

TOPOLOGICAL RESONANCE ENERGY APPROACH TO HOMOAROMATICITY

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Abstract - The notion of nonclassical structures resulting from through-space interactions has been approached from a topological resonance energy point of view. The phenomenon of homoaromaticity has been simplified to competitive tendencies of aromatic stabilization and minimal-strain conformation. The formation of a polygon-like pattern by through-space interactions among disjoint intramolecular fragments has been recognized as the essential stage in the course of aromatic stabilization/destabilization. Introduction of the original combinatorial-topological manipulations enabled the use of first order perturbation treatment. This constructed procedure was used in calculating the intrinsic topological contribution due to closing polygonal patterns gemane to most homoaromatic systems.

INTRODUCTION

Homoaromaticity is generally considered to be related to the phenomenon of through-space interaction. Such interactions are those between molecular fragments that are not directly bonded. The prerequisites are propinquity of interacting fragments, conformable symmetry of interacting orbitals and compatible energy ranges of interacting orbitals. Such interactions can occur mostly between i) an ethylenic fragment and a positively charged carbon center at the β position (Ref. 1), ii) an ethylenic fragment and small rings, particularly that of trigonal topology (Ref. 2), and iii) ethylenic fragments (Ref. 3). This variability of situations has led to some argumentation on the orbital character of the through-space interactions in terms of σ -, π -orbitals separability (Refs. 4 & 5). If we consider aromaticity as a common name for cumulative physical effects that are experienced by species possessing a system of conjugated carbon-carbon π -bonds, homoaromaticity is then usually referring to those effects that are experienced by species possessing adjacent nonconjugated carbon-carbon π -bonds. Because of the primacy of effects characterizing conjugated systems some people tend to refer to analogous effects that appear in systems without strict conjugation as second-order effects. Such would be effects in the tricyclo/5.2.1.0^{4,10}/deca-2,5,8-triene, (1), for instance, by allowing for a possibility of through-space interactions among the three ethylenic fragments. In employing the rigorous approach of MO formalism to this system, one has to solve the secular equation, $\det(\hat{F}_{\kappa\mu} - E\hat{S}_{\kappa\mu}) = 0$, which requires the evaluation of the through-space interactions quantitatively. The entries of the secular determinant, constructed upon the premises of general orbital interaction formalism, which describe the through-space interaction are of a form,



(1)

$$\langle \psi_{\kappa\mu}^{(i)} | \hat{F}_i + \hat{F}_j + \hat{F}_{ij} | \psi_{1\mu}^{(j)} \rangle - E \langle \psi_{\kappa\mu}^{(i)} | \psi_{1\mu}^{(j)} \rangle \quad (1)$$

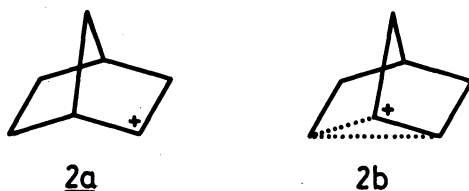
which describes a mixing of orbitals at different ethylenic fragments, $i \neq j$, ($i, j = 1, 2, 3$), but of the same occupancy, $\mu = \mu$, and,

$$\langle \psi_{\kappa\mu}^{(i)} | F_i + F_j + F_{ij} | \psi_{\lambda\nu}^{(j)} \rangle - E \langle \psi_{\kappa\mu}^{(i)} | \psi_{\lambda\nu}^{(j)} \rangle \quad (2)$$

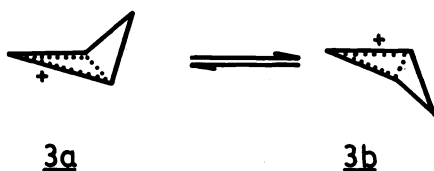
which describes a mixing of orbitals at different ethylenic fragments, $i \neq j$, and with different occupancy, $\mu \neq \nu$. The mutual interaction among the three ethylenic fragments is dissected to pairwise interactions, as given in the form of Fock operator,

$$\hat{F} = \sum_i \hat{F}_i + 1/2 \sum_{i < j} \hat{F}_{ij} \quad (3)$$

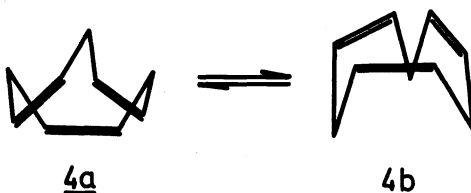
In many practical situations such a "hard" approach effected by ab initio calculations appears to be both complex and "inordinately expensive" (Ref. 4). Therefore there is a paucity of such calculations. On the other hand, the results of detailed MO calculations do not seem to be recognized as sufficient arguments in ambiguous cases. An illustrative example is that of 2-norbornylcation (2a, b), (Refs. 6 & 7).



