

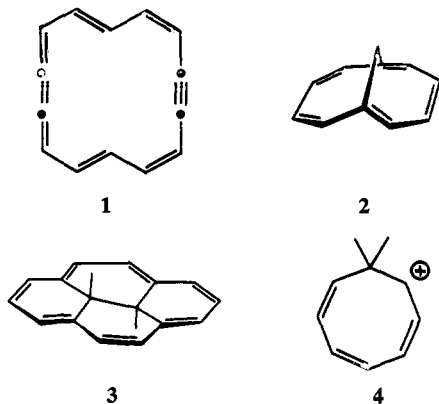
Symmetry, Topology, and Aromaticity¹

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Abstract: The $4q + 2$ π -electron prerequisite for cyclic stabilization is shown to be a necessary consequence whenever orbitals of π 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.² Through the ingenuity and the diligence of organic chemists, the "aromatic character" of fully conjugated, monocyclic hydrocarbons containing $4q + 2$ π 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**³) and of spanning alkyl fragments (as in **2**⁴ and **3**⁵) to prevent intramolecular cyclization. Distortions from coplanarity have thus become commonplace and even the otherwise continuous polyene conjugation has been interrupted (cf. **4**⁶). Indeed, only the essentially pericyclic π -electron topology has been left more or less intact.



More recently, two further developments have appeared. First, orbital symmetry control of transi-

(1) Presented in part at the International Symposium on the Chemistry of Nonbenzenoid Aromatic Compounds, Sendai, Aug 1970.

(2) (a) E. Hückel, "Grundzüge der Theorie ungesättigter und aromatischer Verbindungen," Verlag Chemie, Berlin, 1938, and references therein; (b) "Kekulé Symposium on Theoretical Organic Chemistry," Butterworths, London, 1959; (c) D. Ginsburg, Ed., "Non-Benzenoid Aromatic Compounds," Interscience, New York, N. Y., 1959; (d) "Aromaticity," Special Publication No. 21, The Chemical Society, London, 1967; (e) P. J. Garratt and M. V. Sargent, *Advan. Org. Chem.*, **6**, 1 (1969); (f) G. M. Badger, "Aromatic Character and Aromaticity," Cambridge University Press, London, 1969; (g) J. P. Snyder, Ed., "Nonbenzenoid Aromatics," Academic Press, New York, N. Y., 1969.

(3) F. Sondheimer and Y. Gaoni, *J. Amer. Chem. Soc.*, **82**, 5765 (1960); F. Sondheimer, Y. Gaoni, L. M. Jackman, N. A. Bailey, and R. Mason, *ibid.*, **84**, 4595 (1962).

(4) E. Vogel and H. D. Roth, *Angew. Chem.*, **76**, 145 (1964); *Angew. Chem., Int. Ed. Engl.*, **3**, 228 (1964); E. Vogel and W. A. Böll, *Angew. Chem.*, **76**, 784 (1964); *Angew. Chem., Int. Ed. Engl.*, **3**, 642 (1964).

(5) V. Boekelheide and J. B. Phillips, *J. Amer. Chem. Soc.*, **89**, 1695 (1967); J. B. Phillips, R. J. Molyneux, E. Sturm, and V. Boekelheide, *ibid.*, **89**, 1704 (1967).

(6) J. L. Rosenberg, J. E. Mahler, and R. Pettit, *ibid.*, **84**, 2842 (1962); J. D. Holmes and R. Pettit, *ibid.*, **85**, 2531 (1963); C. E. Keller and R. Pettit, *ibid.*, **88**, 604 (1966).

tion-state stabilization has been recognized as a fundamental phenomenon.⁷ Second, each of the authors has noted that stabilization, akin to classical aromaticity, might be detected in rather different environments (spirarenes,⁸ bicycloaromaticity⁹). 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 phosphonitrilic 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 *longicyclic* 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

(7) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(8) R. Hoffmann, A. Imamura, and G. D. Zeiss, *J. Amer. Chem. Soc.*, **89**, 5215 (1967); cf. H. E. Simmons and T. Fukunaga, *ibid.*, **89**, 5208 (1967).

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

(10) D. P. Craig, *J. Chem. Soc.*, 997 (1959); A. J. Ashe, III, *Tetrahedron Lett.*, 359 (1968).

(11) S. Winstein, H. M. Walborsky, and K. Schreiber, *J. Amer. Chem. Soc.*, **72**, 5795 (1950).

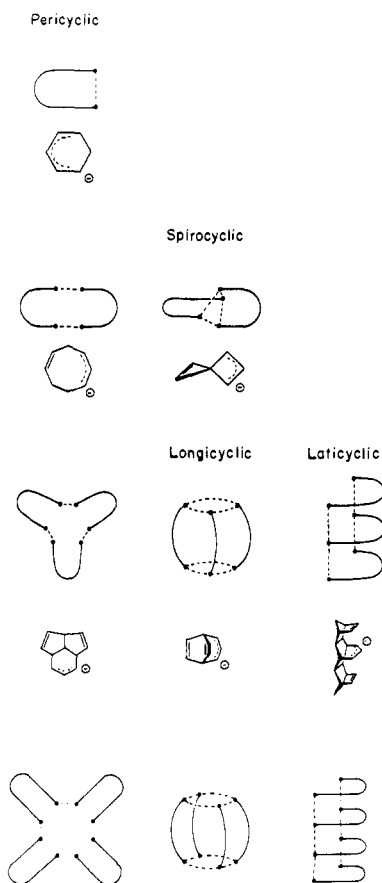
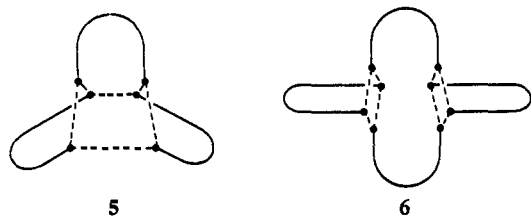


Figure 1. Some topologies for interacting ribbons.

