Graph Theory and Molecular Orbitals. 19.[1] Nonparametric Resonance Energies of Arbitrary Conjugated Systems

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Abstract: The topological resonance energy, TRE, concept is introduced. TRE values depend solely on topology of a conjugated system and do not contain any additional parameters outside the MO method used (in the present work Hückel theory is employed). TRE values are reported for a number of conjugated hydrocarbons, heterocycles, conjugated ions, and radicals. Analysis shows that in the case of conjugated systems with Kekulé structures TRE's and Dewar resonance energies, DRE's, lead to identical predictions. However, TRE's are also obtained for conjugated ions and radicals giving a good agreement with experimental findings, while the DRE concept cannot be extended to charged species.

I. Introduction

The resonance energy, RE, concept is a traditional notion in the molecular orbital theory of conjugated molecules.[3] This concept has often been utilized for understanding and predicting aromatic stability of various conjugated structures.[3,4] Furthermore, it had a great impact on the preparative efforts of several generations of organic chemists interested in chemistry of conjugated compounds. However, a number of recent studies concerning the RE concept[5-19] indicates that there are certain difficulties and unsettled questions in its theoretical foundations.

RE is defined, in general, as the difference between the total π-electron energy, E_π, of a given conjugated molecule and of a corresponding hypothetical reference structure, respectively,

$$\mathrm{RE} = E_\pi \text{ (conjugated molecule)} - E_\pi \text{ (ref structure)} \quad (1)$$

Since the reference structure is, in general, a hypothetical and nonexisting entity, its choice is to some extent arbitrary. Thus, resonance energy defined in the classical way,[20] CRE, given by

$$\mathrm{CRE} = E_\pi - 2n_= \quad (2)$$

is based on a reference structure which contains $n_=$ isolated double bonds with π-electron energy of ethylene (2β). However, CRE criterion is shown to fail in many cases because rather unstable molecules are predicted to be aromatic on the grounds of their CRE values being large.[3,4,21] Thus, several attempts[22] have been made to redefine RE in order to obtain better agreement between theory and experiment. Dewar's suggestion[4,5,23] to use a reference structure that resembles an acyclic polyene and which has led to the introduction of the quantity called[24] "Dewar resonance energy", DRE, has proved[4,25] to be the most valuable one; the DRE values obtained from (3) (either in the framework of Dewar's variant[4] of the SCF π molecular orbital method[26] or within the HMO approximation) correlated well with experimental behavior of conjugated systems.[4,5,7,27-33]

$$\mathrm{DRE} = E_\pi - (n_=E_= + n_-E_-) \quad (3)$$

In eq 3 $n_=$ and n_- are the number of double and single bonds in a Kekulé structure of the considered π system while $E_=$ and E_- are parameters usually interpreted[34] as the π energies of "polyene" double and single bonds, respectively.

The fundamental idea in the Dewar concept (which has been also expressed by Breslow and Mohacsi,[35] but not further elaborated) is to substract from E_π of a conjugated molecule that energy part which corresponds to an acyclic polyene-like reference structure. Therefore in the proper approach to this problem, one has to devise such a parametrization scheme which should give zero (or nearly zero) DRE values for acyclic polyenes. Similarly, in such a parametrization scheme DRE must contain *all* cyclic contributions to E_π. DRE approaches of Dewar and Hess and Schaad fulfill the above requirements only approximately. In addition, we wish to point out here several other limitations which are in common to most DRE methods proposed in the literature:

(i) One has to use the *empirical* parameters for reference structure bond energies determined by (least-squares) fitting of numerical data.

(ii) The necessary number of parameters increases rapidly when heteroatoms are considered. Thus, for example, the parametrization scheme of Hess and Schaad requires eight parameters for hydrocarbons[7,31,36] but at least an additional seven for heteroconjugated systems containing only one kind of heteroatom at the time.

(iii) Because of the form of eq 3 DRE values can be calculated for molecules possessing Kekulé structures only. Therefore, radicals, ions, etc., are automatically excluded from DRE considerations. This is a serious failure of currently used DRE methods in the light of a recent interest in chemistry of conjugated ions and radicals.[37]

We are now able to offer a novel variant of the DRE method that is free from the above limitations and that has some additional interesting features. Our variant of DRE concept is a nonparametric one and is directly related to topology of the molecular π network. Thus, we wish to call it "topological resonance energy", TRE, and in the next section we will give a theoretical derivation of TRE.

II. Theory

The theory which will be exposed in this section may seem at first to be a rather abstract and complicated one. We wish to note, however, that it is just a consequent translation of the ideas originally proposed by Dewar[4] and Breslow[35] into the language and formalism of graph theory which is a branch of pure mathematics.[38] One can pose the question about the meaning of the notion "acyclic polyene-like reference structure". The exact mathematical formulation of such a notion will automatically result in a nonparametric variant of DRE, the advantages of which will be seen throughout the later discussion.

For the sake of simplicity, we will derive the full theory only for TRE's of conjugated hydrocarbons calculated within the framework of Hückel MO theory. In Appendix 1 it is indicated how the results obtained can be generalized to MO models different from HMO theory.

(1) Definitions. We follow the terminology of ref 39, where also the additional details about the applications of graphs[40] in the theory of conjugated compounds may be found. Note, however, that the use of the mathematical apparatus of graph theory is only a convenient way of formulating Hückel-type MO theories.[41]

Let G be the so called "molecular graph",[39] that is the graph representing the π-electron network of a conjugated system. Let its vertices be denoted as $v_1, v_2, \ldots, v_N$ and its edges $e_1, e_2, \ldots, e_\nu$. The adjacent matrix[40a] $\mathbf{A}$ of G is defined as

$$A_{ij} = \begin{cases} 1 \text{ if } v_i \text{ and } v_j \text{ are adjacent} \\ 0 \text{ otherwise} \end{cases} \tag{4}$$

Then the characteristic polynomial $P(G,x)$ of the graph G is

$$P(G,x) = \det(x\mathbf{I} - \mathbf{A}) = \sum_{j=0}^{N} a_j(G)x^{N-j} \tag{5}$$

with $\mathbf{I}$ being a unit matrix and $a_j(G)$ ($j = 0, 1, 2, \ldots, N$) the coefficients of $P(G,x)$. The roots of $P(G,x)$ form the spectrum of the graph G and the branch of mathematics investigating the relations between the structure of a graph and its spectrum is called the graph-spectral theory.[42] We denote the roots x_j of $P(G,x)$ in such a way that $x_1 \geqslant x_2 \geqslant \ldots \geqslant x_N$. Note that x_j's are necessarily real numbers.

The relations between the spectrum of the molecular graph and the HMO theory are well known.[39,43,44] Hence, the energy of the jth HMO is $E_j = \alpha + x_j\beta$ and, therefore, the total π-electron energy, E_π, is given by

$$E_\pi = \sum_{j=1}^{N} g_jE_j = N\alpha + \sum_{j=1}^{N} g_jx_j\beta \tag{6}$$

where g_j is the occupation number of the jth MO. Moreover,[45] Σg_jx_j can be replaced by $\Sigma|x_j|$ either exactly (e.g., for all alternant and the majority of nonalternant hydrocarbons) or as a satisfactory approximation (e.g., for the majority of heteroconjugated systems). One may take $\alpha = 0$ and $\beta = 1$, which results finally in

$$E_\pi = \sum_{j=1}^{N} g_jx_j \tag{7}$$

Coulson[46] has obtained an integral formula relating E_π with the characteristic polynomial

$$E_\pi = (1/\pi) \int_{-\infty}^{+\infty} \left[N - \frac{ixP'(G,ix)}{P(G,ix)}\right] \mathrm{d}x \tag{8}$$

which can be rewritten as

$$E_\pi = (1/\pi) \int_{-\infty}^{+\infty} \frac{\mathrm{d}x}{x^2} \ln |H(G,x)| \,\mathrm{d}x \tag{9}$$

where

$$H(G,x) = (-ix)^N P(G,-i/x) \tag{10}$$

A simple derivation of eq 8 and 9 is given in Appendix 2.

There is a theorem[44,47] in graph-spectral theory relating the coefficients a_j of the characteristic polynomial with the structure of the graph.[48] A Sachs graph of the graph G is a subgraph of G, the only components of which are cycles (of the size 3, 4, 5, . . .) and complete graphs of degree one.[52] Let $c(s)$ and $r(s)$ be the total number of components and the number of cyclic components, respectively, of the Sachs graph s. Let S_j be the set of all Sachs graphs with j vertices (of the molecular graph). Then, $a_0 = 1$ and

$$a_j = \sum_{s \in S_j} (-1)^{c(s)}2^{r(s)} \tag{11}$$

Equation 11, the Sachs theorem, has been presented in more detail and exemplified elsewhere.[39,44,53]

Let us introduce the following definitions. $n(s)$ is the number of vertices in the Sachs graph s. Then the set S of all Sachs graphs (of the molecular graph) and the sets S_{even} and S_{odd} of all Sachs graphs with even and odd number of vertices, respectively, are defined as

$$S = \bigcup_{j=0}^{N} S_j \tag{12a}$$

$$S_{\text{even}} = \{s \in S \,|\, n(s) = \text{even}\} \tag{12b}$$

$$S_{\text{odd}} = \{s \in S \,|\, n(s) = \text{odd}\} \tag{12c}$$

We call a Sachs graph s acyclic if $r(s) = 0$. Let the sets $S_j{}^{\text{ac}}$, S^{ac}, $S_{\text{even}}{}^{\text{ac}}$, and $S_{\text{odd}}{}^{\text{ac}}$ be the subsets of S_j, S, S_{even}, and S_{odd}, respectively, containing only acyclic Sachs graphs:

$$S_j{}^{\text{ac}} = \{s \in S_j \,|\, r(s) = 0\} \tag{12d}$$

$$S^{\text{ac}} = \{s \in S \,|\, r(s) = 0\} \tag{12e}$$

$$S_{\text{even}}{}^{\text{ac}} = \{s \in S_{\text{even}} \,|\, r(s) = 0\} \tag{12f}$$

$$S_{\text{odd}}{}^{\text{ac}} = \{s \in S_{\text{odd}} \,|\, r(s) = 0\} \tag{12g}$$

(2) Topological Analysis of E_π. The Sachs formula 11 gives the dependence of a_j's on the graph structure. The Coulson formulas 8 and 9 give the dependence of E_π on a_j's. Thus, by combining these formulas one gets insight into the dependence of E_π on the structure of the molecular graph or, in other words, on the molecular topology. This topological analysis of E_π turns out not to be simple.[54,55] Here we present only the details necessary for the later definition of TRE.

