Symmetry, Topology, and Aromaticity

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Abstract: The $4q + 2 \pi$-electron prerequisite for cyclic stabilization is shown to be a necessary consequence whenever orbitals of $\pi$ symmetry are constrained to interact within a pericyclic topology. Corresponding symmetry-imposed rules are then derived for three other topologies in a way that permits still further extension. Finally, a topological definition of aromaticity is provided as a stimulus and guide to further experiments.

For more than two decades, the Hückel rule has helped to fashion the development of contemporary organic chemistry. Through the ingenuity and the diligence of organic chemists, the “aromatic character” of fully conjugated, monocyclic hydrocarbons containing $4q + 2 \pi$ electrons has now been opened to scrutiny for values of $q$ from 0 to 7. During this process, the original structural prerequisite for the $4q + 2$ rule has also been subjected to extensive variations. Among these, we note the use of dehydro derivatives (e.g., $1^4$) and of spanning alkyl fragments (as in $2^4$ and $3^3$) to prevent intramolecular cyclization. Distortions from coplanarity have thus become commonplace and even the otherwise continuous polyene conjugation has been interrupted (cf. $4^9$).

Indeed, only the essentially pericyclic $\pi$-electron topology has been left more or less intact.

More recently, two further developments have appeared. First, orbital symmetry control of transition-state stabilization has been recognized as a fundamental phenomenon.$^3$ Second, each of the authors has noted that stabilization, akin to classical aromaticity, might be detected in rather different environments (spirarenes,$^4$ bicycloataromaticity)$^5$. In this paper, we first abstract some fundamentals from our previous studies. We then apply these to a third topology and, in this way, come to the discovery of newer Hückel rules, each in its own environment.

Most fundamentally, the conditions for stabilizing a system of interacting orbitals will depend upon: (1) the symmetry properties of the component orbitals, (2) the topology of their interaction, and (3) the magnitude of their overlap. The first factor is demonstrated by contrasting the orbital pattern of cyclic polyenes which contain some $d$ orbitals, such as the phosphorilic halides, with those that do not.$^10$ The second factor, the topology of orbital interaction, is our principal concern. We later return to see how its consequences are modified by the third factor, the magnitude of the orbital overlap.

Our fundamental building block is an intact conjugated polyene segment, here to be designated by an unbroken line, called a ribbon. Such ribbons may be joined directly by single bonds to form still longer ribbons or, more germane to the ensuing discussion, they may be connected by insufficiently insulating (homoconjugating)$^{11}$ saturated centers, here to be denoted by broken lines.

Of the great variety of topologies which may be envisaged for the linkage of several ribbons, we single out four (Figure 1). The simplest pericyclic topology is the only one available to a single ribbon; the two termini are linked. Two ribbons may be linked in either a pericyclic or in a spirocyclic array. In the latter, each terminus is connected to two others rather than only to one. The possibilities increase again when three ribbons are used. In the laticyclic topology, only the termini of the central ribbon are doubly linked. The longyclic restores a connectivity of two at each terminus. Below each topology is an appropriately constructed hydrocarbon representative, arbitrarily chosen to be a stabilized anion. Finally, at the bottom of Figure 1, we also note that each

(9) M. J. Goldstein, ibid., 89, 6357 (1967).

Goldstein, Hoffmann / Symmetry, Topology, and Aromaticity
topology is capable of further annelation, here arbitrarily halted at four ribbons.

Numerous other topological possibilities become available as the number of ribbons increases. For example, even for three ribbons there are alternate linkages (e.g., 5); for four ribbons a logical extension of the spirocyclic topology is 6. We defer discussion of these and other possibilities not only for reasons of brevity but because their analysis follows logically from the arguments we will present for the principal four.

**Figure 2** We display the well-known pattern of molecular orbitals for ribbons containing as many as seven centers. It is apparent that the orbitals of any one ribbon alternate between $\sigma$ and $\pi$ with increasing energy.