There seems to be another, quite general, weak point in the rigorous MO approach to the homoaromaticity. It is implied in this sort of questions: if the inversion of the cyclobutenylcation (3a, b) through a structure with a wholly planar carbon skeleton is calculated to require $1.9 \text{ kJ} \cdot \text{mol}^{-1}$ (Ref. 8), what



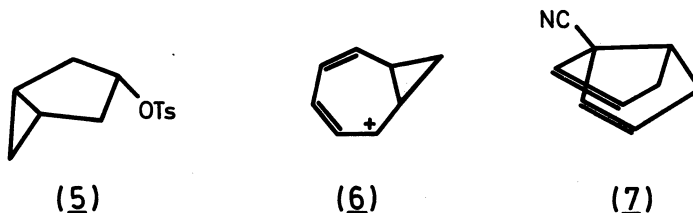
would be the energy barrier for the crown-crown flip-flopping of the *cis,cis,cis*-cyclonona-1,4,7-triene (4a, b)?



It follows that there has been an obvious necessity for constructing a set of simple, practical rules that could be used to make an accurate prediction of homoaromatic stabilization/destabilization for any species of interest. Thus the strictness of the rigorous MO approach frequently succumbs to the use of empirical quantities introduced at various levels of sophistication (Refs. 4, 9, 10, 11 & 12). Simple methods which are based more on intuition than on mathematical justification have been employed too. Within the formalism of the Hückel MO method, the through-space interaction has been treated by introducing a variable β -parameter, $\beta' = k \cdot \beta$; $k \leq 1.0$. The k could be determined from UV spectral data (Ref. 13) by use of linear relationship established between λ_{max} and the HOMO-LUMO

separation value (Ref. 14). One could exploit the perturbation treatment and express such an interaction by a linear combination of bonding orbitals, LCBO. The numerical calibration of the off-diagonal entry, $\langle \psi_i | H_{\mu} | \psi_j \rangle$ in the Hückel secular determinant could be done by use of PES data (Refs. 15 & 16). The attempts to interpret the detailed MO calculations in a more intuitive way have proved the usefulness of the qualitative orbital representation (Refs. 17 & 18). The fact that homoaromaticity is associated with species which are neither of cycloalkyl- nor of aromatic character has been reflected through different approaches by attempts, more or less justified, to block out the energy of a system under consideration to a simple union of linearized contributions. Thus, by the Hückel MO method the "aromatic contribution" is dissected from the rest of a system while in some other approaches various strain situations have been found the main factor to be accounted for (Refs. 19 & 20).

Certain dissection of the through-space interaction phenomenon is made in our approach to homoaromaticity. The dissection is but fictive, it does not presume any physical situation and is essentially an algebraic procedure. It is completely different from any other method used. It was based on the trivial fact that some kinetic, spectroscopic and structure-determination data in the pertinent literature had been rationalized by invoking "nonclassical structures" to come into play. This is well illustrated by the i) kinetic observations in the acetolysis of the *cis*-bicyclo[3.1.0]hex-3-yl toluenesulphonate (5), (Ref. 21); ii) by the ^1H nmr data of the bicyclo[5.1.0]



octadienyl cation (6), (Ref. 22), and iii) by the structure-determination data of the 1-cyanotricyclo[3.3.0.0^{2,8}]octa-3,6-diene (7), (ref. 23). In the cases (i) and (iii) homoaromaticity is believed to contribute to transition states while the nonclassical representative of (6) is an isolable species. What is common to all three examples is that new chemical bonds are presupposed. If we consider a transition state as a chemical species, the essential quality in all three examples is a change in both the number and the arrangement of chemical bonds. In approaching this situation from the topological point of view one should say that molecular topologies are changed.

OUTLINE OF THEORY

Molecular topology of a conjugated system is effectively represented by an unoriented connected graph. Vertices in such a graph stand for carbon atoms while edges stand for carbon-carbon bonds. The maximal valency in such a graph is naturally three. There exists a copious literature relevant to the Hückel MO theory-graph theory alliance (Refs. 24, 25, 26 & 27). This connection is based on numerical identity of the HMO energy levels and the spectrum of a graph representing the carbon skeleton of a conjugated species. Graph theoretical techniques were successfully employed when dealing with the problem of representing a cyclic structure and its reference structure. By use of combinatorial topological rules we have for a characteristic polynomial of a generally oriented graph, \vec{G} (ref. 28),

$$f(x) = \sum_{k=0}^N \sum_{\vec{L}_k \subset \vec{G}} (-1)^k (-1)^{g(\vec{L}_k)} x^{N-k} \quad (4)$$

\vec{L}_k being a "linear element" (see Note a) of a graph \vec{G} , that is, subgraphs built up exclusively of subgraphs such as are $G_i = G_i(u, v)$; where outdegree and indegree are equal, $d^+(u_i) = d^-(u_i) = 1$, for $i = 0, 1, 2, \dots, N$.

$g(\vec{L}_k)$ number of components in a subgraph \vec{L}_k .

Note a. There is no such thing as nonlinear graph.