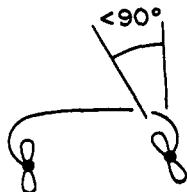
topology is capable of further annelation, here arbitrarily halted at four ribbons.

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.

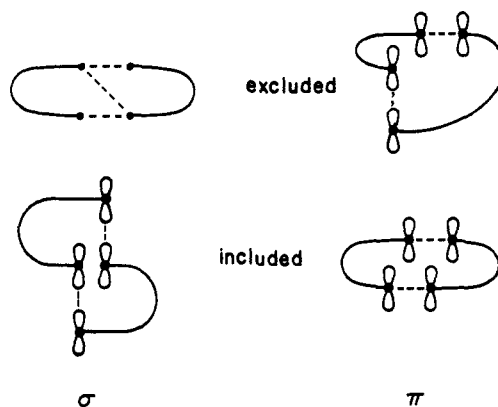


Ribbons and Their Interaction

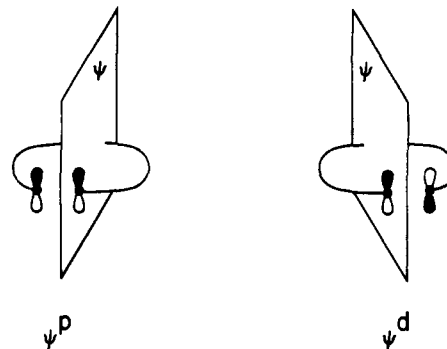
A ribbon is defined as an intact conjugated polyene segment, subject to the following constraints on its structure and on its mode of interaction: (1) interaction between ribbons must occur only at their



termini; (2) the twisting of any ribbon must remain less than 90° (Möbius ribbons¹² are excluded); (3) the two termini of any ribbon must remain indistinguishable, both in the number of their connections and in the sense (σ or π) that such connections are made.



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.⁷ We therefore define the symmetry of any ribbon orbital to be either ψ_p (pseudo-p) or ψ_d (pseudo-d) according to whether the phase relations at the termini resemble those of a p or a d atomic orbital. Alternatively, these may be regarded as either symmetric (ψ_p) or antisymmetric (ψ_d) with respect to the pseudo-plane ψ .¹³



In 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 ψ_p and ψ_d with increasing energy.

The lesson of perturbation theory¹⁴ 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

(12) E. Heilbronner, *Tetrahedron Lett.*, 1923 (1964).

(13) Since the ribbon may be variously twisted as well as substituted, this need not be a true symmetry plane.

(14) (a) E. Heilbronner and H. Bock, "Das HMO-Modell und seine Anwendung," Verlag Chemie, Weinheim/Bergstr., Germany, 1968; (b) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969; (c) K. Fukui, *Fortsch. Chem. Forsch.*, 15, 1 (1970); K. Fukui in "Molecular Orbitals in Chemistry, Physics and Biology," P.-O. Löwdin and B. Pullman, Ed., Academic Press, New York, N. Y., 1964, p 513, and references therein; (d) L. Salem, *J. Amer. Chem. Soc.*, 90, 543, 553 (1968).

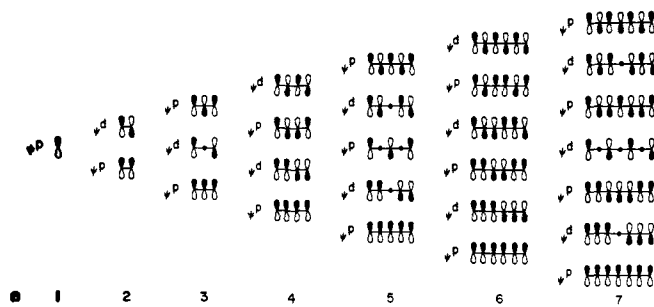


Figure 2. The π orbitals of the shortest ribbons. The atomic orbital coefficients for any given molecular orbital are distorted to the same magnitude in order to emphasize nodal properties.

| Orbitals | | | | |
|-----------|------------|------------|------------|------------|
| LUMO | ψ^d — | ψ^d — | ψ^p — | ψ^p — |
| HOMO | ψ^p + | ψ^p + | ψ^d + | ψ^d + |
| Examples: | 2^+ | 2^0 | 2^- | 2^- |
| | $3^+, 5^-$ | 3^+ | 3^0 | 3^- |
| n^2 | 4^- | $4^+, 4^-$ | 4^+ | 4^0 |
| | 5^0 | 5^- | $5^+, 5^-$ | 5^+ |
| | 6^+ | 6^0 | 6^- | $6^+, 6^-$ |
| | $7^+, 7^-$ | 7^+ | 7^0 | 7^- |
| Mode: | 1 | 2 | 3 | 0 |

Figure 3. The four patterns of orbital symmetry and occupancy illustrated by some representative ribbons.

singly or doubly occupied. And it must be either ψ^p or ψ^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 (6^0) is also that of ethylene (2^0), 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 $(n - z) \text{ modulo } 4$.¹⁵ For example, the butadienyl radical anion (4^-) mode is given by: $4 - (-1) = 5 \text{ (modulo } 4) = 1$. 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 μ_1 and μ_2 interact, even weakly but in an acyclic way, the new composite ribbon is of mode $\mu_1 + \mu_2 \text{ (modulo } 4)$.

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."^{14,16} In an acyclic topology, this node is buried somewhere within the new composite

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

(16) R. Hoffmann, *Accounts Chem. Res.*, 4, 1 (1971).