The lesson of perturbation theory now points to the crucial roles of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Their symmetry will depend both on the number of centers ($n$) and on the electron occupancy, as measured by the resulting charge ($z$). Only four patterns are possible. The HOMO must be either

![HOMO and LUMO patterns](image)

Restriction 1 implies that the effectiveness of any ribbon depends only upon the electron density at its termini. The lesson of orbital symmetry control points to the crucial role of the relative phase of the wave function at these termini. We therefore define the symmetry of any ribbon orbital to be either $\sigma$ or $\pi$ according to whether the phase relations at the termini resemble those of a $\sigma$ or a $\pi$ atomic orbital. Alternatively, these may be regarded as either symmetric or antisymmetric with respect to the pseudo-plane $\psi$.

Ribbons and Their Interaction

A ribbon is defined as an intact conjugated polyene segment, subject to the following constraints on its structure and on its mode of interaction: (1) interaction between ribbons must occur only at their termini; (2) the twisting of any ribbon must remain less than $90^\circ$ (Möbius ribbons are excluded); (3) the two termini of any ribbon must remain indistinguishable, both in the number of their connections and in the sense ($\sigma$ or $\pi$) that such connections are made.

![Ribbons and Their Interaction](image)
singly or doubly occupied. And it must be either $\psi p$ or $\psi d$. The LUMO must be vacant and of opposite symmetry to the HOMO. As indicated in Figure 3, each of the four patterns also has a homologation factor of four electrons. The pattern of hexatriene (6') is also that of ethylene (2'), of the allyl cation (3+), or of the pentadienyl anion (5-).

It therefore becomes convenient to represent the mode of a ribbon as one of the four integers 0, 1, 2, or 3, computed as $(n - z) \mod 4$. For example, the butadienyl radical anion (4-) mode is given by: $4 - (-1) = 5 \mod 4 = 1$. The LUMO–HOMO pattern of any ribbon is unambiguously defined by its mode.

Implicit in this definition is the necessary additivity of modes by the acyclic extension of ribbons, i.e., by the overlap between one terminus of each of two ribbons. We think it nevertheless useful to digress briefly in order to provide a more formal proof of the theorem: when two ribbons of modes $\mu_1$ and $\mu_2$ interact, even weakly but in an acyclic way, the new composite ribbon is of mode $\mu_1 + \mu_2 \mod 4$.

The proof consists in the construction of an addition table (Figure 5), whose rows and columns contain each of the four modes. The elements of the table are then deduced by the analysis of orbital symmetry interactions appropriate to the topology in question, here the acyclic one. The general rule is that whenever two orbitals interact, the higher energy combination “takes the node.” In an acyclic topology, this node is buried somewhere within the new composite ribbon whose symmetry is always revealed at its termini. As shown in Figure 4, this requires interacting orbitals of identical symmetry to generate $\psi p$ below $\psi d$. Those of opposite symmetry generate $\psi p$ above $\psi d$.

When this rule is now applied to the ten possible LUMO–HOMO combinations of two ribbons, the addition table of Figure 5 is constructed. The numbers in the lower right-hand corner of each element are the modes of the new composite ribbons as defined by Figure 3. The proof is then completed by verifying that each such mode is indeed the sum of those defined by its row and column ($\mod 4$).

Since this proof can be extended to any number of acyclically connected ribbons it provides an alternative proof.

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(15) Arithmetic operations, $\mod 4$, are the conventional ones but then completed by subtracting the highest multiple of 4.

derivation of the orbital patterns of Figure 2. More important, the proof is independent of the relative energies of the interacting orbitals. (These were arbitrarily set at identical levels in Figure 5.) It is also independent of the magnitudes of their interaction. Finally, we note that the logic involved is reversible so that the converse of the theorem is equally valid. Ribon orbital symmetry remains unchanged upon the partitioning of a ribbon into any number of shorter but still interacting ones. A particularly powerful application of this converse is described in the next section.

Prerequisites for Electronic Stabilization. It must be noted immediately that emphasis has been directed solely to electron count and not at all to the one-electron energy of the orbital. In particular, a Hückel calculation of a mode 0 ribbon can make the HOMO bonding (40,80), nonbonding (31,73), or even antibonding (2°, 6°), and similarly for the LUMO. It would thus appear that no great energetic significance could be attached to these interaction diagrams.