Substitution of eq 11 back into eq 5 with regard to (12a) produces

$$P(G,x) = \sum_{s \in S} (-1)^{c(s)}2^{r(s)}x^{N-n(s)} \tag{13}$$

Therefore, taking into account (12b) and (12c),

$$H(G,x) = \sum_{s \in S_{\text{even}}} (-1)^{n(s)/2+c(s)}2^{r(s)}x^{n(s)} - i \sum_{s \in S_{\text{odd}}} (-1)^{(n(s)-1)/2+c(s)}2^{r(s)}x^{n(s)} \tag{14}$$

which combined with eq 9 yields

$$E_\pi = (1/2\pi) \int_{-\infty}^{+\infty} \frac{\mathrm{d}x}{x^2} \times \ln \left\{ \left[\sum_{s \in S_{\text{even}}} (-1)^{n(s)/2+c(s)}2^{r(s)}x^{n(s)}\right]^2 + \left[\sum_{s \in S_{\text{odd}}} (-1)^{(n(s)-1)/2+c(s)}2^{r(s)}x^{n(s)}\right]^2 \right\} \tag{15}$$

Equation 15 may be interpreted as if every Sachs graph (of the molecular graph) contributes to E_π. On the other hand, every Sachs graph represents a distinct detail of the molecular topology. Therefore, the way in which every structural detail of a conjugated molecule affects the value of E_π is given by eq 15.

The above consideration enabled us to offer a simple mathematical formulation of a "acyclic polyene-like reference structure". Evidently, "acyclic polyene-like" means that all structural details of a molecule should be taken into account, except the presence of cycles. However, in all earlier variants of DRE the way to ignore the presence of cycles in polycyclic topologies in building the corresponding reference structure was not completely clarified and the offered solutions of the problem were on a semiempirical level. Within the Sachs graph formalism, the ignoring of cycles means simply the use of the set S^{ac} instead of S. Hence, from eq 15 we obtain the exact mathematical expression for the energy of the reference structure.

$$E_\pi \text{ (ref structure)} = (1/2\pi) \int_{-\infty}^{+\infty} \frac{\mathrm{d}x}{x^2} \times \ln \left\{ \left[\sum_{s \in S_{\mathrm{even}}{}^{\mathrm{ac}}} (-1)^{n(s)/2+c(s)} x^{n(s)} \right]^2 + \left[\sum_{s \in S_{\mathrm{odd}}{}^{\mathrm{ac}}} (-1)^{(n(s)-1)/2+c(s)} x^{n(s)} \right]^2 \right\} \quad (16)$$

By analogy to eq 14 it is convenient to define the polynomial H^{ac},

$$H^{\mathrm{ac}}(G,x) = \sum_{s \in S_{\mathrm{even}}{}^{\mathrm{ac}}} (-1)^{n(s)/2+c(s)} x^{n(s)} - i \sum_{s \in S_{\mathrm{odd}}{}^{\mathrm{ac}}} (-1)^{(n(s)-1)/2+c(s)} x^{n(s)} \quad (17)$$

By utilizing eq 17 the above expression for E_π (ref structure) becomes

$$E_\pi \text{ (ref structure)} = (1/\pi) \int_{-\infty}^{+\infty} \frac{\mathrm{d}x}{x^2} \ln |H^{\mathrm{ac}}(G,x)| \quad (18)$$

Substitution of the formulas 15 and 16 back into eq 1 yields an expression for the Dewar resonance energy. Since it is in fact a topological definition of DRE, we feel that the name *topological resonance energy,* TRE, is justified to be used. Thus,

$$\mathrm{TRE} = (1/\pi) \int_{-\infty}^{+\infty} \frac{\mathrm{d}x}{x^2} \ln \left| \frac{H(G,x)}{H^{\mathrm{ac}}(G,x)} \right| \quad (19)$$

It is to be expected that the numerical values of TRE's are close to DRE's obtained by Hess and Schaad using a semiempirical parametrization scheme. This is indeed the case as it will be demonstrated in a subsequent section.

As the actual application of eq 19 will not be required, we can omit further details concerning it.

(3) **The Acyclic Polynomial.** The calculation of TRE's by means of eq 19 is possible but for obvious reasons rather tedious. Fortunately, there exists a much easier procedure for the evaluation of TRE.

Let us define *the acyclic polynomial* $P^{\mathrm{ac}}(G,x)$ of the graph G in the following way,

$$H^{\mathrm{ac}}(G,x) = (-ix)^N P^{\mathrm{ac}}(G,-i/x) \quad (20)$$

This definition enables one to apply eq A2-12 from Appendix 2, and hence,

$$\mathrm{TRE} = (1/\pi) \int_{-\infty}^{+\infty} \ln \left| \frac{P(G,x)}{P^{\mathrm{ac}}(G,ix)} \right| \mathrm{d}x \quad (21)$$

In fact, there is a far-reaching analogy between P^{ac} and P. From eq 20 we simply obtain

$$P^{\mathrm{ac}}(G,x) = \sum_{s \in S^{\mathrm{ac}}} (-1)^{c(s)} x^{N-n(s)} \quad (22)$$

P^{ac} is a polynomial of degree N and one can write

$$P^{\mathrm{ac}}(G,x) = \sum_{j=0}^{N} a_j(G) x^{N-j} \quad (23)$$

which yields

$$a_j{}^{\mathrm{ac}}(G) = \sum_{s \in S_j{}^{\mathrm{ac}}} (-1)^{c(s)} \quad (24)$$

The comparison of eq 22 and 24 with eq 13 and 11 shows that there exists a full analogy between the characteristic polynomial and the acyclic polynomial of a graph. However, according to the definition of a Sachs graph, $S_j{}^{\mathrm{ac}}$ contains only complete graphs of degree one, the $j/2$ edges which are nonincident in G. Therefore,

$$a_j{}^{\mathrm{ac}}(G) = \begin{cases} (-1)^{j/2} b_{j/2}(G) & \text{if } j = \text{even} \\ 0 & \text{if } j = \text{odd} \end{cases} \quad (25)$$

Thus, we obtain an important relation for the acyclic polynomial,

$$P^{\mathrm{ac}}(G,x) = \sum_{j=0}^{N/2} (-1)^j b_j \quad (26)$$

Let e be an edge of the graph G, and G–e denotes the graph obtained by deletion of e from G. Similarly, G–(e) denotes the graph obtained by deletion of both vertices incident to e from G.

The following theorem about b_k's has been proved by Hosoya[56]

$$b_k(G) = b_k(G\text{-}e) + b_{k-1}(G\text{-}(e)) \quad (27)$$

Substitution of eq 27 into eq 26 leads to a recurrence relation for the acyclic polynomial,

$$P^{\mathrm{ac}}(G,x) = P^{\mathrm{ac}}(G\text{-}e,x) - P^{\mathrm{ac}}(G - (e),x) \quad (28)$$

In Appendix 3 it is demonstrated how the application of this formula makes possible evaluation of P^{ac}'s without difficulty.

Note that eq 28 is a generalization of the Heilbronner formula[57]

$$P(G,x) = P(G\text{-}e,x) - P(G\text{-}(e),x) \quad (29)$$

which is valid for acyclic polyenes only.

The analogy between P^{ac} and P can be extended even further. Suppose all roots $x_j{}^{\mathrm{ac}}$ ($j = 1, 2, \ldots, N$) of $P^{\mathrm{ac}}(G,x)$ are real.[58] Then the reasonings analogous to those in Appendix 2 show that

$$(1/\pi) \int_{-\infty}^{+\infty} \frac{\mathrm{d}x}{x^2} \ln |H^{\mathrm{ac}}(x)| = \sum_{j=1}^{N} |x_j{}^{\mathrm{ac}}| \quad (30)$$

from which the final TRE formula follows

$$\mathrm{TRE} = \sum_{j=1}^{N} g_j (x_j - x_j{}^{\mathrm{ac}}) \quad (31)$$

Thus, knowing the roots of the characteristic polynomial and the acyclic polynomial, one can calculate the TRE's for arbitrary conjugated systems. Depending on the occupation numbers, one can calculate TRE's for conjugated species with an arbitrary number of π electrons (any kind of radicals and ions). Ground and excited states could be equally treated by eq 31. It should be evident that the existence or not of Kekulé structures in the considered conjugated system is irrelevant for the application of eq 31.

Finally, this is the very place to emphasize that *no empirical parameter* is required in eq 31.

(4) **TRE's for Acyclic Polyenes.** It is now easy to show that if a conjugated system is acyclic, its TRE value is zero. Namely, for acyclic graphs, $S_j{}^{\mathrm{ac}} = S_j$, $S^{\mathrm{ac}} = S$, etc. Therefore, $H^{\mathrm{ac}}(G,x) \equiv H(G,x)$ and $P^{\mathrm{ac}}(G,x) \equiv P(G,x)$. Any of the formulas 19, 21, or 31 results simplify in the *theorem*

$$\mathrm{TRE \ (acyclic\ polyene)} = 0 \quad (32)$$

III. Results

Extensive tables of resonance energies of various homo- and heteroconjugated structures have been reported by Dewar and co-workers[4,5,27–29] (within the framework of the SCF π approximation) and by Hess and Schaad[7,31–33] (within the HMO approximation). Certain classes of conjugated molecules have also been studied by Herndon[10] (conjugated hydrocarbons) and by Aihara[12] (polyacenes). Results of Dewar were compared by Hess and Schaad with their REPE index and these parallel each other in most of the cases studied. Hence, we decided to compare our results with those reported by Hess and Schaad since we both are working with Hückel MO's. However, they have used a purely empirical eight-bond parameter scheme in order to approximate the reference structure. Their scheme has produced results which agree nicely with experimental facts.