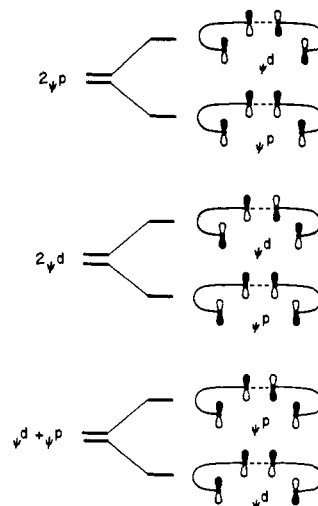


Figure 4. Interaction patterns for acyclic extension.

| | 1 | 2 | 3 | 0 |
|---|---|---|---|---|
| 1 | | | | |
| 2 | | | | |
| 3 | | | | |
| 0 | | | | |

Figure 5. Addition table for the acyclic extension of ribbons; in each interaction diagram the ribbon at left possesses the mode of the row, the ribbon at right the mode of the column.

ribbon whose symmetry is always revealed at its termini. As shown in Figure 4, this requires interacting orbitals of identical symmetry to generate ψ^p below ψ^d . Those of opposite symmetry generate ψ^p above ψ^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 (*modulo* 4).

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

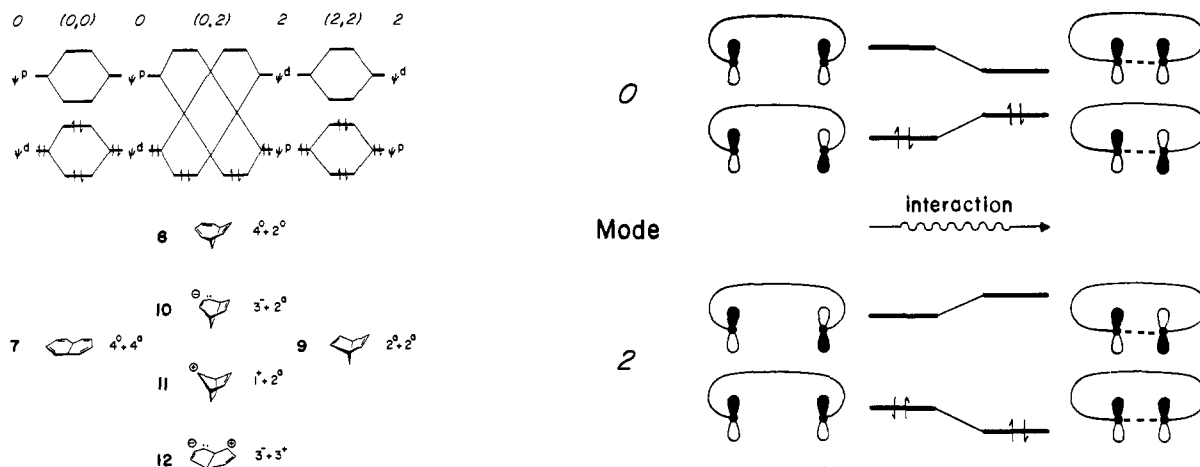


Figure 6. Interaction diagrams for the pericyclic connection of two ribbons.

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. *Ribbon 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 ($4^0, 8^0$), nonbonding ($3^-, 7^-$), or even antibonding ($2^{2-}, 6^{2-}$), 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.¹⁷ We limit ourselves to ribbons of the even modes, 0 and 2.

A Topological Survey

Pericyclics. 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.¹⁸ As shown below, interaction between the termini of a ψ_p orbital lowers the energy of that level, while interaction between the termini of a ψ_d orbital raises its energy. It is apparent that stabilization is then only accessible to a mode 2 ribbon, *i.e.*, to one that contains $4q + 2\pi$ electrons.

(17) It may be noted that this is a more general, if also a somewhat more permissive definition of stabilization than either of those used previously.^{8,9}

(18) Cf. M. J. S. Dewar, ref 14b, p 210 ff.

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.⁷ 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 Winstein¹⁹ or the ultimate in stabilization that is achieved when interactions between ribbons become as great as within them—the $4q + 2\pi$ -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 ψ_p can now no longer interact with ψ_d . 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-dihydronaphthalene (7),²⁰ bicyclo[4.2.1]nonatriene (8),²¹ norbornadiene (9), the bicyclo[3.2.1]octadienyl anion (10),²² the norbornenyl cation (11),²³ and a zwitterionic semibullvalene (12).²⁴ The interaction diagrams at the top lead

(19) S. Winstein, *J. Amer. Chem. Soc.*, **81**, 6524 (1959).

(20) T. L. Burkoth and E. E. van Tamelen, in ref 2f, p 63; S. Masamune and R. T. Seidner, *Chem. Commun.*, 542 (1969).

(21) T. S. Cantrell and H. Schechter, *J. Amer. Chem. Soc.*, **85**, 3300 (1963); L. Cannell, *Tetrahedron Lett.*, 5967 (1966); W. Grimme, *Chem. Ber.*, **100**, 113 (1967).

(22) (a) J. M. Brown and J. L. Occolowitz, *Chem. Commun.*, 376 (1965); 638 (1967); *J. Chem. Soc. B*, 411 (1968); (b) S. Winstein, M. Ogliaruso, M. Sakai, and J. M. Nicholson, *J. Amer. Chem. Soc.*, **89**, 3656 (1967).

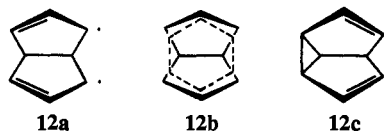
(23) (a) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *ibid.*, **77**, 4183 (1955); (b) H. G. Richey and R. K. Lustgarten, *ibid.*, **88**, 3136 (1966); (c) R. Hoffmann, *ibid.*, **86**, 1259 (1964); *J. Chem. Phys.*, **40**, 2480 (1964); (d) S. Winstein, in ref 2c, p 5.