Nevertheless, it will be our central thesis that the topological prerequisites for electron stabilization can be derived in precisely this way. Explicitly and deliberately we now assume all HOMO's to lie at one level and all LUMO's at a higher but still uniform level. Electronic stabilization will be expected only when symmetry-allowed interactions decrease the total one-electron energies. We limit ourselves to ribbons of the even modes, 0 and 2.

A Topological Survey

Pericycles. This is the only closed topology accessible to a single ribbon and is analyzed, most simply, by considering an acyclic ribbon of the same length perturbed by interaction between its termini. As shown below, interaction between the termini of a orbital lowers the energy of that level, while interaction between the termini of a orbital raises its energy. It is apparent that stabilization is then only accessible to a mode 2 ribbon, i.e., to one that contains 4q + 2 electrons.

We now recall the theorem proved above. The symmetry properties of any ribbon are invariant to subsequent partitioning. Electronic stabilization must then also be expected for any number of interacting ribbons that are constrained to a pericyclic topology, just so long as their modal sum is 2. Equivalently, we can say that an odd number of such ribbons must be mode 2. This last version of the Hückel rule corresponds precisely to the requirement for stabilizing a totally suprafacial pericyclic transition state. The value of the theorem, then, is that it permits us to ignore the otherwise real but inherently only quantitative distinctions between transition-state stabilization and the interrupted, conjugative stabilization termed "homoaromaticity" by Winstein or the ultimate in stabilization that is achieved when interactions between ribbons become as great as within them—the 4q + 2 electron Hückel hydrocarbons.

An alternate derivation of Hückel's rule, one that more easily lends itself to application in the more complicated topologies, begins with an obvious expectation. Ring formation of any kind must impose a symmetry restraint. If two ribbons are joined in a pericyclic topology, the single connections of Figure 4 are replaced by two connections. It is then apparent that a orbital can now no longer interact with a orbital. Every bonding interaction would otherwise be accompanied by an antibonding one. Only orbitals of the same pseudosymmetry can interact.

Only three interaction diagrams are possible. These are shown at the top of Figure 6. Beneath them are some realistic examples: cis-9,10-dihydropyphenalene (7), bicyclo[4.2.0]nonatriene (8), norbornadiene (9), the bicyclo[3.2.0]octadienyl anion (10), the norbornadienyl cation (11), and a zwitterionic semibullvalene (12). The interaction diagrams at the top lead

\[ \text{Figure 6. Interaction diagrams for the pericyclic connection of two ribbons.} \]
to the expected prediction: only \((0 + 2)\) is stabilized. Two of the examples, 11 and 12, are chosen to demonstrate the versatility of the modal formalism.

The \(1^+\) ribbon of the norbornyl cation 11, for example, lacks the fully occupied \(\phi d\) orbital indicated in the interaction diagram above it. It does, however, contain the vacant \(\phi p\) orbital (here, indeed, a \(p\)-atomic orbital at C-7) and this suffices to stabilize the occupied \(\phi p\) orbital of the \(2^+\) ribbon.

The zwitterionic representation 12, forced upon us by our neglect of the odd modes, is necessarily ambiguous. It may be interpreted to be either the singlet biradical 12a, or 12b, the transition state for the Cope rearrangement of 12c.

**Spirocyclic.** We next consider the alternative cyclic interaction of two ribbons, this time with each terminus doubly connected. An added symmetry restriction is to be expected. As revealed below, orbital interaction is now further limited to that between two \(\phi d\) levels. Previous conclusions, deduced from the interaction diagrams of Figure 6, require only minor modification. Once again, neither \(0 + 0\) nor \(2 + 2\) but only \(0 + 2\) is stabilized, if indeed by virtue of only one of the two possible interactions of Figure 6, that between the occupied and unoccupied \(\phi d\) levels. Realistic (if as yet unknown) examples of stabilized spirocyclics are shown below.

Longicyclics. These are generated by requiring three or more ribbons to retain the two characteristic spirocyclic properties: doubly connected termini and topological indistinguishability. Our strategy for three ribbons begins by first permitting two of them to interact. The resulting composite orbitals are then allowed to interact further with orbitals of the third ribbon. The result must of course be independent of any permutation of the three ribbons.

