations were mimicked by the simple Hückel model, particularly the graph theoretical approximation to it described in the previous section.

Dewar and Gleicher considered two measures of the relative thermodynamic stability of fused cyclobutadienes. The first was a resonance energy, E_R, computed by subtracting from the calculated π-energy the estimated energy of a single classical Kekulé structure. Their procedure included a correction for sigma compression energies but made no correction for variation in branching from one species to the next. Because of these differences the E_R values are not directly comparable to the resonance energy calculated from equation (2). Their second measure of relative thermodynamic stability was the quantity E_R' defined as the difference between E_R for the fused hydrocarbon and the E_R's for the component aromatic residues. Since the E_R' value for biphenylene was close to zero it was concluded that positive E_R' values corresponded to stable molecules. Yet another measure of stability would be to take the difference in π-energy of the fused cyclobutadiene and the π-energies of the component aromatic residues. This quantity, E_R'' differs from Dewar's E_R' values by the bond energies of the two single σ-bonds that

hold the aromatic residues together. Because this reference σ-contribution is constant from one molecule to next the variation in E_R'' is identical to the variation in E_R'. Use of the E_R'' values has the advantage here of being conceptually close to the resonance energies calculated via equation (2). It can be seen that in terms of equation (2) where $(ASC)_{A-4-B}$ is the algebraic structure count for a fused cyclobutadiene and $(ASC)_A$ and

$$ E_R'' = 0.45 \ln \left[\frac{(ASC)_{A-4-B}}{(ASC)_A \, (ASC)_B} \right] - 0.17 \qquad (3) $$

$(ASC)_B$ are the structure counts for the component aromatic residues A and B. The constant in equation (3) arises from the loss of a four-membered ring. The published values of E_R' are plotted in Figure 2 against the corresponding E_R'' values calculated from eq. 3*.

Two features of Figure 2 stand out. First, there are two distinct correlation lines. One is for the fused cyclobutadienes containing two aromatic residues
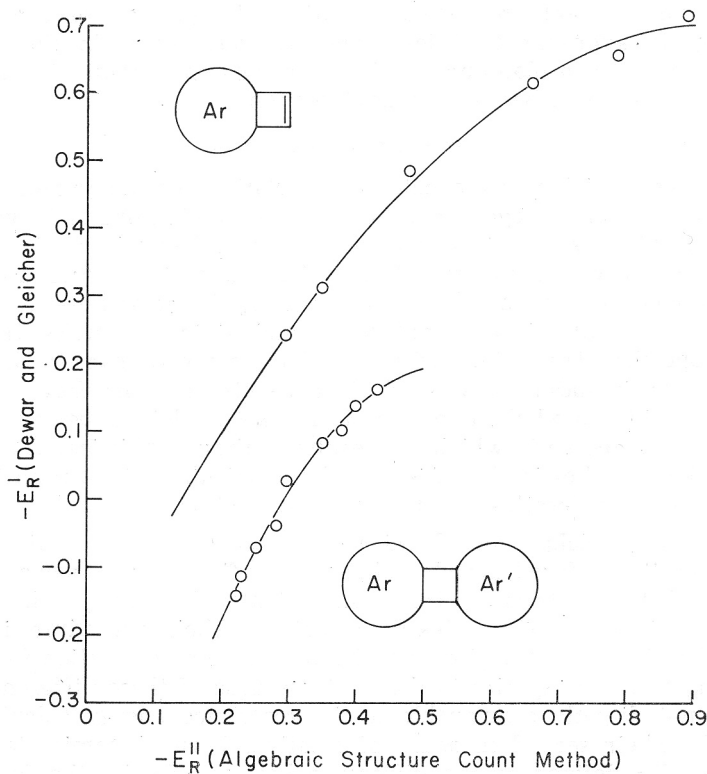

Fig. 2

* This figure does not include the Dewar-Gleicher values for the three diphenyl-monoarylcyclobutadienes, their compounds XVII—XIX. The E_R'' values of these three compounds are identical to the E values of the corresponding monoaryl-cyclobutadienes without the phenyl substituents. The E_R' values are 0.30 ± 0.01 units more negative the corresponding monoarylcyclobutadienes.

and the second is for molecules with only one residue. This splitting into two lines results probably from the inclusion of explicit electron repulsion terms in the Dewar-Gleicher model compared to the averaged value implicit in equation (3).

The second feature of the correlation lines in Figure 2 is that they are not straight. They are, however, over the range observed well aproximated by simple monotonic functions* indicating that although the Hückel model and the PPP SCF model are not identical, conclusions regarding *relative* reactivity can be drawn with almost equal confidence from either model. The same ordering would follow from consideration of the algebraic structure counts alone since E_R'' as expressed in equation (3) is also a monotonic function of ASC. Because the algebraic structure count requires *no* computation, the correlation described here frees the chemist to *design* interesting molecules, confident that the more sophisticated calculations would yield a very similar conclusion regarding relative reactivity.