(24) H. E. Zimmerman and G. L. Grunewald, *J. Amer. Chem. Soc.*, **88**, 183 (1966); H. E. Zimmerman and H. Iwamura, *ibid.*, **90**, 4763 (1968); H. E. Zimmerman, R. W. Brinkley, R. S. Givens, G. L. Grunewald, and M. A. Sherwin, *ibid.*, **91**, 3316 (1969).

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.

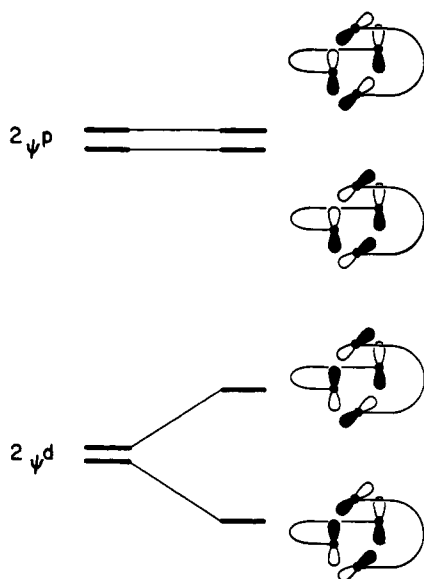
The 1^+ ribbon of the norbornenyl cation **11**, for example, lacks the fully occupied ψ_d orbital indicated in the interaction diagram above it. It *does*, however, contain the vacant ψ_p orbital (here, indeed, a p-atomic orbital at C-7) and this suffices to stabilize the occupied ψ_p orbital of the 2^0 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

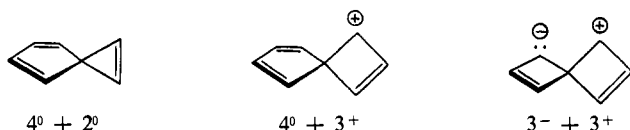


rearrangement of **12c**.

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



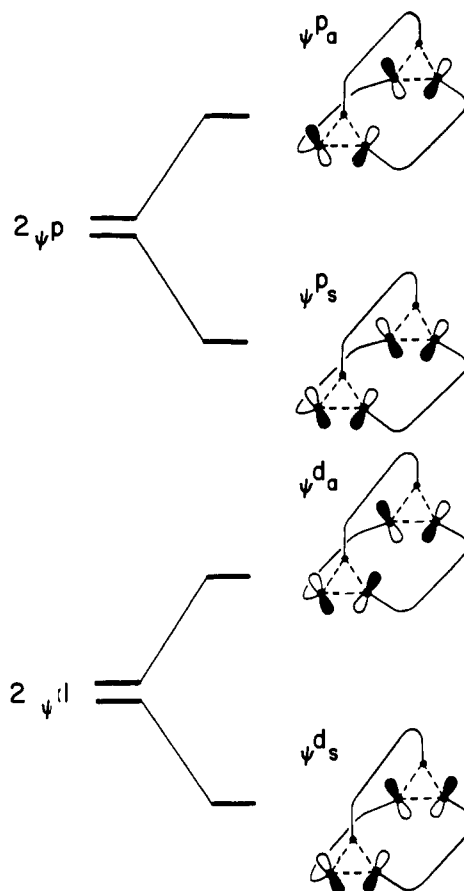
is now further limited to that between two ψ_d levels. Previous conclusions, deduced from the interaction diagrams of Figure 6, require only minor modification. Once again, neither $0 + 0$ nor $2 + 2$ but only $0 + 2$ is stabilized, if indeed by virtue of only one of the two possible interactions of Figure 6, that between the occupied and unoccupied ψ_d levels. Realistic (if as yet unknown) examples of stabilized spirocyclics are shown below.



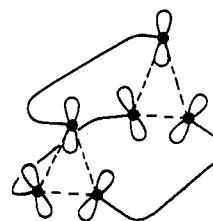
Longicyclics. These are generated by requiring three or more ribbons to retain the two characteristic spirocyclic properties: doubly connected termini and topological indistinguishability. Our strategy for three ribbons begins by first permitting two of them to interact. The resulting composite orbitals 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 ψ_p or ψ_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.^{25a} It is apparent



that the lower symmetric combinations never interact with any π orbital of the third ribbon. Only the anti-symmetric combinations possess the proper symmetry^{25b} Only two possibilities will then be allowed: ψ_{p_a} with a ψ_p orbital from the third and ψ_{d_a} with a ψ_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 com-

(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.

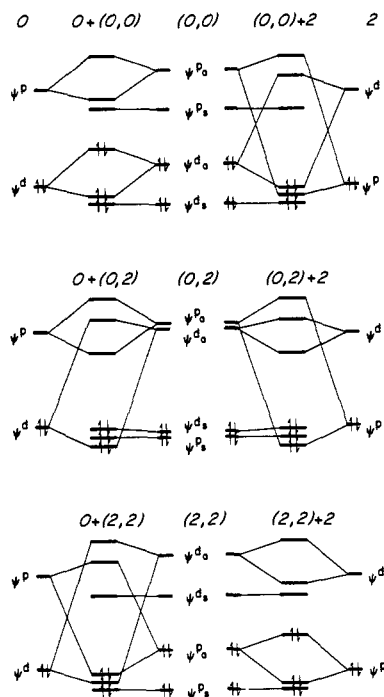


Figure 7. Interaction diagrams for the longicyclic topology. See text for explanation.

posite occupied orbitals of $(0,0)$ or $(2,2)$ are split above and below our universal HOMO level. The ψ_{d_s} and ψ_{p_s} occupied orbitals of $(0,2)$ are degenerate and already stabilized below this level. The interactions shown are those allowed for longicyclics: ψ_{p_a} with ψ_p and ψ_{d_a} with ψ_d . As required by permutational invariance, longicyclic interactions are seen to be both associative and commutative; $(0,0) + 2 = 0 + (0,2)$ and $(0,2) + 2 = 0 + (2,2)$.