TRE values are calculated[59] in a way described in section II using expression 31. x_j's corresponding to the characteristic polynomials associated with conjugated systems have been obtained either from the available HMO tables[60] or using a standard Hückel program. The roots of the acyclic polynomials related to particular conjugated molecules are obtained using a standard computer program. We have studied more than 400 diverse conjugated topologies.[61] Here we report only 135 examples, most of which are the classical ones. Structures of all studied molecules, conjugated hydrocarbons (45 examples), heteroconjugated molecules (45 examples), and conjugated radicals and ions (45 examples), are given in Figures 1-3.

We report TRE (per electron), TRE(PE), and Hess and Schaad REPE values of selected conjugated hydrocarbons (**1-45**) and heterocycles (**46-90**) in Tables I and II. Similarly, TRE(PE) values of selected conjugated radicals and ions (**91-135**) are given in Table III.

First, we have compared TRE(PE) and REPE indices of conjugated hydrocarbons and heteroconjugated molecules. A plot of TRE(PE) vs. REPE for 45 hydrocarbons is presented in Figure 4, and a similar plot for 45 heteroconjugated systems can be found in Figure 5. A least-squares fit for conjugated hydrocarbons gives

$$\text{TRE(PE)} = 1.068\text{REPE} - 0.0086 \qquad (33)$$

with the correlation coefficient 0.978. Similarly, for heteroconjugated molecules

$$\text{TRE(PE)} = 1.086\text{REPE} - 0.0054 \qquad (34)$$

with the correlation coefficient 0.968. This analysis shows that in most cases our results parallel REPE predictions. Hence, the TRE approach, though conceptually very different from REPE, has in practice the same predictivity power as the REPE index for neutral conjugated species. Thus, compounds with large TRE(PE) values (TRE(PE) $> 0.01\beta$) are predicted to be of high aromatic stability. Those TRE(PE) values which are close to zero should be nonaromatic ($-0.01\beta <$ TRE(PE) $< 0.01\beta$) and in their stability similar to acyclic polyenes. Finally, compounds with large negative TRE(PE) values (TRE(PE) $< -0.01\beta$) should be quite unstable and antiaromatic and, thus, very reactive.

The TRE method allows also the estimation of the aromatic stability of conjugated radicals and ions, a class of interesting and important compounds in chemistry of conjugated structures.[37,62] This is the advantage of TRE(PE) over REPE index.

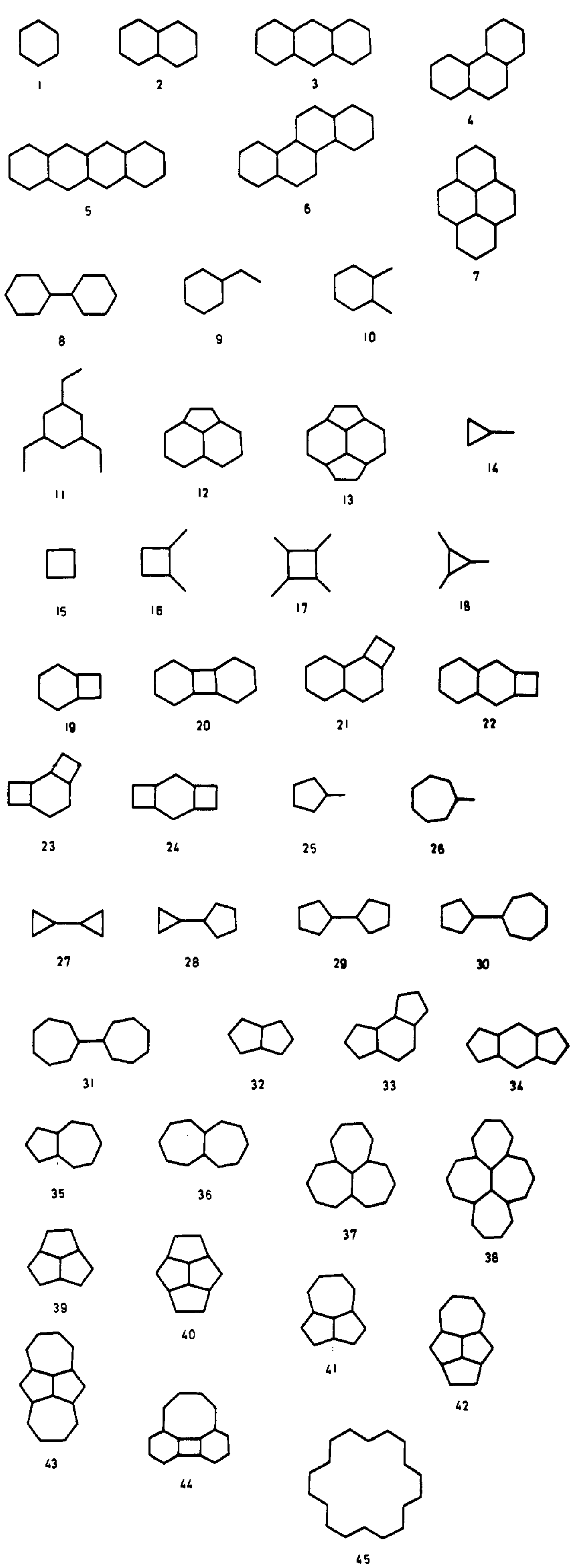


Figure 1. Conjugated hydrocarbons.

It is interesting to note that the first topological definition of resonance energy, proposed by Wilcox,[13] is to a certain extent arbitrary.[63] Wilcox wanted to introduce a resonance energy index which will be directly related to the molecular topology and thus has proposed the following expression for calculation of what we call here WRE ("Wilcox's resonance energy"),

$$\text{WRE} = a_1 \ln(\text{ASC}) + a_2 n_4 \qquad (35)$$

where ASC and n_4 are the algebraic structure count[64] and the number of four-membered rings of the molecule, respectively. The coefficients a_1 (0.445) and a_2 (-0.17) are obtained by a least-squares fitting to REPE values of 40 randomly selected alternant hydrocarbons. WRE has some advantages over REPE: (i) ASC and n_4 may be easily obtained from the molecular topology (they are simple topological parameters of a conjugated molecule) and (ii) by definition WRE (acyclic

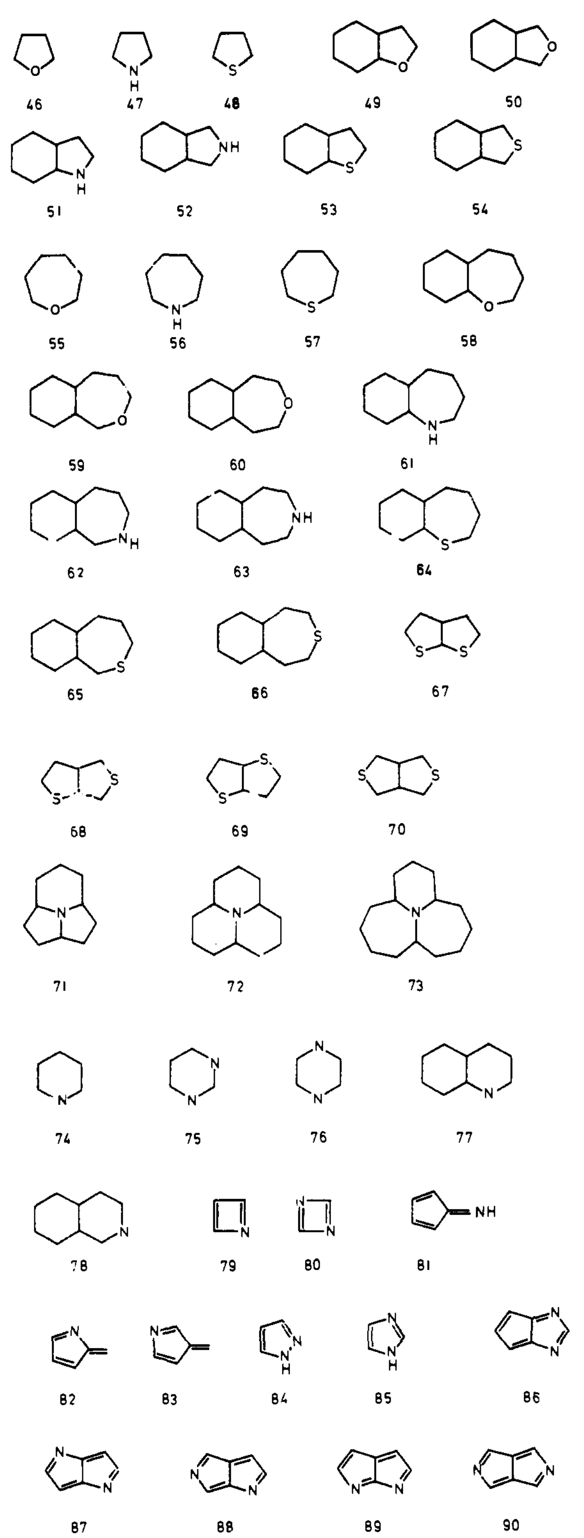


Figure 2. Heteroconjugated molecules.