In the first stage, the pericyclic constraint still applies: only orbitals of common pseudo-symmetry can interact. As shown below, these result in a new pair of orbitals which retain the \(\phi p\) or \(\phi d\) symmetry of their precursors. They are classified further as symmetric (s) or anti-symmetric (a) with respect to the pseudo-mirror plane in which the third ribbon must lie. It is apparent that the lower symmetric combinations never interact with any \(\pi\) orbital of the third ribbon. Only the anti-symmetric combinations possess the proper symmetry. Only two possibilities will then be allowed: \(\phi p_a\) with a \(\phi p\) orbital from the third and \(\phi d_a\) with a \(\phi d\).

To return now to the initial stage, the composite orbitals produced by pericyclic interaction of two ribbons are abstracted from the top of Figure 6. These are now appropriately labeled for a longicyclic topology in the central column of Figure 7. At the extreme left are the orbitals of the third ribbon, should it be mode 0 (they are at the right if mode 2). Note that the combination 23 cannot occur.

(25) a) This is only a pseudo-plane because the first two ribbons need not be of identical length, nor need the dihedral angles to be equal; cf. ref 13. (b) In an alternate arrangement, shown below, the symmetric combinations become the potent ones.
Figure 7. Interaction diagrams for the longicyclic topology. See text for explanation.

Table I. The Simplest Stabilized Longicyclics

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<thead>
<tr>
<th>(0,0,0)</th>
<th>(2,2,2)</th>
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<tbody>
<tr>
<td>Molecules</td>
<td>Ions</td>
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<td>(4^0)</td>
<td>(3^+)</td>
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Experimental support, curiously enough, is now most convincingly available for the simplest longicyclic molecule that is not stabilized, the \(2^22^20^2\) barrelene (13). Hydrogenation of its first double bond is more exothermic than that of any other alkene (excluding only the more highly strained cyclopropenes or methylenecyclopropanes).\(^{24,27}\) Only negative evidence can be cited for the other entries of Table II. Various otherwise reasonable attempts to prepare 14 have failed.\(^{28}\) Correspondingly reasonable precursors of 15 have instead provided evidence for the exclusive generation of the barbaralyl cation (16, the collapsed stabilized \(3^+3^--1^+\)), whether judged by low-temperature nmr\(^{29}\) or by solvolytic capture.\(^{30-32}\)

Turning now to more positive evidence, we note the abundantly documented stability of the simplest realization of \(2^22^10^1\)—the 7-norbornadienyl cation (17).\(^{34,35}\) Amusingly, a suggested alternate struct-


\(^{27}\) This rationalization of its thermodynamic instability (cf. ref 9) has since been abundantly supported by photoelectron spectroscopy and by MINDO/2 calculations. Cf. E. Haselbach, E. Heilbronner, and G. Schröder, Helv. Chim. Acta, 54, 153 (1971).


\(^{32}\) 15 has been invoked, perhaps unnecessarily, to help rationalize both the apparent total degeneracy of 16 under some\(^{34}\) (but not all\(^{35}\)) conditions, as well as the otherwise anomalous\(^{11}\) isolation of a covalent derivative\(^{13}\) in low and irreproducible yield (0-20%), ref 31 and especially footnote 8). Alternative explanations for both phenomena remain to be excluded.

\(^{33}\) Note: The Simplest Stabilized Longicyclics That Are Not Stabilized

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\(^{a}\) We restrict ourselves to at most singly charged ribbons of length 4 or less and to a total molecular charge of at most \(\pm 1\).
ture for this ion, 18,19,9 is recognized to be a collapsed form of $3^+1^-$, also expected to be stabilized.

Evidence for stabilization of the anion 19, a realization of $3^22^0$, is more recent.8 Nevertheless, the available data for both ions already suffice to confirm a more general prediction of relative stability, also accessible from Figure 7.

If we compare occupied levels of the stabilized pericyclic (0,2) with those of the two stabilized longicyclics (0,0,2) and (0,2,2) at either side of it, it appears that more stabilization is available in a longicyclic topology than in a pericyclic one.