For unoriented graphs that are spectral representatives of systems based on the nearest-neighbour approximation, Sachs (Ref. 28) established the following relation:

$$P(G; x) = \sum_{i=0}^N \sum_{U_i \subset G} (-1)^{c(U_i)} 2^{r(U_i)} x^{N-i} \quad (5)$$

c, r being the total number of components and the number of ring components, respectively in a subgraph U_i ; $U_i \subset G$,

U_i being the unoriented analog of \vec{L}_k .

The problem of the linear reference structure (Refs. 29, 30, 31 & 32), (vide supra) has been avoided by singling out the non-ring components of the U_i (Ref. 33). In such a way the formed polynomial,

$$P^{ac}(G; x) = \sum_{i=0}^N \sum_{U_i \subset G} (-1)^{c(U_i)} x^{N-i} \quad (6)$$

has coefficients constructed by all possible disjoint selection of the subgraphs K_2 (two vertices linked by an edge), such that $K_2 \subset G$. With the K_2 subgraph given a name dimer (Ref. 34) the $P^{ac}(G; x)$ polynomial could be expressed as,

$$Q(G; x) = (i)^{-N} \sum_{d=0} Z_d(ix)^{N-2d} \quad (7)$$

i being the imaginary unit,

Z_d being a d -dimer partition function associated with dimer covering of a graph G .

The zeros of such a polynomial are given the meaning of a spectrum of reference graph (see Note a). Pursuing the previously mentioned connection, these roots are given the meaning of energy levels of the reference structure of the conjugated system under consideration. The final step, being very simple, gives topological resonance energy, TRE, as a sum of pairwise subtracted values of the HMO characteristic polynomial zeros and the zeros of the $P^{ac}(G; x)$.

$$TRE = \sum_{i=1}^N g_i (x_i - x_i^{ac}) \quad (8)$$

x_i, x_i^{ac} being zeros of characteristic and reference polynomial, respectively,

g_i being "orbital" occupancy number.

The sum is over occupied levels. The "orbital occupancy" number, g_i , is determined with respect to the principle of maximal resonance. It should be clear that $P^{ac}(G; x)$ is not the characteristic polynomial of a graph G , it is generally not a characteristic polynomial of any finite, unoriented graph. However, for certain special cases a reverse procedure could be performed, that is, an acyclic graph

Note a. Matching polynomial, matching graph are probably more correct names for structures we call reference (acyclic) polynomial, reference graph, respectively.

could be constructed from the reference polynomial. We start with the difference between the characteristic and reference, acyclic polynomial. It could be easily shown (Refs. 35 & 36) that this difference is, in general, given by

$$\begin{aligned} \Delta &= P(G; x) - P^{ac}(G; x) = \\ &= (-1)^{\sum i} \sum_{i, j(i)} m_{ij(i)} \sum_{k=0}^{m_{ij(i)}} (-1)^{k+n_{ij(i)}} p(G - R_{ij(i)}; k) x^{N-2k-n_{ij(i)}} \end{aligned} \quad (9)$$

$i = 1, 2, 3, \dots, r, r+1, \dots, r+q.$

r number of principal (chemical) rings in G ,

q increment in the number of principal rings due to possible fusion of rings.

The $ij(i)$ index have the following meaning:

$i = 1; j(i) = j(1), j(2), \dots, j(r+q)$, i.e. denote piecewise numbering;

$i = 2; j(i) = j(k1), j(mn), \dots, j(pq)$, i.e. denote pairwise numbering;

$i = 3; j(i) = j(klm), \dots$, etc.

$k1, mn, \dots, klm, mnp, \dots$ - denote disjoint (ring) components.

k number of K_2 components,

$p(G; k)$ number of disjoint K_2 selections in G ,

$G-R_{ij(i)}$ graph obtained by excising the ring(s) $R_{ij(i)}$ from G ,

$m_{ij(i)}$ maximum number of K_2 in the graph $G-R_{ij(i)}$,

$n_{ij(i)}$ number of vertices in the ring(s) $R_{ij(i)}$,

N number of vertices in G .

Inspection of the equation (9) reveals a possibility for constructing the acyclic graphs, at least in certain cases. The necessary prerequisites for such a possibility is stated in the following proposition.

Proposition. For any polygon-type graph the difference between the characteristic and the acyclic polynomial is linear and unique.

Proof. A proof may be constructed either from the Sachs' formula (5) or from the relation (9). It follows from (5) that, if the characteristic polynomial of a graph G is given as:

$$f(x) = a_0 x^N + a_1 x^{N-2} + \dots + a_{N-k} x^{N-N+k} \quad (10)$$

where $k = \begin{cases} 0, & \text{for } N \text{ even,} \\ 1, & \text{for } N \text{ uneven,} \end{cases}$

the difference between the characteristic and the acyclic polynomial is given by, at least, x^{N-p} term, where p is the girth (Ref. 37) of the smallest ring in a graph. It is easily seen in the relation (9) that the difference,

$$P(G; x) - P^{ac}(G; x) = f\left(\sum_k a_k x^{N-k}\right) \quad (11)$$

is linear and unique when $ij(i) = 0$. The index $ij(i)$ is equal to zero for a graph containing but one ring. Hence the proposition.