More important, Figure 7 reveals that there are two stabilizing partitions of three ribbons, $(0,2,2)$ and $(0,0,2)$. The two other partitions, $(0,0,0)$ and $(2,2,2)$, are not stabilized. In contrast to both the pericyclics and the spirocyclics, the stabilizing total number of π electrons can be either $4q$ or $4q + 2$. Other differences become more apparent if we pause to make these conclusions more explicit. Tables I and II list the simplest stabilized and nonstabilized examples.

Table I. The Simplest Stabilized Longicyclics^a

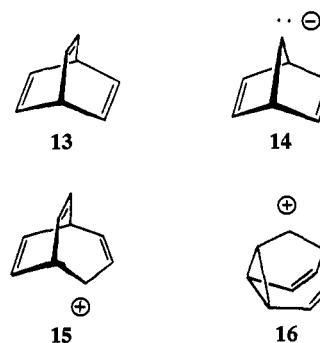
| $(0,0,2)$ | | | $(0,2,2)$ | | |
|----------------|----------------|----------------|----------------|----------------|----------------|
| Molecules | | | | | |
| 4 ⁰ | 4 ⁰ | 2 ⁰ | 4 ⁰ | 2 ⁰ | 2 ⁰ |
| 1 ⁺ | 3 ⁻ | 2 ⁰ | 1 ⁺ | 1 ⁻ | 2 ⁰ |
| 1 ⁺ | 4 ⁰ | 1 ⁻ | 3 ⁻ | 3 ⁺ | 2 ⁰ |
| 3 ⁻ | 4 ⁰ | 3 ⁺ | 4 ⁰ | 1 ⁻ | 3 ⁺ |
| Ions | | | | | |
| 4 ⁰ | 4 ⁰ | 1 ⁻ | 1 ⁺ | 2 ⁰ | 2 ⁰ |
| 4 ⁰ | 4 ⁰ | 3 ⁺ | 3 ⁻ | 2 ⁰ | 2 ⁰ |
| 1 ⁺ | 4 ⁰ | 2 ⁰ | 4 ⁰ | 2 ⁰ | 1 ⁻ |
| 3 ⁻ | 4 ⁰ | 2 ⁰ | 4 ⁰ | 2 ⁰ | 3 ⁺ |
| 1 ⁺ | 1 ⁺ | 1 ⁻ | 1 ⁺ | 1 ⁻ | 1 ⁻ |
| 1 ⁺ | 3 ⁻ | 1 ⁻ | 1 ⁺ | 1 ⁻ | 3 ⁺ |
| 1 ⁺ | 3 ⁻ | 3 ⁺ | 3 ⁻ | 1 ⁻ | 3 ⁺ |
| 3 ⁻ | 3 ⁻ | 3 ⁺ | 3 ⁻ | 3 ⁺ | 3 ⁺ |

^a We restrict ourselves to at most singly charged ribbons of length 4 or less and to a total molecular charge of at most ± 1 .

Table II. The Simplest Longicyclics That Are Not Stabilized

| $(0,0,0)$ | | | $(2,2,2)$ | | |
|----------------|----------------|----------------|----------------|----------------|----------------|
| Molecules | | | | | |
| 4 ⁰ | 4 ⁰ | 4 ⁰ | 2 ⁰ | 2 ⁰ | 2 ⁰ |
| 4 ⁰ | 1 ⁺ | 3 ⁻ | 2 ⁰ | 1 ⁻ | 3 ⁺ |
| Ions | | | | | |
| 4 ⁰ | 4 ⁰ | 1 ⁺ | 2 ⁰ | 2 ⁰ | 1 ⁻ |
| 4 ⁰ | 4 ⁰ | 3 ⁻ | 2 ⁰ | 2 ⁰ | 3 ⁺ |
| 1 ⁺ | 1 ⁺ | 3 ⁻ | 1 ⁻ | 1 ⁻ | 3 ⁺ |
| 3 ⁻ | 3 ⁻ | 1 ⁺ | 3 ⁺ | 3 ⁺ | 1 ⁻ |

Experimental support, curiously enough, is now most convincingly available for the simplest longicyclic molecule that is *not* stabilized, the $2^0 2^0 2^0$ 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).^{26,27} 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 nmr²⁹ or by solvolytic capture.³⁰⁻³²



Turning now to more positive evidence, we note the abundantly documented stability of the simplest realization of $2^0 2^0 1^+$ —the 7-norbornadienyl cation (17).^{23d,33-35} Amusingly, a suggested alternate struc-

(26) R. B. Turner, *J. Amer. Chem. Soc.*, **86**, 3586 (1964); R. B. Turner, P. Goebel, B. J. Mallon, W. E. Doering, J. F. Coburn, Jr., and M. Pomerantz, *ibid.*, **90**, 4315 (1968).

(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).

(28) G. Wittig and E. Hahn, *Angew. Chem.*, **72**, 781 (1960); R. A. Finnegan and R. S. McNees, *J. Org. Chem.*, **29**, 3234 (1964); A. Streitwieser, Jr., and R. A. Caldwell, *ibid.*, **27**, 3360 (1962); G. Wittig and J. Otten, *Tetrahedron Lett.*, 601 (1963); G. Wittig and G. Klumpp, *ibid.*, 607 (1963).

(29) P. Ahlberg, D. L. Harris, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 4454 (1970).