This prediction of relative stability must be regarded more cautiously than our previous qualitative judgement—stabilized or not. In addition, the traditional experimental tests of relative ionic stability are most indirect. For cations, the solvolysis rate of a neutral precursor should depend on the rate at which a dianionic form of the above conclusion would appear to be that bulvalene, 22,45 should undergo its degenerate Cope rearrangement at a faster rate than semibulvalene, 12c. The transition state for the rearrangement of 12c is a realization of the pericyclic $3^+3^-$, while that of 22 is one of $3^+3^-$. The observed activation energies are in fact 12.8 kcal/mol for 2241,42 and 6.4 kcal/mol for the octamethyl derivative of 12c.43 Clearly both transition states are stabilized, as they should be, but the extent of stabilization appears anomalously great in the case of semibulvalene. An important effect, which we neglect in this paper and which we think is significant in this case, is the electronic stabilization of the reactants, whether by framework constraints, by through-bond coupling, or by substituents.44

A more obvious role for substituents is apparent from the zwitterionic formalism. Thus, an interesting feature of Table I and II is the presence of some stabilized species, e.g., $4^33^-$, 23a, whose collapse products are identical with those of some destabilized species, e.g., $4^33^+, 12c$. This collapse product, 23b, is the recently synthesized isobulvalene.45 The differ-

The conclusion that more stabilization is available in a longicyclic topology than in a pericyclic one must be tempered by a consideration of numerous other factors. For instance, a straightforward corollary to the above conclusion would appear to be that bulvalene, 22,45 should undergo its degenerate Cope rearrangement at a faster rate than semibulvalene, 12c. The transition state for the rearrangement of
As an appropriate example, we predict stabilization to fall off in the sequence $24 \ (20^1+2^2) > 25 \ (2^20^1) > 26 \ (2^3+2^9)$. Although many other similar predictions are equally accessible, no currently available experimental evidence that we know bears on any of them.

We therefore go on to consider the transformation of a laticyclic into its isomeric longicyclic (Figure 9). The only important pseudo-plane for this transformation is now that of the central ribbon and so we can ignore any distinction between $p$ and $d$. Those occupied orbitals which are $s$ with respect to this plane are stabilized by the transformation. Those which are $a$ are destabilized.

Referring back to Figure 8, we see that the singly stabilized laticyclics, $(0 + 0 + 2)$ and $(2 + 2 + 0)$, possess two occupied $s$ orbitals and one occupied $a$. These laticyclics will therefore be stabilized by longicyclic formation. The doubly stabilized laticyclics, $(0 + 2 + 0)$ and $(2 + 0 + 0)$, possessing two $a$'s and one $s$, will be destabilized. Yet, clearly, one and the same longicyclic must surely result from either $(0 + 0 + 2)$ or from $(0 + 2 + 0)$, from $(2 + 2 + 0)$ or from $(2 + 0 + 2)$. As a result, we can expand the laticyclic hierarchy to include longicyclics as well.

The most stable array of three ribbons is symmetrically laticyclic: $(0 + 2 + 0)$ or $(2 + 0 + 2)$. Less stable are the isoconjugate longicyclics and, following these, the isomeric unsymmetrical laticyclics: $(0 + 0 + 2)$ and $(2 + 2 + 0)$. Least stable of all are the homogeneous partitions, $(0 + 0 + 0)$ and $(2 + 2 + 2)$, but especially so in a longicyclic topology. We thus expect the order of cationic stability to fall off in the series $24 > 17 > 25 > 26$.

Generalization and Other Topologies

It is now apparent that the three-ribbon laticyclics and longicyclics have been constructed by an annelation procedure that is implicitly pericyclic. Throughout this process, only one version of the Hückel rule has survived: stabilization can come only from $(0 + 2)$ interactions. It then follows that one can always construct a hierarchy of stabilities simply by counting the number of these stabilizing interactions and then subtracting the number of those, $(0 + 0)$ or $(2 + 2)$, that are not. It is then a trivial exercise to show, for example, that the relative stabilities of the four-ribbon