For the particular case when no more than one ring exists in a graph G , the difference between the characteristic and the acyclic polynomial is given by:

$$\Delta = \det(x_i I - A) - \sum_{i=0}^{\lfloor N/2 \rfloor} (-1)^i \prod_{U_i \subset G} b(E)x^{N-2i} - 2(-1)^{N+1} \tag{12}$$

$b(E)$ combinatorial contribution due to subgraph E , $E \subset U_i$;

$\lfloor N/2 \rfloor$ maximum integer of $N/2$,

that is, it figures in the absolute coefficient only. The simple consequence follows that the acyclic polynomial could be constructed from a linear graph with an edge given a weight, $w = (\Delta)^{1/2}$. To determine the position of the weighted edge, a combinatorial procedure based on generalization of Hosoya's (Ref. 39) formulae is used (Ref. 36). From there follows the combinatorial formula for constructing the coefficients of the characteristic polynomial of a linear, weighted graph:

$$f(x) = \sum_{i=0}^{\lfloor N/2 \rfloor} (-1)^i \left\{ \frac{w^2}{(i-1)!} \prod_{j=i-1}^{2i-3} (N-2-j) + \frac{1}{i!} \prod_{j=i}^{2i-1} (N-1-j) \right\} x^{N-2i} \tag{13}$$

Such a selectively weighted graph possesses combinatorial properties analogous to those of an imaginary, acyclic graph. If the previous relation is properly equated with the formula for constructing the characteristic polynomial of a p -polygon,

$$f(x) = \sum_{i=0}^{\lfloor N/2 \rfloor} (-1)^i \cdot \frac{1}{i!} \prod_{j=i}^{2i-1} N(N-1-j) \cdot x^{N-2i} - 2(-1)^N \tag{14}$$

and solved for the weight w , one gets:

$$w = \left\{ \frac{\frac{1}{i!} \prod_{j=i-1}^{2i-1} N(N-1-j) - \frac{1}{i!} \prod_{j=i}^{2i-1} (N-1-j)}{\frac{1}{(i-1)!} \prod_{j=i-1}^{2i-3} (N-2-j)} \right\}^{1/2} \tag{15}$$

RESULTS AND DISCUSSION

We proceed by operating on both the molecular graph representing the carbon sigma skeleton of a conjugated compound and the linear weighted graph bearing the combinatorial properties of a fictitious graph representing the reference structure of a conjugated compound. Describing the homoaromatic effects in terms of cycle forming/breaking (vide supra) we proceed by introducing variations of the Hückel parameters; these variations specifically concern β - parameters that are ascribed to the "nonclassical" linking of directly disjoint molecular fragments. These variations built into the Hückel secular determinant result in exact values; however, we are more interested in the trend that obey topological resonance energy values with the "nonclassical bonds" weakening. We thus come upon a perturbation calculation. The first order perturbation, FOP, treatment adapted to the HMO theory gives the standard Hückel energy levels, E_j ; $j = 1, 2, \dots, N$; corrections due to changing the β - parameters (Refs. 39 & 40).

$$E_j = E_j + \delta E_j \quad (16)$$

$$\delta E_j = 2c_{jk}c_{jl} \delta \beta_{kl} \quad (17)$$

or, in the case of more than one simultaneously varied β - parameter,

$$\delta E_j = 2 \sum_i c_{jk_i} c_{jl_i} \delta \beta_{k_i l_i} \quad (18)$$

j MO levels, $j = 1, 2, \dots, N$,

c_{jk} LCAO coefficient corresponding to the j -th MO orbital and the k -th atom,

i the number of simultaneously varied β - parameters.

Thus, the topological resonance energy values for the firstly used example, the tricyclo/5.2.1.0^{4,10}/deca-2,5,8-triene (1), are to be calculated in the following way; the Hückel energy levels are,

$$\delta E_h = 2c_{h1}c_{h2} \delta \beta_{12} + 2c_{h3}c_{h4} \delta \beta_{34} + 2c_{h5}c_{h6} \delta \beta_{56} \quad (19)$$

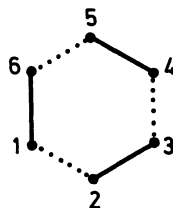
$$h = 1, 2, 3.$$

An analogous formula is used in calculating the "energy levels" of a reference, acyclic graph,

$$\delta E_r = 2c_{r1}c_{r2} \delta \beta_{12} + 2c_{r3}c_{r4} \delta \beta_{34} + 2c_{r5}c_{r6} \delta \beta_{56} \quad (20)$$

$$r = 1, 2, 3.$$

Three ethylenic groups of the triene are schematized as in (8) and the first order perturbed topological resonance energy, FOPTRE, is obtained as follows,