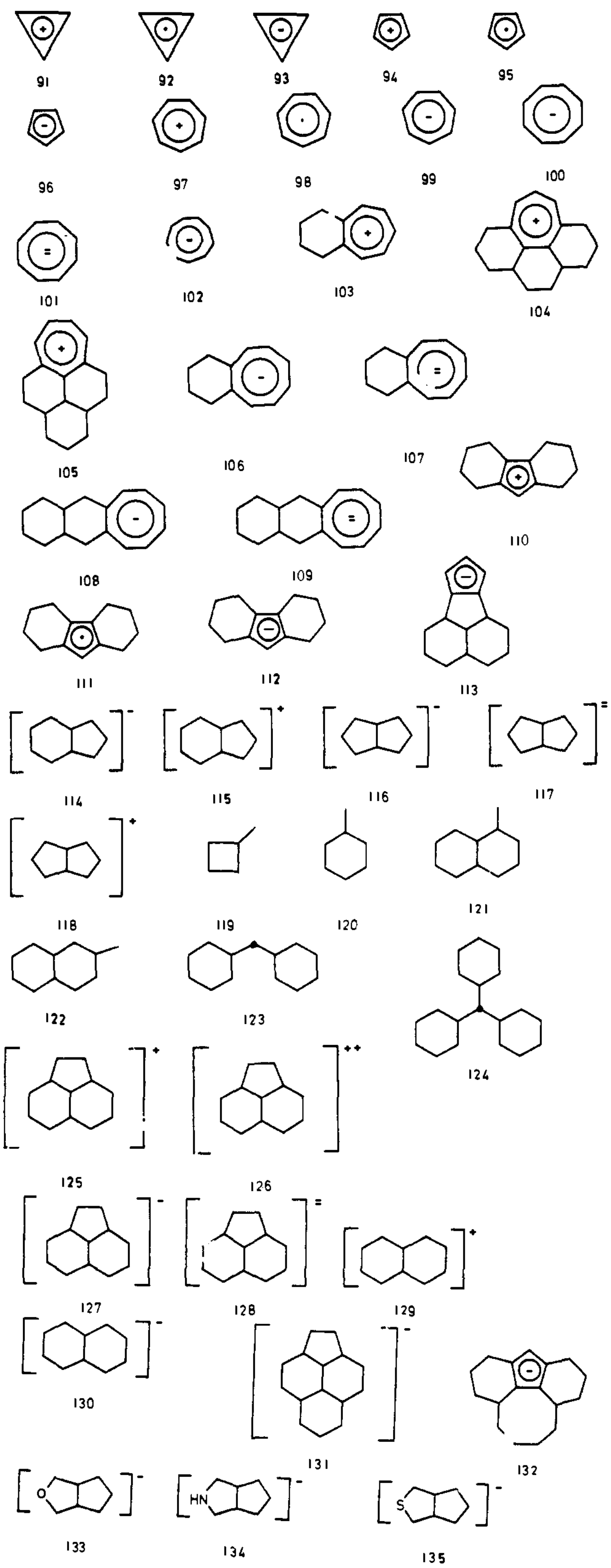


Figure 3. Conjugated radicals and ions.

polyene) = 0. However, it is not likely that all cyclic contributions to E_π are contained in WRE. Similarly, WRE does not work for radicals and ions. In addition, we point out that the final expressions for both DRE and WRE are obtained by a least-squares fitting of some coefficients using a selected set of conjugated molecules. TRE, in comparison with DRE and WRE, does not require fitting parameters and is mathematically defined in such a way that the energy of the TRE reference structure contains exactly *all* acyclic and *no* cyclic contributions to E_π(molecule), and finally, its application is not stipulated by the existence of Kekulé structures. Thus, *the topological resonance energy may be understood as the optimal nonempirical realization of the Dewar resonance energy concept, and not as a new definition of resonance energy.* In addition, the TRE values when calculated in the framework of Hückel theory depend *only* on the employed HMO parameters (α_x and β_{xy}). In the present work the heteroatom parameters (h and k) used are taken from Hess and Schaad.[32,33]

Table I. TRE(PE) and REPE Indices of Some Conjugated Hydrocarbons

Molecule	TRE(PE), β	REPE,[a] β	Status[b]	Ref to the preparative work	Molecule	TRE(PE), β	REPE,[a] β	Status[b]	Ref to the preparative work
1	0.046	0.065	i	*c*	**24**	−0.079	−0.060	u	*q*
2	0.039	0.055	i	*c*	**25**	0.003	−0.002	u	*r*
3	0.034	0.047	i	*c*	**26**	0.001	−0.002	u	*s*
4	0.039	0.055	i	*c*	**27**	−0.077	−0.100	-	
5	0.031	0.042	i	*c*	**28**	0.054	0.043	i	*t*
6	0.038	0.053	i	*c*	**29**	−0.030	−0.033	u	*u*
7	0.037	0.051	i	*c*	**30**	0.023	0.022	i	*v*
8	0.042	0.060	i	*c*	**31**	−0.016	−0.014	-	
9	0.031	0.046	i	*d*	**32**	−0.027	−0.018	u	*w*
10	0.007	0.005[e]	u	*f*	**33**	−0.025	−0.021	-	
11	0.017	0.027	i	*g*	**34**	0.005	0.009	u	*x*
12	0.030	0.039	i	*h*	**35**	0.015	0.023	i	*y*
13	0.009	0.019	u	*i*	**36**	−0.012	−0.004	u	*z*
14	0.016	0.005	u	*j*	**37**	−0.027	−0.019	-	
15	−0.307	−0.268	u	*k*	**38**	−0.018	−0.011	-	
16	−0.027	−0.028	u	*l*	**39**	−0.073	−0.036	-	
17	−0.009	−0.010	u	*m*	**40**	−0.045	−0.036	-	
18	0.002	−0.002	u	*n*	**41**	0.008	0.018	u	*aa*
19	−0.049	−0.027	u	*o*	**42**	−0.011	−0.002	-	
20	0.010	0.027	i	*k*	**43**	0.013	0.021	i	*bb*
21	−0.032	−0.012	-		**44**	−0.011	−0.014	u	*cc*
22	−0.010	0.007	u	*p*	**45**	0.005	0.012	i	*dd*
23	−0.032	−0.070	-						

[a] REPE values are taken from: B. A. Hess, Jr., and L. J. Schaad, *J. Am. Chem. Soc.*, **93,** 305, 2413 (1971); *J. Org. Chem.*, **36,** 3418 (1971). [b] i, isolated (either parent compound or its derivatives); u, unstable (either parent compound or its derivatives); -, unknown. [c] E. Clar, "Polycyclic Hydrocarbons", Academic Press, London, 1964. [d] A. Klages and A. Keil, *Ber.*, **36,** 1632 (1903). [e] REPE value of *o*-xylylene is taken from the work: G. J. Gleicher, D. D. Newkirk, and J. C. Arnold, *J. Am. Chem. Soc.*, **95,** 2526 (1973). [f] C. R. Flynn and J. Michl, *ibid.*, **95,** 5802 (1973). [g] V. A. Dombrovskij and L. A. Janovskaja, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 1886 (1975). [h] K. Dziewoński and G. Rapalski, *Ber.*, **45,** 2941 (1912). [i] B. M. Trost, G. M. Bright, C. Frihart, and D. Bertelli, *J. Am. Chem. Soc.*, **93,** 737 (1971). [j] M. Battiste, *ibid.*, **86,** 942 (1964). [k] M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds", Academic Press, New York, N.Y., 1967. [l] W. D. Huntsman and H. J. Wristers, *J. Am. Chem. Soc.*, **89,** 342 (1967). [m] G. W. Griffin and L. I. Peterson, *ibid.*, **85,** 2268 (1963). [n] G. Köbrich and H. Heinemann, *Angew. Chem.*, **77,** 590 (1965). [o] O. L. Chapman, C. C. Chang, and N. R. Rosenquist, *J. Am. Chem. Soc.*, **98,** 261 (1976). [p] M. P. Cava, B. Hwang, and P. J. VanMeter, *ibid.*, **85,** 4032 (1963). [q] F. Toda and M. Ohi, *J. Chem. Soc., Chem. Commun.*, 506 (1975). [r] J. Thiec and J. Wiemann, *Bull. Chem. Soc. Fr.*, 177 (1956). [s] W. von E. Doering, "Theoretical Organic Chemistry", Kekulé Symposium, 1958, p 35; R. B. Turner, W. von E. Doering, L. H. Knox, J. R. Mayer, and D. W. Wiley, *J. Am. Chem. Soc.*, **79,** 4127 (1957). [t] A. S. Kende, P. T. Izzo, and P. T. MacGregor, *ibid.*, **88,** 3359 (1966). [u] G. M. Badger, "Aromaticity", University Press, Cambridge, 1969, p 112. [v] E. K. von Gustorf, M. C. Henry, and P. V. Kennedy, *Angew. Chem., Int. Ed. Engl.*, **6,** 627 (1967). [w] R. Bloch, R. A. Marty, and P. de Mayo, *J. Am. Chem. Soc.*, **93,** 3072 (1971); K. Hafner, R. Donges, E. Goedecke, and R. Kaiser, *Angew. Chem., Int. Ed. Engl.*, **12,** 337 (1973). [x] K. Hafner, K. H. Häfner, C. König, M. Kreuder, G. Ploss, G. Schulz, E. Sturm, and K. H. Vöpel, *ibid.*, **2,** 123 (1963). [y] W. Keller-Schierlein and E. Heilbronner, "Non-Benzenoid Hydrocarbons", D. Ginsburg, Ed., Interscience, New York, N.Y., 1959, p 277. [z] H. J. Dauben and D. J. Bertelli, *J. Am. Chem. Soc.*, **83,** 4659 (1961). [aa] K. Hafner and J. Schneider, *Justus Liebigs Ann. Chem.*, **624,** 37 (1959). [bb] H. Reel and E. Vogel, *Angew. Chem.*, **84,** 1064 (1972). [cc] C. F. Wilcox, Jr., J. P. Uetrecht, and K. K. Grohmann, *J. Am. Chem. Soc.*, **94,** 2532 (1972). [dd] F. Sondheimer, *Pure Appl. Chem.*, **7,** 363 (1963).

IV. Discussion

Conjugated Hydrocarbons. Compounds **1–9, 11, 12, 20, 28, 30, 35,** and **43** are all predicted to have high values of TRE(PE) and they should be considered as stable atomatic molecules. Experimental results are in accord with this prediction. REPE values for these molecules are, in general, slightly lower than the corresponding TRE(PE) values. Nonaromatic compounds are predicted to be the following ones: **10, 18, 25, 26,** and **34.** Experimental data and REPE indices support this prediction. Finally, compounds **15–17, 19, 21–24, 27, 29, 31–33, 37–40,** and **44** have large negative values of TRE(PE) and thus they all should be antiaromatic and very reactive species. Available experimental data are in accord with this prediction. For example, recent preparation of benzocyclobutadiene (**19**) indicated that this molecule is extremely unstable.[65] Similarly, REPE indices parallel our results.

There are several cases (molecules **13, 14, 36, 41,** and **42**) in which TRE(PE) and REPE somewhat differ leading to incongruous predictions.