(46) This corresponds precisely to a scheme for establishing the bonding or antibonding character of Hückel molecular orbitals; cf. ref 14a, Chapter 8.
Table III. Relative Stabilities of the Four-Ribbon Longicyclics and Laticyclics

<table>
<thead>
<tr>
<th>Most stable</th>
<th>Laticyclic</th>
<th>Longicyclic</th>
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<tr>
<td>Laticyclic</td>
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<td>(0, 2, 0, 2)</td>
</tr>
<tr>
<td>Longicyclic</td>
<td>(0 + 2 + 2 + 0)</td>
<td>(2 + 0 + 0 + 2)</td>
</tr>
<tr>
<td>Laticyclic</td>
<td>(2 + 2 + 0 + 2)</td>
<td>(0 + 0 + 2 + 2)</td>
</tr>
<tr>
<td>Longicyclic</td>
<td>(0, 2, 2, 0)</td>
<td>(0, 0, 2, 0)</td>
</tr>
<tr>
<td>Laticyclic</td>
<td>(0 + 0 + 0 + 0)</td>
<td>(2 + 2 + 2 + 2)</td>
</tr>
<tr>
<td>Longicyclic</td>
<td>(0, 0, 0, 0)</td>
<td>(2, 2, 2, 2)</td>
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</table>

Least stable

| Laticyclic | (0 + 2 + 0 + 2) |
| Longicyclic | (2 + 0 + 2 + 2) |

* No distinction is made among those hydrocarbons grouped together.

laticyclics and longicyclics fall in the order shown in Table III.

Every topology requires its own analysis of the constraints on orbital interaction. For example, the array 27 precludes all interactions except those between ϕp of the unique central ribbon with the ϕd composite of the other two, or ϕd of the central ribbon with ϕd of the exterior two. As a result, Table IV reveals an amusing contrast to the hierarchy of stabilities determined for the laticyclic case.

Ancillary Considerations

The modal formalism has thus provided us with an internally rigorous technique for seeking stabilization in a way that can be applied to any topology. It should be clear that our exclusive preoccupation with unrealistically invariant HOMO and LUMO levels served principally to avoid distraction by other, more quantitative matters. In the three sections that follow, we draw attention to some of these, if only in a qualitative way, being now much more strongly guided by empirical fact.

Destabilization. One now knows the Hückel rule to be a double-edged sword. With 4q π electrons, fully conjugated pericyclics become dramatically inaccessible, highly transient when at all formed.47 This behavior approximates the description, "destabilized," that we used when such pericyclics were constructed by joining the termini of a single mode 0 ribbon. The gentler description, "not stabilized," was used when the same pericyclic was instead constructed from two or more ribbons. The resolution of this ambiguity reveals a much more general principle.

The error is to be found in our description of occupied level interactions as nonstabilizing. In the most general case shown below, ε' is always greater than ε. This follows from the inclusion of overlap in any quantum mechanical calculation.14,48 The destabilization of two interacting electron pairs is further emphasized when electron interaction is explicitly included at higher levels of approximation.49 However its origin is described, interaction between occupied levels is always destabilizing.

We can now look below the LUMO-HOMO levels to find any number of other levels, σ as well as π, more in longer ribbons than in shorter ones. When ribbons are joined, some of these must interact and all of them are filled. Destabilization must therefore be regarded as the natural consequence of ribbon interactions except when overwhelmed by explicitly required stabilization.

Such destabilization will most often be revealed as high chemical reactivity but the converse is not true. Several of the molecules and ions which we expect to be stabilized may well prove to be highly reactive for quite another reason. Their ground states may be triplets.