(30) J. C. Barborak, J. Daub, D. M. Follweiler, and P. von R. Schleyer, *ibid.*, **91**, 7760 (1969); J. C. Barborak and P. von R. Schleyer, *ibid.*, **92**, 3184 (1970).

(31) J. B. Grutzner and S. Winstein, *ibid.*, **92**, 3186 (1970).

(32) 15 has been invoked, perhaps unnecessarily, to help rationalize both the apparent total degeneracy of 16 under some²⁹ (but not all)³⁰ conditions, as well as the otherwise anomalous³¹ isolation of a covalent derivative^{32a} in low and irreproducible yield (0–20%, ref 31 and especially footnote 8). Alternative explanations for both phenomena remain to be excluded.

(32a) NOTE ADDED IN PROOF. This covalent derivative has since been shown to be an experimental artifact: J. B. Grutzner, private communication; J. B. Grutzner and S. Winston, *J. Amer. Chem. Soc.*, in press.

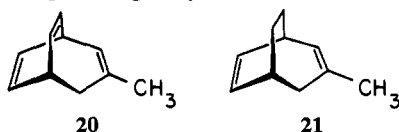
ture for this ion, **18**,^{36,37} is recognized to be a collapsed form of $3^+1^-1^+$, also expected to be stabilized.



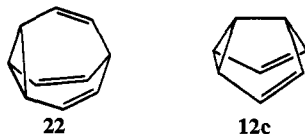
Evidence for stabilization of the anion **19**, a realization of 3^-2^0 , is more recent.³⁸ Nevertheless, the available data for both ions already suffice to confirm a more general prediction of *relative stability*, also accessible from Figure 7.

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 is usually compared with that of an appropriately hydrogenated derivative. For anions, comparative rates of hydrocarbon–deuterium exchange have been used. Nevertheless, it is gratifying to recall that 7-norbornadienyl chloride produces **17** at 760 times the rate at which 7-norbornenyl chloride generates the stabilized pericyclic 7-norbornenyl cation, **11**.³⁹ Equally consistent, the hydrocarbon **20** exchanges its allylic protons for deuterium 750 times faster than does its corresponding dihydro derivative **21**.⁴⁰



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 of the above conclusion would appear to be that bullvalene, **22**,⁴¹ should undergo its degenerate Cope rearrangement at a faster rate than semibullvalene, **12c**. The transition state for the rearrangement of



(33) P. R. Story and M. Saunders, *J. Amer. Chem. Soc.*, **82**, 6199 (1960); **84**, 4876 (1962).

(34) P. R. Story, L. C. Snyder, D. C. Douglass, E. W. Anderson, and R. L. Kornegay, *ibid.*, **85**, 3630 (1963).

(35) S. Winstein and C. Ordroneau, *ibid.*, **82**, 2084 (1960).

(36) H. C. Brown and H. M. Bell, *ibid.*, **85**, 2324 (1963); N. C. Deno, *Progr. Phys. Org. Chem.*, **2**, 129 (1964).

(37) A historical perspective is available in P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, New York, N. Y., 1965.

(38) (a) J. B. Grutzner and S. Winstein, *J. Amer. Chem. Soc.*, **90**, 6562 (1968); (b) S. W. Staley and D. W. Reichard, *ibid.*, **91**, 3998 (1969).

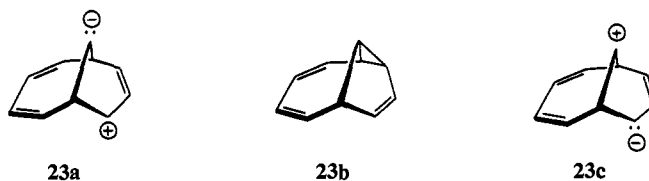
(39) "80% aqueous" acetone at 25°, ref 35.

(40) Potassium *tert*-butoxide catalysis in dimethyl sulfoxide at 25°, ref 38b.

(41) W. E. Doering and W. R. Roth, *Angew. Chem.*, **75**, 27 (1963); *Angew. Chem., Int. Ed. Engl.*, **2**, 115 (1963); *Tetrahedron*, **18**, 715 (1963); G. Schröder, *Chem. Ber.*, **97**, 3140 (1964); G. Schröder and J. F. M. Oth, *Angew. Chem.*, **77**, 774 (1965); **79**, 458 (1967); *Angew. Chem., Int. Ed. Engl.*, **4**, 752 (1965); **6**, 414 (1967).

12c is a realization of the pericyclic 3^+3^- , while that of **22** is one of $3^+3^-2^0$. The observed activation energies are in fact 12.8 kcal/mol for **22**^{41,42} 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 semibullvalene. 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., $4^03^+1^-$, **23a**, whose collapse products are identical with those of some destabilized species, e.g., $4^03^-1^+$, **23c**. This collapse product, **23b**, is the recently synthesized isobullvalene.⁴⁵ The differ-



ence in stability between **23a** and **23c** should clearly be enhanced by electron-donating substituents on the 3^+ ribbon and electron-withdrawing substituents on the 1^- ribbon.

Laticyclics. This last topological domain that we consider introduces us to the more general consequences of topologically distinguishable ribbons—here the interior and exterior ones (*cf.* Figure 1). The strategy we employ closely follows that used for longicyclics.

We begin by mixing appropriate orbitals of two ribbons, now explicitly identified as the exterior ones. Obviously, the energetic consequences of this operation, over so great a distance, are likely to be negligible. Comparison with the corresponding interaction of two ribbons in a longicyclic topology reveals, once again, that ψp mixes with ψp to produce ψp_s and ψp_a . Two ψd 's similarly provide ψd_s and ψd_a . Now, however, ψp_s and ψp_a are both at the same level as are ψd_s and ψd_a .