We predict pyracylene (**13**) to be nonaromatic (TRE(PE) = 0.009β) while the REPE index (0.019β) indicates this molecule is aromatic. The chemistry of pyracylene[66] appears to be in agreement with our prediction. Besides, some other theoretical studies[67] also indicated a nonaromatic stability of this molecule. In addition, pyracylene has one nonbonding MO in its HMO energy level diagram the existence of which per se is the indication of low stability. Methylcyclopropene (**14**) has a TRE(PE) value (0.016β) of an aromatic compound while the REPE value (0.005β) indicates this compound to be nonaromatic. Methylcyclopropene (**14**) is not known, but the diphenyl derivative is prepared[68] and is unstable unless carefully stored in a highly pure solid form. In addition, alkylmethylcyclopropene's are remarkably stable at 253 K but polymerize at room temperature and in the absence of solvent.[69] Therefore, it appears that methylcyclopropene could be considered borderline aromatic. However, some additional structural factors not taken into account by the TRE(PE) approach, but otherwise very important for the stability of small ring compounds (e.g., ring strain), may be grossly responsible for its instability.[68-70]

Heptalene (**36**) is predicted by us (TRE(PE) = −0.012β)

Table II. TRE(PE) and REPE Indices of Some Heteroconjugated Molecules

Molecules	TRE(PE), β	REPE,[a] β	Status[b]	Ref to the preparative work	Molecules	TRE(PE), β	REPE,[a] β	Status[b]	Ref to the preparative work
46	0.007	0.007	i	*c*	**68**	0.026	0.015	i	*s*
47	0.040	0.039	i	*d*	**69**	0.031	0.024	i	*r*
48	0.033	0.032	i	*e*	**70**	0.004		-	
49	0.027	0.036	i	*f*	**71**	0.033	0.040	i	*t*
50	0.011	0.002	u	*g*	**72**	0.010	0.001	u	*u*
51	0.038	0.047	i	*h*	**73**	−0.008	−0.003	-	
52	0.032	0.029	i	*i*	**74**	0.038	0.058	i	*v*
53	0.035	0.044	i	*j*	**75**	0.032	0.049	i	*w*
54	0.029	0.025	i	*k*	**76**	0.022	0.049	i	*x*
55	−0.004	−0.006	u	*l*	**77**	0.036	0.052	i	*y*
56	−0.029	−0.036	u	*m*	**78**	0.033	0.051	i	*z*
57	−0.023	−0.029	u	*cc*	**79**	−0.193	−0.160	-	
58	0.018	0.024	i	*n*	**80**	−0.136	−0.113	-	
59	0.003	−0.004	-		**81**	−0.033	−0.032	-	
60	0.017	0.026	i	*o*	**82**	0.008	0.008	-	
61	0.006	0.014	-		**83**	0.007	0.002	-	
62	−0.023	−0.024	-		**84**	0.047	0.055	i	*aa*
63	0.005	0.015	u	*n*	**85**	0.033	0.042	i	*bb*
64	0.022	0.016	i	*p*	**86**	−0.047	−0.037	-	
65	−0.018	−0.019	-		**87**	−0.041	−0.033	-	
66	0.008	0.017	u	*q*	**88**	−0.022	−0.016	-	
67	0.031	0.022	i	*r*	**89**	−0.042	−0.036	-	
					90	−0.008	−0.001	-	

[a] REPE values are taken from: B. A. Hess, Jr., L. J. Schaad, and C. W. Holyoke, Jr., *Tetrahedron,* **28** 3657 (1972); **31,** 295 (1975). [b] i, isolated (either parent compound or its derivatives); u, unstable (either parent compound or its derivatives); -, unknown. [c] R. C. Elderfield and T. N. Dodd, Jr., "Heterocyclic Compounds", Vol. 1, R. C. Elderfield, Ed., Wiley, New York, N.Y., 1950, p 277. [d] A. H. Corwin, "Heterocyclic Chemistry", R. C. Elderfield, Ed., Wiley, New York, N.Y., 1950, p 119. [e] H. D. Hartough, "Thiophene and Its Derivatives", Interscience, New York, N.Y., 1952. [f] A. Baeyer, *Justus Liebigs Ann. Chem.,* **140,** 295 (1866). [g] R. N. Warrener, *J. Am. Chem. Soc.,* **93,** 2346 (1971). [h] A. G. Perkin, *J. Chem. Soc.,* 368 (1870); 295 (1871). [i] R. Kreher and J. Seubert, *Z. Naturforsch.,* **20,** 15 (1965); L. A. Carpino and D. E. Barr, *J. Org. Chem.,* **31,** 764 (1966). [j] L. Gatterman and A. E. Lockhart, *Chem. Ber.,* **26,** 2808 (1893). [k] R. Mayer, H. Kleinert, S. Richter, and K. Gewald, *Angew. Chem.,* **74,** 118 (1962); M. P. Cava, N. M. Pollock, O. A. Mamer, and M. J. Mitchell, *J. Org. Chem.,* **36,** 3932 (1971). [l] G. Maier, *Angew. Chem., Int. Ed. Engl.,* **6,** 402 (1967). [m] A. Hafner, *Angew. Chem.,* **75,** 1041 (1963). [n] K. Dimroth and H. Frayschlag, *Chem. Ber.,* **89,** 2602 (1956); **90,** 1628 (1957); K. Dimroth and G. Pohl, *Angew. Chem.,* **73,** 436 (1961). [o] E. Vogel, M. Biskup, W. Pretzer, and W. Böll, *Angew. Chem., Int. Ed. Engl.,* **3,** 642 (1964); F. Sondheimer and A. Shani, *J. Am. Chem. Soc.,* **86,** 3168 (1964). [p] H. Hofmann, B. Meyer, and P. Hoffmann, *Angew. Chem., Int. Ed. Engl.,* **11,** 423 (1972); D. N. Reinhoudt and C. G. Kouwenhoven, *J. Chem. Soc., Chem. Commun.,* 1232 (1972). [q] V. J. Traynelis, "Heterocyclic Compounds", A. Rosowsky, Ed., Wiley, New York, N.Y., 1972, p 667. [r] S. Gronowitz, U. Rudén, and B. Gestblom, *Ark. Kemi,* **20,** 297 (1963). [s] H. Wynberg and D. J. Zwanenburg, *Tetrahedron Lett.,* 761 (1967). [t] R. J. Windgassen, Jr., W. H. Saunders, Jr., and V. Boekelheide, *J. Am. Chem. Soc.,* **81,** 1459 (1959). [u] D. Farquhar and D. Leaver, *Chem. Commun.,* **24** (1969). [v] W. Ramsay, *Philos. Mag.,* **2,** 269 (1876). [w] E. Frankland and H. Kolbe, *Justus Liebigs Ann. Chem.,* **65,** 269 (1848). [x] J. K. Dixon, U.S. Patent 2 414 522; *Chem. Abstr.,* **41,** 2756 (1974). [y] Z. H. Skraup, *Monatsh. Chem.,* **1,** 316 (1880). [z] A. Bischler and B. Napieralski, *Chem. Ber.,* **26,** 1903 (1893). [aa] E. Buchner, *ibid.,* **22,** 486 (1889). [bb] B. Radziszewski, *ibid.,* **15,** 2706 (1882). [cc] J. M. Hoffmann, Jr., and R. H. Schlessinger, *J. Am. Chem. Soc.,* **92,** 5203 (1970).

to be antiaromatic and by Hess and Schaad (REPE = −0.004β) to be nonaromatic. The experimental fact[71] is that heptalene is a very unstable molecule.

Aceazulylene (**41**) has a nonaromatic value of TRE(PE) (0.005β) and an aromatic value of REPE (0.018β). The parent compound is not known, but the dimethyl derivative is a moderately stable species.[72]

Pentalenoazulene (**42**) is also predicted by us (TRE(PE) = −0.011β) to be antiaromatic; REPE (−0.002β) however, indicates this molecule to be nonaromatic. Unfortunately, experimental data for this pentalenoazulene are not yet available.

We wish to point out here that in all discussed cases, i.e., **13, 14, 36, 41,** and **42,** the incongruency between TRE(PE) and REPE predictions was not very severe. The trend of both predictions was in the right direction and disagreement originated from the consideration of which should be the threshold value for aromatic, nonaromatic, and antiaromatic species.

Interesting results are reached for [18]annulene (**45**). TRE(PE) (0.005β) indicates smaller delocalization in the [18]annulene ring system than the REPE value (0.012β). Our prediction that [18]annulene is an acyclic polyene opposes currently accepted opinion[73] that this molecule is aromatic. However, [18]annulene fails to undergo electrophilic substitution reactions[74] (which is a property of classical aromatic substances) unless the reaction is carried out under special conditions.[75] Besides, a recent very thorough MINDO/3 study[76] on [18]annulene (its geometry has been calculated by minimizing the energy with respect to all 102 internal coordinates) indicated a very small π-electron delocalization in the [18]annulene ring.

Heteroconjugated Molecules. Compounds **47–49, 51–54, 58, 60, 64, 67–69, 71, 72, 74–78, 84,** and **85** are all predicted by both TRE(PE) and REPE indices to be aromatic while compounds **46, 55, 59, 73, 82, 83,** and **90** are predicted also by both indices to be nonaromatic. Abundant experimental evidence for compounds **47–49, 51–54, 58, 60, 64, 67–69, 71, 72, 74–78, 84,** and **85** is in agreement with the theoretical predictions. On the other hand, experimental data for the nonaromatic class of heterocycles studied here (i.e., **46, 55, 59, 73, 82, 83,** and **90**) are very limited.[77,78]

TRE(PE) and REPE correctly differentiated between furan (a nonaromatic molecule) and pyrrole and thiophene (aromatic molecules). While furan undergoes Diels–Alder reactions,[79] pyrrole and thiophene are rather inert in the Diels–Alder sense.[80,81]