As an example consider the question of whether any monoaryl fused cyclobutadiene can be designed that would be stable in the Dewar-Gleicher sense and stil be capable of isolation. Since by definition[10] the cyclobutadiene ring introduces structures of opposing parity, the ASC ratio in equation (3) will always be less than unity for any aryl group composed only of 6-membered rings and chains. In the limit the most stabilizing benzenoid group will have an ASC ratio of unity, which gives a limiting value for $-E_R''$ of $0.17\,\beta$ and by extrapolation of the line in Figure 2 a value for $-E_R'$ of about 0.05 eV. Thus by the Dewar-Gleicher criteria of stability it should not be possible to synthesis a stable monoaryl cyclobutadiene. As noted above, however, their conservative criterion places biphenylene close to the borderline of stability when in fact it is a particularly stable hydrocarbon with enhanced but not extraordinary reactivity[11]. In order to define a borderline value of E_R' (and E_R'') that more realistically reflects an isolatability criterion of stability it is necessary to find a less stable reference species.

Straub[12] has recently prepared a tetramethyl derivative of 1,2-diphenylbenzocyclobutadiene and isolated it as an unstable red solid. Dewar and Gleicher calculated the $-E_R'$ value of the parent unmethylated hydrocarbon to be 0.91 eV. This value of $-E_R'$ can be taken to represent the approximate upper limit of isolatability. From the correlation line developed above this value of $-E_R'$ corresponds to a value of $-E_R''$ of $0.26\,\beta$. On this basis it seems that a hydrocarbon such as I ($-E_R'' = 0.22$) might be barely capable of isolation**. The more reactive anthracene analog II ($-E_R'' = 0.29$) should be still more difficult. Cava[13] has recently reported the isolation of the 1,2-diphenyl derivative of II as a stable but reactive red hydrocarbon. Although this diphenyl derivative was not included in the Dewar-Gleicher study the

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* The lines drawn through the points are given

    by $-E_R'$ (monoaryl) $= -0.277 + 2.094\,(-E_R'') - 1.117\,(-E_R'')^2$

    and $-E_R'$ (diaryl) $= 0.790 + 3.727\,(-E_R'') - 3.523\,(-E_R'')^2$

** Some portion of the stability of Staub's hydrocarbon must be related to steric hindrance to dimerization offered by the phenyl groups. Hydrocarbon I, without added bulky groups like t-butyl, might still therefore prove too reactive to isolate. The question of planarity of the phenyls introduces further ambiguities.
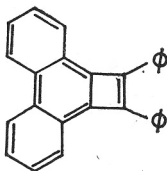
correlation reported here* suggests that it should have an $-E_R'$ value of about $+0.06$ and should be stable by their criterion. The highly reactive and non-isolatable hydrocarbon III[14] is estimated to have an $-E_R'$ value of about $+0.40$ eV ($-E_R'' = +0.42\,\beta$) and should be unstable by both the original Dewar-Gleicher and the present criteria.

I   II

III
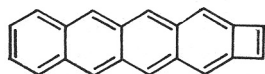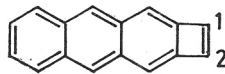
The pesimistic situation described above is entirely different when the restriction on 6-membered rings and chains is relaxed. For example, when cycloocta[def]biphenylene[15] is fused onto a cyclobutadiene to give IV, the calculated $-E_R''$ value is $+0.01\,\beta$ ($-E_R' = -0.27$ eV). This corresponds to an extremely stable compound by either the conservative criterion of Dewar and Gleicher or the risky one set forth here*. The difference, of course, of compounds such as IV lies with the presence of negative structures contributing to the algebraic structure count[10b] of the cycloocta[def]biphenylene. When fused to cyclobutadiene their destabilizing interaction is diminished.
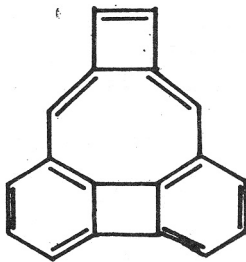

IV

Another example of the design potential of the present approach is to note that the ASC ratio in equation (3) can be transformed into a function of the fraction of double bond character in the fusion bonds of the parent aromatic residues. Thus if F_A represents the fraction of double bond character (i. e. Pauling bond order) in the fusion bond of residue A, and F_B the same quantity for residue B it is a straightforward matter to transform the ASC ratio of (3) to give

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* The *caveat* of footnote above applies to hydrocarbon III. The rearranged dimer of III, however, would be an extremely interesting products in itself.

$$\frac{(ASC)_{A-Y-B}}{(ASC)_A (ASC)_B} = \frac{(ASC)_A (ASC)_B [1 - F_A F_B]}{(ASC)_A (ASC)_B} = 1 - F_A F_B \qquad (4)$$

An interesting application of equation (4) is to molecules containing two aryl groups fused to the central cyclobutadiene ring. For such molecules application of the conservative Dewar-Gleicher criterion ($E_R' = 0.0$ eV) corresponds to an E_R'' value of about $-0.30\,\beta$ or a value of the expression in equation (4) of close to 0.75. It follows that any structure in which the product $F_A F_B \leq 0.25$ will be stable in the Dewar-Gleicher sense. For example, the Pauling bond order of the 2—3 bond of anthracene is $^1/_4$ so that any diaryl species in which one of the fused residues is anthracene, V, should be stable regardless of the nature of the other residue.
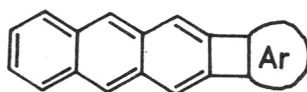
V

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SAŽETAK

Topološka definicija energije rezonancije

C. F. Wilcox, Jr.

Predložena je topološka definicija energije rezonancije koja se može linearno korelirati s definicijom Hessa i Schaada. Pokazano je da su izvedeni topološki parametri u korelaciji s rezultatima jednoga SCF π-elektronskog modela.

INSTITUT »RUĐER BOŠKOVIĆ«
41000 ZAGREB