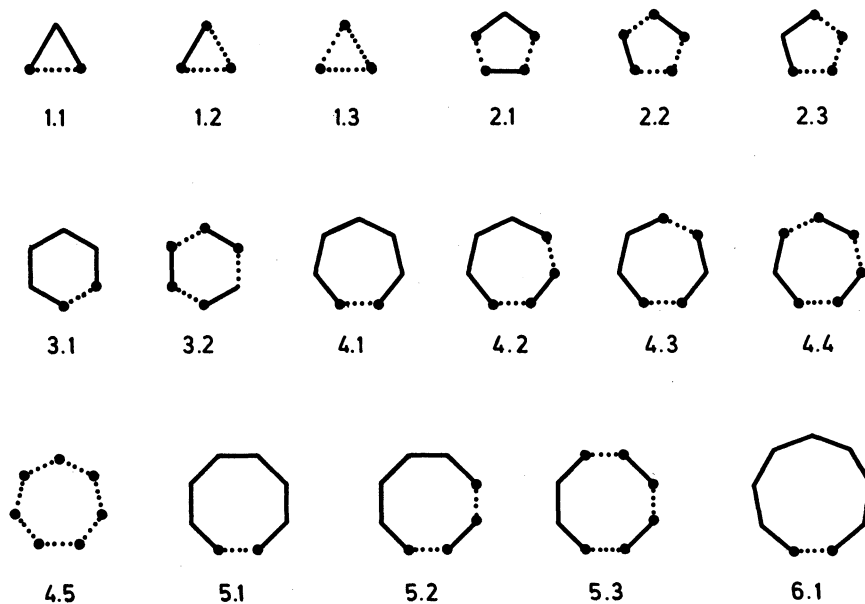


(8) (21)

$$\text{FOPTRE} = \sum_h g_{h,r} (E'_h - E_r)$$

The first order perturbation treatment has been thus used within the Hückel MO theory formalism applied to a conjugated system represented by its molecular graph and simultaneously applied to a fictitious linear structure represented by an edge-weighted graph bearing the required combinatorial properties. This procedure should not be mistaken (Ref. 42) for graph-perturbation which is an essentially different thing. Our calculations were based on the conceptual approaches (i) presuming the existence of a poly-

gon made up of directly disjoint molecular fragments, (ii) allowing for β - parameter variations extending far over the values taken in rigorous perturbation treatment. The presumption of yet the existing through-space connected intramolecular fragments is an approach apparently antithetic to the previous work on the homoaromaticity. However, considering either a ring that is opening to a chain or a chain that is closing to a ring is merely two ways of looking at essentially the same process. These two different approaches give no rise to conceptual difficulties, at least not within the formalism of the first order perturbation treatment. The allowance for large β - parameter variations is unjustified from the angle of rigorous perturbation treatment; however we believe that such variations are of minor significance compared with the approximation inherent to the Hückel MO method which is the basis of our approach. In the Table are given the first order perturbation topological resonance energy, FOPTRE, values for a selected set of structures. This set is probably not a complete one but it covers most of the experimentally observed or suggested homoaromatic systems. The systems are basically arranged with respect to their presumed topologies and then subdivided to mono-, bi-, and polyhomo structures, as is illustrated in the Figure.



TABLE

SYSTEM	$\delta\beta_{\mu\nu}$	FOPTRE	REFERENCE
1. TRIGONAL CATION			
1.1. Monohomo-	0.90	0.56570	a
	0.70	0.62531	
	0.30	0.74453	
	0.10	0.80414	
1.2. Bishomo-	0.90	0.47932	b
	0.70	0.36612	
	0.30	0.13975	
	0.10	0.02656	
1.3. Trishomo-	0.90	0.50911	c
	0.70	0.45554	
	0.30	0.34840	
	0.10	0.29483	
2. PENTAGONAL ANION			
2.1. 1,3-Bishomo-	0.90	0.21610	d
	0.70	0.00012	
	0.30	-0.43186	
	0.10	-0.64784	