Table III. TRE(PE) Indices of Some Conjugated Radicals and Ions

Molecule	TRE(PE), β	Status	Ref to the preparative work
91	0.268	Stable	*a*
92	−0.155	Unknown	
93	−0.366	Transient species	*ee*
94	−0.153	Transient intermediate (at −60 °C)	*b*
95	−0.049	Transient intermediate	*c*
96	0.094	Stable	*d*
97	0.032	Stable	*e*
98	−0.031	Short-lived species	*f*
99	−0.097	Transient intermediate (at −20 °C)	*g*
100	−0.023	Observed in solution	*h*
101	0.019	Stable in solution	*h*
102	0.018	Stable in an inert atmosphere	*i*
103	0.029	Stable	*j*
104	0.023	Stable	*k*
105	0.018	Stable	*l*
106	0.003	Unstable	*m*
107	0.014	Unstable	*n*
108	0.009	Unstable	*o*
109	0.011		
110	0.008		
111	0.022		
112	0.036	Sensitive to oxygen	*p*
113	0.026	Stable	*q*
114	0.040		
115	−0.025		
116	0.016		
117	0.046	Stable	*r*
118	0.016		
119	−0.081		
120	0.022	Stable	*s*
121	0.026	Stable	*t*
122	0.024	Stable	*u*
123	0.030	Stable in an inert atmosphere	*v*
124	0.033	Stable	*w*
125	−0.003		
126	−0.041		
127	−0.025		
128	0.021	Stable	*x*
129	−0.014	Unstable	*y*
130	−0.011	Unstable	*z*
131	0.014	Unstable	*aa*
132	−0.011	Unstable	*bb*
133	0.004	Unstable	*cc*
134	0.007		
135	0.003	Unstable	*dd*

[a] R. Breslow and J. T. Groves, *J. Am. Chem. Soc.*, **92,** 984 (1970). [b] K. Ziegler and B. Schnell, *Justus Liebigs Ann. Chem.*, **445,** 266 (1925). [c] B. A. Trash, *Nature (London)*, **178,** 155 (1956). [d] J. Thiele, *Ber. Dtsch. Chem. Ges.*, **33,** 660 (1900). [e] W. von Doering and L. H. Knox, *J. Am. Chem. Soc.*, **76,** 3203 (1954). [f] G. Vincow, M. L. Morrell, W. V. Volland, H. J. Dauben, and F. R. Hunter, *ibid.*, **87,** 3257 (1965). [g] H. J. Dauben and M. R. Rifi, *ibid.*, **85,** 3041 (1963). [h] T. J. Katz, *ibid.*, **82,** 3784, 3785 (1960). [i] E. A. LaLancette and R. E. Benson, *ibid.*, **85,** 2853 (1963); **87,** 1941 (1965). [j] G. Wittig and W. Reuther, *Justus Liebigs Ann. Chem.*, **765,** 47 (1972). [k] I. Murata, K. Yamamoto, Y. Kayane, and H. Ori, *Tetrahedron Lett.*, 131 (1975). [l] I. Murata, K. Yamamoto, and Y. Kayane, *Angew. Chem.*, **86,** 862 (1974). [m] L. B. Anderson and L. A. Paquette, *J. Am. Chem. Soc.*, **94,** 4915 (1972). [n] J. P. N. Brewer, H. Heaney, S. V. Ley, and T. J. Ward, *J. Chem. Soc., Perkin Trans. 1*, 2688 (1974). [o] G. R. Stevenson, M. Colon, I. Ocasio, J. G. Concepcion, and A. McB. Block, *J. Phys. Chem.*, **79,** 1685 (1975). [p] H. Staudinger, A. Gaule, and J. Siegwart, *Helv. Chim. Acta*, **4,** 212 (1921). [q] K. Yamamoto, M. Morioka, and I. Murata, *Tetrahedron Lett.*, 3009 (1975). [r] T. J. Katz and M. Rosenberger, *J. Am. Chem. Soc.*, **84,** 865 (1962). [s] J. A. Grace and M. C. R. Symons, *J. Chem. Soc.*, 958 (1959). [t] A. G. Harrison and F. P. Lossing, *J. Am. Chem. Soc.*, **82,** 1052 (1960). [u] N. Buu-Hoi, *Justus Liebigs Ann. Chem.*, **556,** 18 (1944). [v] J. Holmes and R. Pettit, *J. Org. Chem.*, **28,** 1695 (1963). [w] T. L. Chu and S. I. Weissman, *J. Chem. Phys.*, **22,** 21 (1954). [x] T. S. Cantrell, *Tetrahedron Lett.*, 1803 (1973). [y] W. Ij. Aalbersbeg, G. J. Hoijtink, E. L. Mackor, and W. P. Weijland, *J. Chem. Soc.*, 3049 (1959). [z] P. Balk, G. J. Hoijtink, and J. W. H. Schreus, *Recl. Trav. Chim. Pays-Bas.*, **76,** 813 (1957). [aa] I. Murata, K. Yamamoto, M. Morioka, and T. Hirotsu, *Tetrahedron Lett.*, 2287 (1975). [bb] I. Willner and M. Rabinovitz, *Tetrahedron Lett.*, 1223 (1976). [cc] T. S. Cantrell and B. L. Harrison, *ibid.*, 1299 (1969). [dd] T. S. Cantrell and B. L. Harrison, *ibid.*, 4477 (1967). [ee] R. Breslow and M. Battiste, *Chem. Ind. (London)*, 1143 (1958).

Compounds **56, 57, 62, 65, 79–81,** and **86–89** are predicted by both TRE(PE) and REPE to be antiaromatic, reactive species. All these compounds, except azepine (**56**) and thiepin (**57**), are virtually unknown. This only confirms the theoretical result that they should be very poor candidates for synthesis. However, N derivatives of azepine are known but are very reactive species.[84] Interest in azepine itself and its derivatives is greatly stimulated by their potential pharmacological properties.[85] Thiepin (**57**) is not prepared as yet, but the thiepin nucleus has appeared in the annelated thiepins, e.g., the furanothiepin derivatives.[86] Thus, as in the case of five-membered heterocycles containing σ-bivalent atoms (e.g., Ö, N̈H, S̈), we have correctly differentiated between seven-membered heterocycles containing either Ö, N̈H, or S̈. In this case, however,

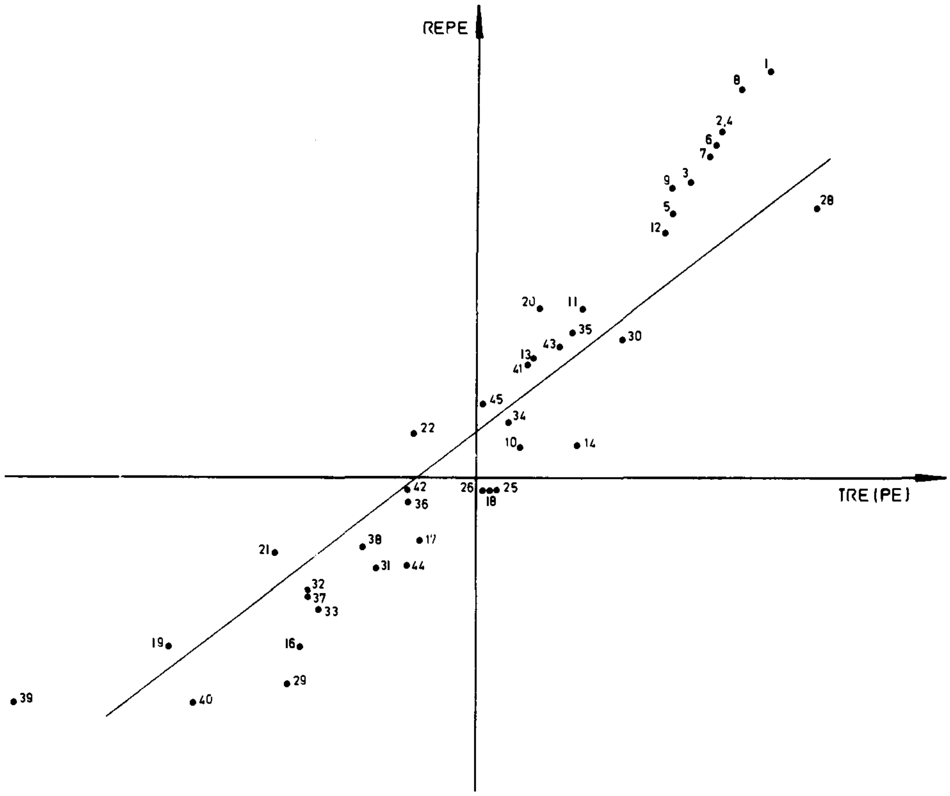


Figure 4. A plot of TRE(PE) vs. REPE for studied conjugated hydrocarbons; the line is representing a linear least-squares fit.

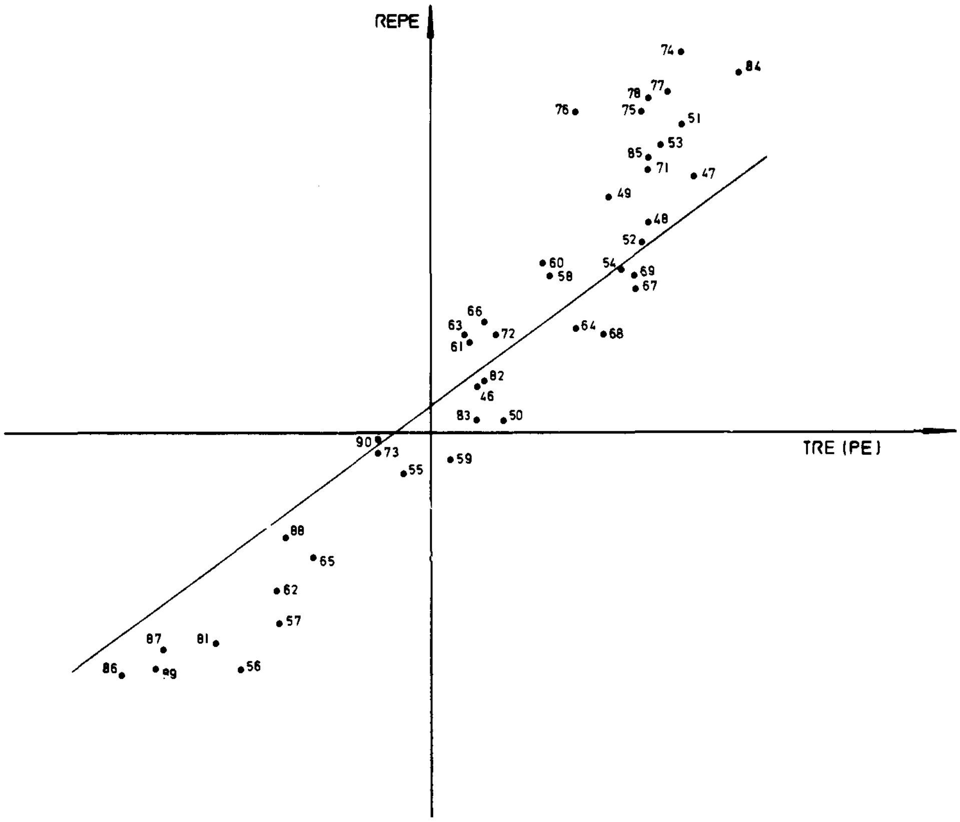


Figure 5. A plot of TRE(PE) vs. REPE for studied heterocycles; the line is representing a linear least-squares fit.