An example from one such class is the spirocyclic 28, which we classify as 5+5- of modal sum 2. A conventional orbital interaction diagram for 28a (Figure 10), one in which the assumption of universal energies for LUMO and HOMO is not made, shows the results of restricting interaction to those between ϕd orbitals. The formally nonbonding ϕp levels cannot now be split, yet must accommodate two electrons. This is a typical diradical situation.40 The degeneracy is most simply

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50 R. Hoffmann, J. Amer. Chem. Soc., 90, 1475 (1968); R. Hoffmann, G. D. Zeiss, and G. W. VanDine, ibid., 90, 1485 (1968); R.
which stabilize ions, is then revealed in Figure 11. One
molecules and the neutral-charged ribbon interactions
much smaller energy gap than does either of the two
neutral-neutral ribbon interactions which stabilize
of the two ion-stabilizing interactions operates over a
cursor of
(1
hence an odd number of levels. One of these, the
contain one ribbon with an odd number of atoms,
and the HOMO of any even ribbon with which it in-
HOMO of an anionic ribbon or the LUMO of a cationic
one, is formally "nonbonding," at least in the sense
that its energy must fall somewhere between the LUMO
and the HOMO of any even ribbon with which it in-
teracts.
An important quantitative difference, between the
neutral–neutral ribbon interactions which stabilize
molecules and the neutral–charged ribbon interactions
which stabilize ions, is then revealed in Figure 11. One
of the two ion-stabilizing interactions operates over a
much smaller energy gap than does either of the two
interactions which stabilize neutral molecules. Since
the magnitude of any interaction is inversely related to
the size of such an energy gap, it follows that the stabiliza-
tion of ions should exceed those of neutral molecules,
irrespective of topology. Indeed, the stabilization of neutral,
incompletely conjugated polyenes has thus far been experimentally
detected only in the uniquely most favorable case—1,3,5-
cycloheptatriene (30). With two interruptions (8)
or three (31) no trace of the expected pericyclic stabiliza-
tion is detected, whether measured by the heat of hydrogenation
or by the photoelectron spectroscopically
determined position of the higher occupied lev-
els.
By contrast, we have already encountered cations (11, 17) and anions (10, 19), both pericyclic and longi-
cyclic, whose stability is manifest in spite of two inter-
ruptions. Still others may be cited.62
The anticipated stabilization of molecules such as 31
will be most easily detected, not in their ground-state
properties, but rather in the transition states for their
concerted reactions. For instance, we would expect
a low activation barrier to the as yet unobserved reac-
tion

In this way, we reestablish the connection between
stabilization, as it is discussed here, and the complex
of ideas described as "the conservation of orbital sym-
metry" by one of us as well as in alternate ways by
others.7
Indeed, our formalism may add some further insight
to the analysis of symmetry-controlled reactions. Con-
consider, for example, the following closely analogous pro-
cesses: the rearrangement of 32 to semibullvalene 12c5

(52) Assuming, of course, that the ribbon lengths are roughly com-
parable. For the relationship between interaction energy and energy
gap, see ref 14.
Soc., 61, 1868 (1939); R. B. Turner, W. R. Meador, W. E. Doering,
(54) Perhaps appropriately, it was this hydrocarbon which first
suggested the possibility of interrupted pericyclic stabilization, i.e.,
"homoearamoticity." Cf. W. E. Doering, G. Laber, R. Vonderwahl,
N. F. Chamberlain, and R. B. Williams, ibid., 78, 5448 (1956).
and A. P. Yu, ibid., 86, 3178 (1964).
(57) (a) J. Meinwald and D. Schmidt, J. Amer. Chem. Soc., 91, 5877
(1969); J. Meinwald and H. Tsuruta, ibid., 91, 5877 (1969); (b) H. E.

Gleiter and R. Hoffmann, ibid., 90, 5457 (1968); Tetrahedron, 24, 5899
(1968); Angew. Chem. Int. Ed. Engl., 8, 214 (1969); Angew. Chem., 81,
(51) Only one representative of this series, a phenyl-substituted pre-
cursor of 29b, has been studied: S. Masamune, K. Fukumoto, Y.
and the degenerate transformation of 33. The mechanism indicated for the first reaction is reasonable but remains to be established. The second reaction has not yet even been discovered.

Both reactions require the cleavage of both an allylic and a vinylic C–C bond during a process that is thermally “allowed.” An important difference emerges if we represent the transition state of each one by the formal zwitterion produced if the weaker of the two bonds were to cleave (32a vs. 33a). It is then apparent that these are but the 3+3– and 3+5– pericycles—stabilized and destabilized, respectively. We therefore expect the second reaction (if ever discovered) to be slower than the first.