2.2. 1,2,4-Trishomo-	0.90	0.32701	e
	0.70	0.33286	
	0.30	0.34458	
	0.10	0.35043	
2.3. 1,2,3-Trishomo-	0.90	0.35653	f
	0.70	0.42143	
	0.30	0.55123	
	0.10	0.61613	
3. HEXAGONAL NEUTRAL			
3.1. Monohomo-	0.90	0.32902	g
	0.70	0.42649	
	0.30	0.62145	
	0.10	0.71892	
3.2. 1,3,5-Trishomo-	0.90	0.40152	h
	0.70	0.64401	
	0.30	1.12899	
	0.10	1.37148	
4. HEPTAGONAL CATION			
4.1. Monohomo-	0.90	0.14489	i
	0.70	0.03092	
	0.30	-0.38254	
	0.10	-0.55835	
4.2. 1,3-Bishomo-	0.90	0.31473	j
	0.70	0.47860	
	0.30	0.80632	
	0.10	0.97019	
4.3. 1,4-Bishomo-	0.90	0.27815	k
	0.70	0.36886	
	0.30	0.55028	
	0.10	0.64099	
4.4. 1,3,5-Trishomo-	0.90	0.25351	l
	0.70	0.33754	
	0.30	0.50561	
	0.10	0.58964	
4.5. Heptahomo- (Perhomo-)	0.90	0.17747	m
	0.70	0.06682	
	0.30	-0.15450	
	0.10	-0.26515	
5. OCTOGONAL DIANION			
5.1. Monohomo-	0.90	0.10525	n
	0.70	-0.06946	
	0.30	-0.41876	
	0.10	-0.59339	
5.2. 1,3-Bishomo-	0.90	0.22525	o
	0.70	0.29060	
	0.30	0.42128	
	0.10	0.48663	

5.3. 1,3,5-Trishomo-	0.90	0.19943	p
	0.70	0.21314	
	0.30	0.24054	
	0.10	0.25425	

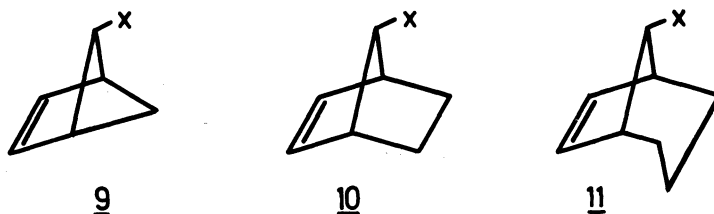
6. NONAGONAL ANION

6.1. Monohomo-	0.90	0.08603	q
	0.70	-0.10692	
	0.30	-0.49280	
	0.10	-0.68575	

a) G.A. Olah, J.S. Stalal, R.J. Spear, and G. Liang, *J. Am. Chem. Soc.*, **97**, 5489 (1975); b) S. Winstein and C. Ordronneau, *J. Am. Chem. Soc.*, **82**, 2084 (1960); c) S. Winstein, J. Sonnenberg, and L. de Vries, *J. Am. Chem. Soc.*, **81**, 6523 (1959); d) J.M. Brown and J.L. Occolowitz, *Chem. Commun.*, 1965, 376; e) P.K. Freeman and T.A. Hardy, *Tetrahedron Lett.*, 1971, 3939; f) L.A. Paquette, H.C. Berk, C.R. Degenhardt, and G.D. Ewing, *J. Am. Chem. Soc.*, **99**, 4764 (1977); g) M. Traeterberg, *J. Am. Chem. Soc.*, **86**, 4265 (1964); h) P. Radlick and S. Winstein, *J. Am. Chem. Soc.*, **85**, 344 (1963); i) J.L. von Rosenberg, Jr., J.E. Mahler, and R. Petit, *J. Am. Chem. Soc.*, **84**, 2842 (1962); j) P. Warner and S. Winstein, *J. Am. Chem. Soc.*, **93**, 1284 (1971); k) P. Ahlberg, D.L. Harris, and S. Winstein, *J. Am. Chem. Soc.*, **92**, 214 (1970); l) L.A. Paquette, P.B. Lavrik, and R.H. Summerville, *J. Org. Chem.*, **42**, 2659 (1977); m) R.W. Thies, M. Gasic, D. Whalen, J.B. Grutzner, M. Sakai, B. Johnson, and S. Winstein, *J. Am. Chem. Soc.*, **94**, 2262 (1972); n) M. Ogliaruse, R. Rieke, and S. Winstein, *J. Am. Chem. Soc.*, **88**, 4731 (1966); o) L.A. Paquette, M.J. Kukla, S.V. Ley, and S.G. Traynor, *J. Am. Chem. Soc.*, **99**, 4756 (1976); p) the same as in (o); q) W.A. Böll, *Tetrahedron Lett.*, 1968, 5531.

We used in our calculations the uniform sequence of $\delta\beta$ values: 0.90, 0.70, 0.30, and 0.10. Since we were considering the opposite process - opening of a ring - the actual β values used were: -0.10, -0.30, -0.70, and -0.90. These figures are not the best choice for each particular case, however, we have chosen them because they are concordant with some values experimentally found (Ref. 13) and because our primary aim has been to compare the influences of β - parameter variations to various topologies, that is, the uniformity of variations was preferred to an adjustment to each particular situation. In analyzing the numerical values we made use of a criterion analogous to that commonly employed by our group (Ref. 43); the trend of decreasing TRE values and eventually taking negative values means the weakening of the aromatic stabilization and vice versa.