an oxygen-containing ring, i.e., oxepin, is a somewhat stabler species[86] than either N-containing ring (azepine) or S-containing ring (thiepin).[84,87,88]

For several heterocycle compounds (i.e., **50, 61, 63,** and **66**) TRE(PE) and REPE values differ somewhat. Thus, isobenzofuran (**50**) certainly behaves like a nonaromatic species.[89] In this case the TRE(PE) value is a little too high (0.011β). REPE (0.002β) correctly indicates isobenzofuran as a nonaromatic molecule. On the other hand, in the case of benzo[*a*]azepin (**61**), benzo[*c*]azepin (**63**), and benzo[*c*]thiepin

(**66**), it seems that REPE values are a bit too high. Benzo[*a*]-azepin is still unknown, but it should be similar in its properties and stability to benzo[*c*]azepin which is apparently a rather unstable species.[90] Some derivatives of benzo[*c*]thiepin are known.[88] For example, benzo[*c*]thiepin-2,4-dicarboxylic acid is prepared,[91] but it appears to be unstable losing sulfur upon standing or more rapidly when heated in solution to form naphthalene-2,3-dicarboxylic acid.

We wish to point out that a rather disappointing result was reached for 2,5-thiophthene (**70**). The TRE(PE) value (0.004β) predicts this molecule to be nonaromatic. However, the experimental fact is that 2,5-thiophthene is observed only as a transient species and a very reactive intermediate.[92] This case may be considered as one of the very few where the TRE(PE) value has failed to give even a tolerable prediction. However, it is clear that the correctness of our predictions to a great extent depends on the HMO heteroatomic parametrization scheme which is certainly not fitted for nonclassical heterocyclic compounds containing σ-bivalent heteroatoms.

Finally, we wish to discuss cycloazines (**71**, **72**, and **73**), since there is a continuous interest in their preparation.[93] Cyclo[3.2.2]azine (**71**), cyclo[3.3.3]azine (**72**), and cyclo-[4.4.3]azine (**73**) are predicted by both TRE(PE) and REPE indices to be of different stabilities, stability order being 71 > 72 > 73. Cyclo[3.2.2]azine is predicted to be aromatic, while the other two compounds are predicted to be nonaromatic, cyclo[4.4.3]azine being the less stable of the two. Experimental evidence is in accord with this prediction. Cyclo[3.2.2]azine prepared some years ago[94] has been found stable and aromatic. Cyclo[3.3.3]azine has, on the other hand, only recently been synthesized[93] and is a rather reactive compound. There is no evidence about the preparation of cyclo[4.4.3]azine or its derivatives.

Conjugated Radicals and Ions. Chemistry of conjugated radicals and ions has flourished in the last decade[37,95] with the improvement of the preparative techniques.[96] We have studied here a selected set of conjugated radicals and ions.

TRE(PE) predictions for monocyclic ring systems C_m ($m = 3, 5, 7, 8, 9$) are in agreement with the Hückel $4n + 2$ π-electron rule.[97] Thus, cyclopropenyl cation, $C_3H_3^+$ (**91**), cyclopentadienyl anion, $C_5H_5^-$ (**96**), tropylium cation, $C_7H_7^+$ (**97**), cyclooctatetraenyl dianion, $C_8H_8^{2-}$ (**101**), and cyclononatetraenyl anion, $C_9H_9^-$ (**102**), are predicted to be aromatic ions. Experimental evidence is in excellent agreement with this prediction. Thus, for example, cyclopropenium hexachloroantimonate,[98] sodium cyclopentadienide,[99] tropylium bromide,[100] dipotassium cyclooctatetraenide,[101] and potassium cyclononatetraenide[102] are all crystalline solids which in solution produce stable ions.

Cyclopropyl radical **92** and anion **93** are predicted to be antiaromatic and reactive species. The predicted stability of cyclopropenyls, $C_3H_3^+ > C_3H_3\cdot > C_3H_3^-$, is fully in agreement with experimental observations. Similarly, the following predicted stability orders, $C_5H_5^- > C_5H_5\cdot > C_5H_5^+$, $C_7H_7^+ > C_7H_7\cdot > C_7H_7^-$, and $C_8H_8^{2-} > C_8H_8^- > C_8H_8$, are in agreement with experimental facts.[95]

Some others results are also interesting to mention. Pentalene anion (**116**), dianion (**117**), and cation (**118**) are all predicted to be more stable than the parent compound. However, only the dianion (**117**) which is quite stable in solution[103] has been prepared.

Acenaphthylene cations and anions are interesting (**125**–**128**). The following prediction concerning the stability order of these species is reached: parent compound **12** > **128** > **125** > **127** > **126**. Besides acenaphthylene only acenaphthylenyl dianion which is predicted to be aromatic is known.[104]

Aromatic hydrocarbons are both capable of donating and of accepting electrons, the products being cation radicals and anion radicals, respectively. Thus, naphthalene cation **129** and radical **130** which can be prepared chemically[105,106] or electrochemically[107,108] are rather sensitive to air. We predict both species considerably less stable than the parent compound and antiaromatic.

Recently reported[109] cycloocta[*def*]fluorenyl anion (**132**) behaves as an antiaromatic species. This supports nicely our result, TRE(PE) (-0.011β) being of an antiaromatic species.

2-Oxa-(**133**), 2-aza- (**134**), and 2-thiapentalenyl (**135**) anions are compounds which belong to the little known class of oxygen-, nitrogen-, and sulfur-containing polycyclic anions. These compounds are thought of as having a cyclic π-electron perimeter. If this is a $(4n + 2)$ π perimeter the corresponding compounds may be good candidates for synthesis. TRE(PE) values, however, indicate all three compounds are nonaromatic. Cantrell and Harrison succeeded to prepare derivatives of 2-oxa- and 2-thiapentalenyl anions.[110] Thus, 1,3-dimethyl-2-oxapentalenyl anion could be stored at 253 K for short periods but disintegrates rapidly above 273 K. Similarly, 1,3-dimethyl-2-thiapentalenyl anion is also unstable though as a lithium salt it could be kept in the appropriate solvent (THF) at 253 K.

Finally, we point out that in all studied cases for which there were experimental data available it has achieved agreement between theory and experiment. This leads to the conclusion that the TRE(PE) index may be used as a powerful theoretical index for predicting aromatic behavior of conjugated radicals and ions.

V. Concluding Remarks

A novel nonempirical variant of the Dewar resonance energy concept, named topological resonance energy, is introduced and applied to a number of conjugated structures. In essence, TRE is the result of the translation of Dewar's definition of the reference structure in the formalism of graph theory. Analysis shows that the TRE index parallels REPE in predicting the chemical behavior of a large number of neutral conjugated systems. However, TRE may be used for studying conjugated radicals and ions without any further adjustment of the theory. Furthermore, it appears that TRE can also be used for studying the aromatic properties[111] of excited states. Thus, we are currently investigating the application of our method to triplet states of hydrocarbons.

Addendum

During the time this paper was being reviewed by editors and referees of this journal and revised by us, a paper by J. Aihara appeared (*J. Am. Chem. Soc.*, **98,** 2750 (1976)), reporting an essentially identical idea. The definitions of "reference polynomial" and "A-II resonance energy" in Aihara's terminology are algebraically fully equivalent to our "acyclic polynomial" and "TRE", respectively. A comparison between the two works shows, fortunately, that the achieved final results were obtained using completely different lines of reasoning.

Appendix 1

Let us consider a quantum-mechanical system Σ, the Hamiltonian operator of which is $\hat{h}$. Let us expand the wave function of Σ in an N-dimensional basis $|j\rangle$ ($j = 1, \ldots N$). Then the Hamiltonian matrix of Σ is $\mathbf{H} = ||\langle i|\hat{h}|j\rangle||$. Without the loss of generality of our consideration, we can assume that the basis set is orthonormal. Hence, the secular polynomial is equal to the characteristic polynomial $P(G,x)$ of the matrix **H**:

$$P(H,x) = \det(x\mathbf{I} - \mathbf{H}) \qquad \text{(A1-1)}$$

Besides, the energy levels of Σ are the roots of $P(H,x)$, that is they form the spectrum of the matrix **H**.

For brevity denote the matrix $x\mathbf{I} - \mathbf{H}$ by $\mathbf{K} = ||K_{ij}||$. Then according to the definition of a determinant

$$P(H,x) = \det\mathbf{K} = \sum_p \sigma(p)K_p \qquad \text{(A1-2)}$$

with

$$K_p = K_{1i_1}K_{2i_2}\ldots K_{Ni_N} \qquad \text{(A1-3)}$$

where $(i_1, i_2, \ldots, i_N)$ is a permutation p of the numbers $(1, 2, \ldots, N)$, $\sigma(p)$ being its parity, and the summation goes over all $N!$ different permutations.

Any term $K_p = K_{1i_1}K_{2i_2}\ldots K_{Ni_N}$ in eq A1-2 is completely determined by the permutation p or what is the same by the set Π_p of N ordered pairs: $\Pi_p = \{(1,i_1), (2,i_2), \ldots, (N,i_N)\}$. We call the term K_p *acyclic* if $(a,b) \in \Pi_p$ implied $(b,a) \in \Pi_p$. If, however, in the set Π_p there exists an element (a,b) such that $(b,a) \overline{\in} \Pi_p$ we call K_p a *cyclic* term. This division of the permutations into acyclic and cyclic is completely consistent with the concept of acyclic and cyclic Sachs graphs. Namely, a one-to-one correspondence exists between Sachs graph and a permutation.[112]

The neglecting of cyclic terms in (A1-2) can be formally achieved by defining a function Ω_p such that

$$\Omega_p = \begin{cases} 1 \text{ if } K_p \text{ is acyclic} \\ 0 \text{ if } K_p \text{ is cyclic} \end{cases} \qquad \text{(A1-4)}$$

Then the acyclic polynomial of the matrix $\mathbf{H}$ is given by

$$P^{\text{ac}}(H,x) = \sum_p \sigma(p)\,\Omega_p K_p \qquad \text{(A1-5)}$$

In other words, the acyclic polynomial (of a matrix) is obtained from the characteristic polynomial (of this matrix) by neglecting all cyclic terms in the corresponding determinant. Since for $\Pi_p = \{(1,1), (2,2), \ldots, (N,N)\}$ K_p is acyclic, $P^{\text{ac}}(H,x)$ is a polynomial of the variable x of degree N.