The results of such negligibly weak exterior interactions comprise the central vertical column of Figure 8. As in Figure 7, the two possible interior ribbons are introduced from the extreme left and right. With permutational invariance incomplete, the new notation ($0 + 2 + 2$) or ($2 + 2 + 0$) explicitly means that the interior ribbon is mode 2 and the exterior ones 0 and 2. We also identify the occupied laticyclic orbitals as symmetric (s) or antisymmetric (a) with respect to the pseudo-plane of the interior ribbon.

The results are revealed as a hierarchal ordering. Two laticyclics lack stabilization: ($0 + 0 + 0$) and ($2 + 2 + 2$). Two others are stabilized because of a single interaction, ($0 + 0 + 2$) and ($2 + 2 + 0$), and two are stabilized by two interactions, ($0 + 2 + 0$) and

(42) A. Allerhand and H. S. Gutowsky, *J. Amer. Chem. Soc.*, **87**, 4092 (1965).

(43) F. A. L. Anet and G. E. Schenck, *Tetrahedron Lett.*, 4237 (1970).

(44) R. Hoffmann and W.-D. Stohrer, to be published.

(45) K. Hojo, R. T. Seidner, and S. Masamune, *J. Amer. Chem. Soc.*, **92**, 6641 (1970); T. J. Katz, J. J. Cheung, and N. Acton, *ibid.*, **92**, 6643 (1970).

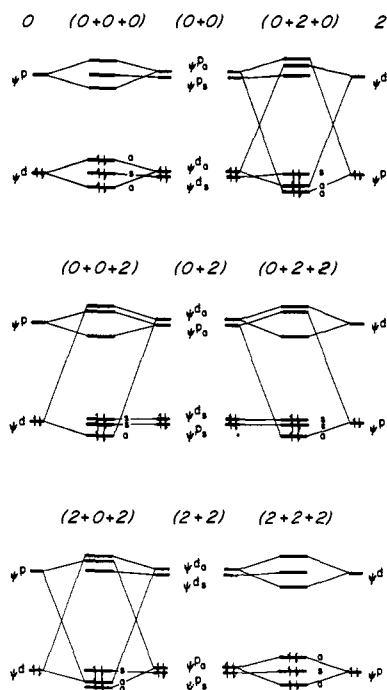


Figure 8. Interaction diagrams for the laticyclic topology. See text for explanation.

(2 + 0 + 2). As an appropriate example, we predict stabilization to fall off in the sequence **24** ($2^0 1 + 2^0$) > **25** ($2^0 2^0 1 +$) > **26** ($2^0 3 + 2^0$). Although many other similar

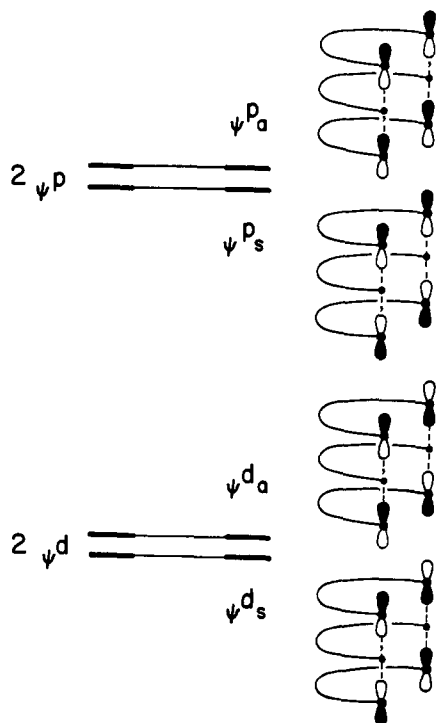


Figure 9. The transformation of a laticyclic topology into a longicyclic one (top) and the corresponding additional interactions for symmetric (middle) and antisymmetric (bottom) orbitals.

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 ψ_p and ψ_d . Those occupied orbitals which are s with respect to this plane are stabilized by the transformation. Those which are a are destabilized.

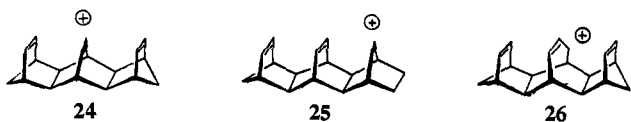
Referring back to Figure 8, we see that the singly stabilized laticyclics, (0 + 0 + 2) and (2 + 2 + 0), possess two occupied s orbitals and one occupied a. These laticyclics will therefore be stabilized by longicyclic formation. The doubly stabilized laticyclics, (0 + 2 + 0) and (2 + 0 + 0), possessing 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.⁴⁶ It is then a trivial exercise to show, for example, that the relative stabilities of the four-ribbon

predictions are equally accessible, no currently available experimental evidence that we know bears on any of them.



(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^a

| Most stable | |
|--------------|--|
| Longicyclic | (0, 2, 0, 2) |
| Laticyclic | (0 + 2 + 0 + 2) |
| Laticyclic | (0 + 2 + 2 + 0) (2 + 0 + 0 + 2) (2 + 2 + 0 + 2) (0 + 0 + 2 + 0) |
| Longicyclic | (0, 2, 2, 0) (2, 2, 0, 2) (0, 0, 2, 0) |
| Laticyclic | (0 + 0 + 0 + 0) (2 + 2 + 2 + 2) |
| Longicyclic | (0, 0, 0, 0) (2, 2, 2, 2) |
| Least stable | |

^a No distinction is made among those hydrocarbons grouped together.

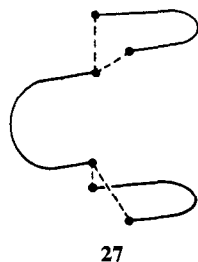
laticyclics and longicyclics fall in the order shown in Table III.