Comparison with experimental facts. The inspection of the first order perturbation topological resonance energy, FOPTRE, values for the monoionized structures of trigonal topology reveals that monohomocyclopropenyl (1.1) cation gains TRE with the bond weakening while trishomocyclopropenyl (1.3) cation decreases in TRE with all three bonds simultaneously and uniformly weakening. The same tendency is even more pronounced in the case of bishomocyclopropenyl (1.2) cation. Experimental evidence concerning the monohomocyclopropenyl cation is somewhat inconclusive; its presence seems to have been established firmly only in a super acid medium (Ref. 44). The ^{13}C nmr spectrum, however, does not indicate a significant diagonal overlap in the cyclobutene cation (Ref. 45). Theoretical work has not shed much more light on that subject (Ref. 8). The weak tendency toward aromatic stabilization should be matched by a particularly feasible geometry giving no rise to significant strain; these requirements seem to be met in the case of bis(tetramethylhomocyclopropenyl)dication (Ref. 46). Diminishing the FOPTRE values with a decrease in β values in the case of bishomotrigonal cation suggests the triangular topology to be strongly supported from the point of homoaromatic stabilization. This topology preference matched with not too rigid and inappropriate geometry should give rise to significant homoaromatic behaviour. There exists strong experimental support for this hypothesis. Solvolytic reactions of three bicyclic systems (9-11) have been studied (Ref. 47). In



going from 11 to 10 to 9 the geometric effect is to bring the carbon bearing the leaving group (X) closer to the two unsaturated carbons. This is very nicely reflected in a marked increase in the rate ratio of the unsaturated system to the saturated system as one proceeds from 11 to 10 to 9 (Ref. 47c). Product studies also support the formation of a bishomotrigonal cation. Similar support is found in the case of solvolytic studies of 7-chloronorbornadiene (Ref. 48). It is of some interest to compare the opinion (Ref. 49) of the two rapidly interconverting classical tricyclic ions with some of our calculations. When calculating the maximum FOPTRE value for the bishomocyclopropenyl cation (which is actually switching off the very perturbation) we obtain unequal β -parameters for C(1) - C(3) and C(2) - C(3) bonds; that is, either $\delta\beta_{13}$ or $\delta\beta_{23}$ is larger by the factor about two. Trishomotriangular topology (1.3) is favoured too and has been experimentally established in at least two cases. It is not that significant in the solvolysis of the cis-bicyclo/3.1.0/hex-3-yl tosylate due possibly to the inappropriate choice of solvent in the original work (Ref. 50). In the case of 9-pentacyclo - /4.3.0.0²,4.0³,8.0⁵,7/ nonane p-nitrobenzoate the preferred topology seems to be a recognizable physical fact (Ref. 51). The FOPTRE calculations for pentagonal anionic structures favor the 1,3-bishomopentagonal topology (2.1) and disfavor the 1,2,4-trishomopentagonal one (2.3). The 1,2,3-trishomo-system is rather insensitive to the three bonds weakening (2.2). The auspicious 1,3-bishomo topology is possibly amenable - besides other factors - for the remarkable rate enhancement in the base-catalyzed deuterium exchange in the bicyclo/3.2.1/ octa-2,6-diene (Refs. 52 & 53) with respect to the same process on the bicyclo/3.2.1/ octa-2-monoene. There seems to be no experimentally observed 1,2,3-trishomoaromatic system (Ref. 54). The same applies to the unfavorable 1,2,4-trishomopentagonal topology. In the process of deprotonation of tricyclo/4.2.1.0³,9/nona-4,7-dien-2-yl "the transition state for exo, H₂ abstraction does not experience significant stabilizing interaction with the proximate double bonds" (Ref. 55); the conclusion which falls in nicely with our calculations. Both hexagonal neutral systems, monohomo- as well as the 1,3,5-trishomo -, appear to be strongly disfavored judging from the FOPTRE results. Traetterberg (Ref. 56) argues against establishing the planar monohomohexagonal system by pointing out the insufficient aromatic stabilization to match the geometric requirements. The monohomohexagonal system occurrence within the cycloheptatriene, CHT, structure is unfavorable for at least two reasons; (i) the propinquity of C(1) - C(6) sufficient for a noticeable through-space interaction would impose on CHT a situation of significant strain, and (ii) strengthening of C(1) - C(6) interaction gives rise to a weaker system, according to FOPTRE calculations. Not much more is to be said of the sym-cis, cis, cis-1,4,7-cyclo-nonatriene (Ref. 3), tricyclo/5.2.1.0⁴,10/deca-2,5,8-triene (Ref. 57) and hexacyclo/4.4.0.0²,4.0³,9.0⁵,7.0⁸,10/decane (Ref. 58) - the alleged trishomohexagonal aromatic systems. Perturbed resonance energy calculations for the heptagonal topology suggest the following: monohomoheptagonal system creation is topologically favored, to somewhat of a less extent this applies to the perhomoheptagonal system. The formation of 1,3-bishomoheptagonal topology (4.2) is rather unfavorable. The formation of the 1,4-bishomo- (4.3) and the 1,3,5-trishomoheptagon (4.4) is not favored either. There is an ample evidence of the yet classical "nonclassical" homotropylium cation (Refs. 22, 59, 60 & 61). Both bishomoheptagonal systems (4.2 and 4.3) occur within flexible enough frameworks (Ref. 62) to allow for required distortions, like that of cis-bicyclo/6.1.0/nona-2,4,6-triene (Ref. 63) which has a 1,3-bishomo-system or those of 1-methylbicyclo/4.3.0/nonatrienyl (Ref. 64), 9-barbaralyl (Ref. 65), and bicyclo/4.3.1./deca-2,4,7-trienyl cation (Ref. 66) which have the 1,4-bishomoheptagon. However, all bishomoaromatic heptagonal systems appear to be significantly attenuated in aromatic stabilization with respect to the homotropylium cation; for instance the chemical shift between inner and outer methylene protons in the cis-bicyclo/6.1.0/nona-2,4,6-triene is more than three times smaller than the corresponding shift in homotropylium cation. We argue that this is due mainly to the unfavorable topologies of 1,3- and 1,4-bishomoheptagon. Furthermore, the intuitively acknowledged difference (Ref. 67) between the two bishomoheptagons in the amount of charge transfer is clearly quantified by our FOPTRE calculations of 1,3- and 1,4-bishomoheptagons (4.2 and 4.3, respectively). There seems to be no experimental evidence supporting the existence of 1,3,5-trishomoheptagonal topology, at least not in the case of tricyclo/5.3.1.0⁴,11/undeca-2,5,8-trienyl cation (Ref. 68). Though favored by FOPTRE results, perhomoheptagonal topology is not as yet experimentally identified. It is possible that either the analyzed tetracyclo/11.1.0.0³,5.0⁷,9/tetradecan-11-ol (Ref. 69) is not of appropriate geometry or that our calculations are misleading. Without reliable computational data of the conformation an answer would be only speculative. In the octagonal series the monohomo system is favored to occur; 1,3-bishomooctagon (5.2) is slightly unfavorable while 1,3,5-trishomooctagon (5.3) is rather insensitive to β - parameter changes. The monohomocyclooctatetraene system is obtainable by a reduction of either cis-bicyclo/6.1.0/nona-2,4,6-triene (Ref. 70) or cis-cyclononatetraene (Ref. 71); that is, rather strong tendency toward forming the octagonal topology matches successfully with the effort required to flatten the anglestrain-free boat conformation (Ref. 72) into nearly planar COT ring. The reduction of the bicyclo/6.2.1/undeca-2,4,6,9-tetraene and the tricyclo/5.4.1.0⁴,12/dodeca-2,5,8,10-tetraene did not give rise to "spectroscopically characterizable" (Ref. 73) 1,3-bishomo COT dianion and 1,3,5-trishomo COT dianion, respectively. The tendency of closing the monohomononagonal topology is strong enough to match the conformational requirements, at least in the structure of 1,6-methano/10/annulene (Ref. 74).