It can be shown that eq A1-5 reduces to the acyclic polynomial of a graph if $\mathrm{H} = \mathrm{A}$ = adjacency matrix. Hence, eq A1-5 is the general algebraic formulation of the problem discussed in the present paper. Obviously this equation applies to arbitrary MO models and is, moreover, not restricted to conjugated systems only. However, only in the case of Hückel-type models, where a one-to-one correspondence exists between a basis vector $|j\rangle$ and a conjugated center, is the meaning of $P^{\text{ac}}(H,x)$ evident. In this case, namely, exactly those contributions to the secular equation are neglected which can be associated with the existence of cycles of the molecular network.

In particular, eq A1-5 enables one to calculate the acyclic polynomials for heteroconjugated molecules, which even in the HMO model cannot be represented by simple graphs. Some necessary details of these calculations are given in Appendix 3.

Appendix 2

The integral formulas necessary for the present discussions are derived in this appendix in an elementary way. Many years ago Coulson[46,113] obtained equivalent results using contour integration of complex functions and the theory of residua. For brevity we denote $(1/\pi)\int_{-\infty}^{+\infty} F(x)\,dx$ by $\langle F(x)\rangle$. Then

$$I_1 = \langle t^2(t^2 + x^2)^{-1}\rangle = |t| \qquad \text{(A2-1)}$$

$$I_2 = \langle tx(t^2 + x^2)^{-1}\rangle = 0 \qquad \text{(A2-2)}$$

Both integrals I_1 and I_2 can be easily calculated by elementary methods. Now, $|t| = I_1 + iI_2$, which gives

$$|t| = \left\langle 1 - \frac{ix}{ix - t}\right\rangle \qquad \text{(A2-3)}$$

and since for any polynomial $P(x)$, the roots of which are $x_1, x_2, \ldots, x_N$,

$$P'(x)/P(x) = \sum_{j=1}^{N} (x - x_j)^{-1} \qquad \text{(A2-4)}$$

we have identity

$$\sum_{j=1}^{N} |x_j| = \left\langle N - ix\frac{P'(ix)}{P(ix)}\right\rangle \qquad \text{(A2-5)}$$

The Coulson integral formula[46] 8 for E_π follows now immediately from relation 7 [(8) ≡ (A2-6)]

$$E_\pi = \left\langle N - ix\frac{P'(G,ix)}{P(G,ix)}\right\rangle \qquad \text{(A2-6)}$$

Another form of this formula is obtained after the substitution $x' = 1/x$ and performing partial integration,

$$E_\pi = \langle x^{-2}\ln H(G,x)\rangle \qquad \text{(A2-7)}$$

where the identity

$$\frac{1}{x}\frac{H'}{H}\,\mathrm{dx} = \frac{\ln H}{x^2}\,\mathrm{d}x + \mathrm{d}\left(\frac{\ln H}{x}\right) \qquad \text{(A2-8)}$$

was used together with the fact that $\ln H/x \to 0$ for $x \to -\infty$, 0, $+\infty$. Finally, since E_π is a real number, eq 9 follows straightforwardly from (A2-8).

Formula A2-6 can be written also in the form

$$E_\pi = \left\langle N - x\frac{\mathrm{d}}{\mathrm{d}x}\ln P(G,ix)\right\rangle \qquad \text{(A2-9)}$$

Hence, if the graphs G and G_1 have an equal number N of vertices,

$$E_\pi(G) - E_\pi(G_1) = -\left\langle x\frac{\mathrm{d}}{\mathrm{d}x}\ln\frac{P(G,ix)}{P(G_1,ix)}\right\rangle \qquad \text{(A2-10)}$$

Partial integration gives

$$E_\pi(G) - E_\pi(G_1) = \left\langle \ln\frac{P(G,ix)}{P(G_1,ix)}\right\rangle \qquad \text{(A2-11)}$$

or finally

$$E_\pi(G) - E_\pi(G_1) = \left\langle \ln\left|\frac{P(G,ix)}{P(G_1,ix)}\right|\right\rangle \qquad \text{(A2-12)}$$

If we set $P(G_1,x) = P^{\text{ac}}(G,x)$, we obtain integral expression 21 for TRE.

Appendix 3

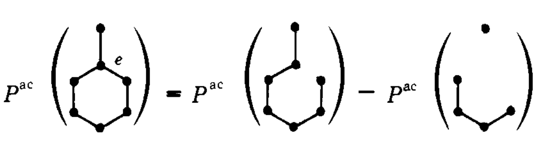
The evaluation of the acyclic polynomial, P^{ac}, is the crucial step in the computation of TRE. We describe and exemplify here a graphical procedure for the determination of P^{ac}'s both for simple graphs (which represent conjugated hydrocarbons) and for weighted graphs (which represent heteroconjugated systems).

(A) Calculation of P^{ac} for Graphs. In order to apply the recurrence relation 28, remember that for acyclic graphs the acyclic and the characteristic polynomials are mutually equal. Hence, by suitable choices of edges e in formula 28, P^{ac} can be expressed in terms of the characteristic polynomials of paths.[114] For brevity we shall denote the characteristic (and acyclic) polynomial of linear graphs by L_n. Then from eq 29,

$$L_n = xL_{n-1} - L_{n-2} \qquad \text{(A3-1)}$$

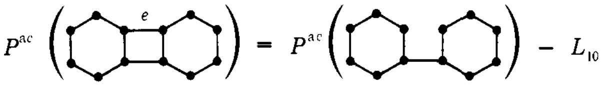
which enables the easy calculation of L_n's starting with $L_0 = 1$ and $L_1 = x$. Moreover, these polynomials are tabulated in ref 57.

For example, we calculate the acyclic polynomial of benzyl:



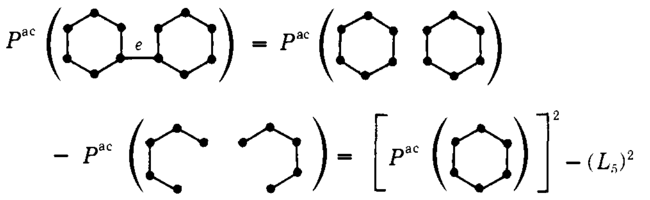
$$= L_7 - L_1L_4 = x^7 - 7x^5 + 13x^3 - 5x$$

As another example, let us evaluate the acyclic polynomial of biphenylene:



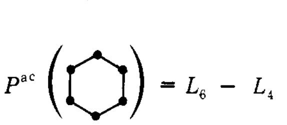
$$- L_{10}$$

The acyclic polynomial of biphenyl can be reduced analogously:



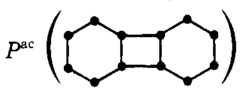
$$-(L_5)^2$$

Since



$$= L_6 - L_4$$

we obtain finally



$$= (L_6 - L_4)^2 - (L_5)^2 - L_{10}$$

$$= x^{12} - 14x^{10} + 71x^8 - 162x^6 + 164x^4 - 60x^2 + 5$$

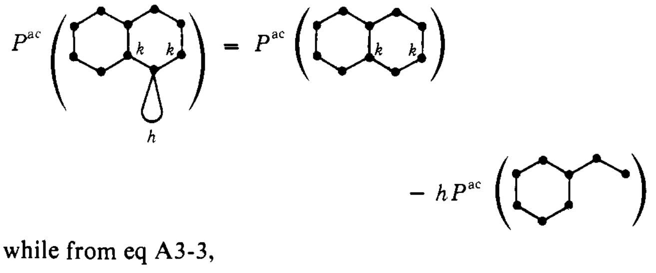
(B) Calculation of P^{ac} for Weighted Graphs. In the graph-theoretical representation of conjugated molecules, a heteroatom is presented by a loop of the weight h attached to the vertex corresponding to the heteroatom.[115,116] Let us consider a graph G_h with a loop of the weight h attached to the vertex v. G_h may contain also other loops or weighted edges. Let G and G-v be obtained from G_h by deleting the loop at the vertex v and by deleting the vertex v, respectively. Then,

$$P^{ac}(G_h,x) = P^{ac}(G,x) - hP^{ac}(G-v,x) \qquad \text{(A3-2)}$$

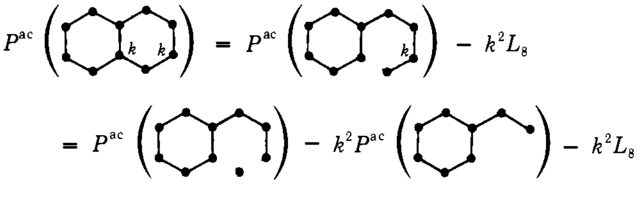
Let G_k be a graph with an edge e of the weight k. G_k may also contain other weighted edges and loops, except that the two vertices incident to e must not possess loops. Then,

$$P^{ac}(G_k,x) = P^{ac}(G-e,x) - k^2P^{ac}(G-(e),x) \qquad \text{(A3-3)}$$

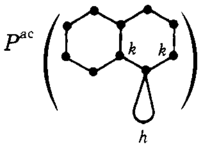
Relations A3-2 and A3-3 present a relatively simple procedure for the calculation of P^{ac}'s for graphs of heteroconjugated systems. As an illustration the graph of a quinoline-like molecule may serve. Application of (A3-2) gives



while from eq A3-3,



Hence, the problem is reduced to obtaining P^{ac}'s of simple graphs. Finally,



$$= L_1L_9 - L_1L_3L_4 - k^2(2L_8 - L_2L_4) - h(L_9 - L_3L_4)$$

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