An alternative mechanism with different stereochemical consequences for the transformation of 32 to 12c involves the formation of a hypothetical diradical intermediate, also represented by 32a. This species could collapse to semibullvalene, not by a shift of a vinylic bond, but by π-radical recombination. The argument we have given for stabilization of 32a can be invoked for this mechanism as well.

Geometry. Surely the most important and the most obvious handicap of the spirocyclic, the laticyclic, and the longicyclic topologies is their interrupted conjugation. Overlap falls off rapidly with distance and with it the magnitude of hoped for stabilization. In partial compensation, typical ribbon interaction geometries permit p–p overlap to be of the more efficient σ kind rather than the less efficient π.62

The hitherto rarely explored laticyclic topology provides unusual opportunities to vary such parameters. We therefore emphasize that our choice of skeletal frameworks to adjust themselves so as to maximize opportunities for stabilization. The 7-norbornadienyl cation 17 provides a well-known, if unusually complicated example. Our previous discussion of longicyclic stabilization noted that interactions between the two 2ν ribbons of 17 were destabilizing while those between the 1+ and either 2ν were stabilizing. If the magnitude of such interactions were solely a function of inter-ribbon distance, the alternative geometry 17a would clearly be preferred. In fact, the ion chooses a geometry which more closely resembles 17b, apparently increasing one stabilizing pericyclic interaction at the expense of the other.33,34,61 A second factor, probably of comparable importance, is the phenomenon of through-bond coupling, the enhanced interaction of ribbons by virtue of appropriately disposed intervening σ orbitals.14,32a,36

The advantages to be gained by such skeletal distortions might well overcome some of the more marginal predictions of relative stability outlined earlier. For example, we would classify the cation 35 together with 25 as unsymmetrically laticyclic (2+2+0) and therefore stabilized, though not so much as the corre-
a set of ribbons into one experimentally realizable topology rather than into another.

This adjective has now long been available, if occasionally abused. It is "aromatic," heretofore appropriately defined (theoretically) as possessing that enhanced stabilization which is achieved whenever an appropriate acyclic ribbon closes to an isoconjugate pericyclic one. The aromaticity of benzene relates its stability to that of 1,3,5-hexatriene, of the cyclopropenyl cation to that of the allyl, etc. Although implicitly quantitative, as well as topological, the definition has most fruitfully been used in a qualitative way. This is because ring closure usually leads to dramatically increased stabilization (aromaticity) or to the converse (antiaromaticity).

The interrupted conjugation of the newer topologies precludes any correspondingly dramatic comparison. In this sense, aromaticity, at least as it has traditionally been manifested, is not likely to be observed.

We would, however, draw particular attention to the contrasting properties of two of the sets of three ribbons: (2,2,2) and (2,2,0). The first of these contains $4q + 2\pi$ electrons and is stabilized in a pericyclic topology but destabilized in either a longicyclic or in a laticyclic one. The second set contains $4q \pi$ electrons and, while stabilized as a longicyclic or laticyclic, is destabilized in a pericyclic topology. As a result, it becomes possible to predict the preferred direction of numerous isoconjugate rearrangements that interconvert topologies. Two well-known examples are the transformations of: the destabilized pericyclic 36 to the stabilized longicyclic 17 and the destabilized longicyclic 15 to the stabilized pericyclic 37.

This is so analogous to the theoretical comparison of acyclic and pericyclic stabilization that it becomes natural to extend the original definition and to call 17 "bicycloaromatic" and 15 "antibicycloaromatic." More generally, bicycloaromatic hydrocarbons are the stabilized laticyclics and longicyclics which contain $4q$ $\pi$ electrons; antibicycloaromatic laticyclics and longicyclics are those that are both destabilized and contain $4q + 2\pi$ electrons.

Such terms introduce a distinction between the two partitions of stabilized longicyclics and laticyclics (2,-2,0) and (2,0,0), and between the two destabilized ones—(2,2,2) and (0,0,0). It is important to recognize that this distinction is not based upon any presumed difference in electronic stabilization or destabilization. Rather, it is intended as a further guide to the experimentalist, warning him of the opportunities and pitfalls of topological interconversion. How useful this will be remains to be established.

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