CONCLUSION

The FOPTRE results for seventeen examples are correlated with the experimental findings concerning the existence and amount of homoaromaticity. In some cases (1.2, 1.3, 2.1, 2.2, 2.3, 3.1, 3.2, 4.1, 4.4, 5.1, 5.2 and 6.1) the FOPTRE results correlate well with experimental facts, in other cases (1.1, 4.2, 4.3 and 5.3) they do not. For system (4.5) our results are contrary to the experimental evidence. One could thus anticipate that either no unambiguous opinion could be formed or that only a tentative premise, based on the relative prevalency of the first group (1.2, 1.3, 2.1, ...etc.) could be postulated. The actual state is, however, differently accented. The tentative conclusion which has been made above can only be tested with pertinent experimental findings. We go ahead by assuming that all the experimental evidence cited is correct and reliable. Now care is to be taken in interpreting the FOPTRE results. FOPTRE calculation results do not refer to any physical quantity of the system under consideration, at least not directly. These results do not quantify the dissected, as a linear term, "aromatic" contribution to certain physical situation of a relevant species. The calculations do not quantify anything, in strict terms. They are given as numbers but should be understood a different way. These numbers do not even express the FOPTRE values for cited topologies, at least not correctly. What is important are the sequels of these numbers. These sequels are sometimes of positive trend, in the other cases of negative trend. They are sometimes steep, sometimes not. They express a tendency of certain chains, or bits of chains to close a ring. We have thus come upon an unobservable property that represents the intrinsic tendency of a certain system to form a closed structure by through-space interaction. Whether this tendency will be realized in the specific situation, concerning a, say, symmetry of interacting orbitals or a strain of particular geometry, that remains to be calculated. Whether the topological tendency should provoke the dispersal of a charge over the polygon-like framework, or should result in equal deuterium scrambling over all the vertices of a hypothetical polygon - remains to be measured. The FOPTRE results are given for the purpose of planning either calculations or the experiment for a specific, alleged homoaromatic system.

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