Every topology requires its own analysis of the constraints on orbital interaction. For example, the array **27** precludes all interactions except those between ψ_p of the unique central ribbon with the ψ_{d_s} composite of the other two, or ψ_d of the central ribbon with ψ_{d_a} of the exterior two. As a result, Table IV reveals an

Table IV. Comparison of Two Three-Ribbon Topologies

| | Laticyclic | 27 |
|-------------------|----------------------------|--|
| Doubly stabilized | (2 + 0 + 2) (0 + 2 + 0) | (0 + 0 + 2) |
| Singly stabilized | (0 + 0 + 2) (0 + 2 + 2) | (0 + 0 + 0) (0 + 2 + 0) (2 + 0 + 2) (2 + 2 + 2) |
| Not stabilized | (0 + 0 + 0) (2 + 2 + 2) | (0 + 2 + 2) |

amusing contrast to the hierarchy of stabilities determined for the laticyclic case.

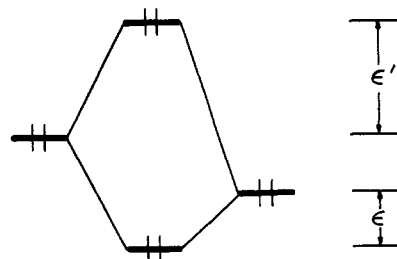


Ancillary Considerations

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

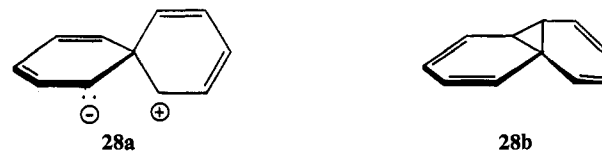


follows from the inclusion of overlap in any quantum mechanical calculation.^{14,48} The destabilization of two interacting electron pairs is further emphasized when electron interaction is explicitly included at higher levels of approximation.⁴⁹ However its origin is described, interaction between occupied 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 ψ_d orbitals. The formally nonbonding ψ_p levels cannot now be split, yet must accommodate two electrons. This is a typical diradical situation.⁵⁰ The degeneracy is most simply

(47) R. Breslow, *Angew. Chem.*, **80**, 573 (1968); *Angew. Chem., Int. Ed. Engl.*, **7**, 565 (1968).

(48) J. N. Murrell, S. F. A. Kettle, and J. M. Tedder, "Valence Theory," Wiley, New York, N. Y., 1965, p 132.

(49) J. C. Slater, "Quantum Theory of Molecules and Solids," Vol. I, McGraw-Hill, New York, N. Y., 1963.

(50) R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968); R. Hoffmann, G. D. Zeiss, and G. W. VanDine, *ibid.*, **90**, 1485 (1968); R.

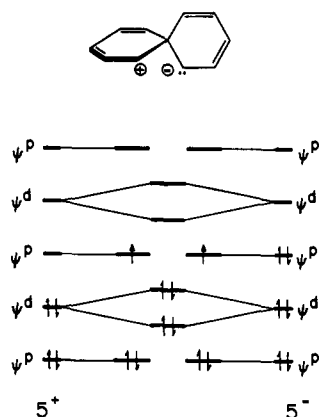
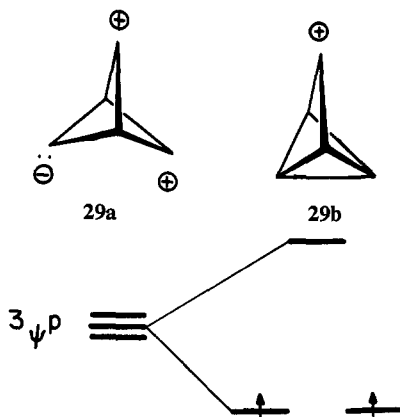


Figure 10. Interaction diagram for the spirocyclic **28**. Note that this is a conventional level diagram, analogous to those drawn in ref 8.

lifted by collapse to the closed form **28b**. More generally, similar conclusions will appear only for those neutral spirocyclics which contain two identical $4q + 1$ ribbons.

The second class also requires odd ribbons of identical length—this time three in a longicyclic array and with a net $1+$ charge. The simplest example here is **29a** whose interaction diagram, shown below, reveals



the half-filled degenerate level pair that results for all such cations of D_{3h} symmetry. Collapse to **29b** again would split the degeneracy.^{44,51}

Charge Type. If we put aside multiply charged species (whether zwitterionic or not), every ion must contain one ribbon with an odd number of atoms, hence an odd number of levels. One of these, the 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 interacts.

An important *quantitative* difference, between the neutral-neutral ribbon interactions which stabilize neutral 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

Gleiter and R. Hoffmann, *ibid.*, 90, 5457 (1968); *Tetrahedron*, 24, 5899 (1968); *Angew. Chem., Int. Ed. Engl.*, 8, 214 (1969); *Angew. Chem.*, 81, 225 (1969); R. Hoffmann, *Chem. Commun.*, 240 (1969).

(51) Only one representative of this series, a phenyl-substituted precursor of **29b**, has been studied: S. Masamune, K. Fukumoto, Y. Yasunari, and D. Darwish, *Tetrahedron Lett.*, 193 (1966).

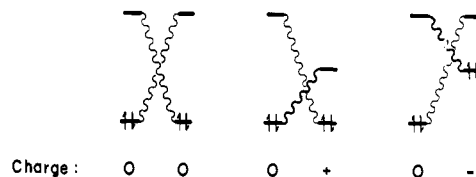
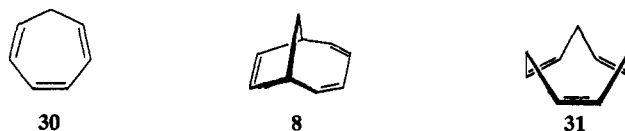


Figure 11. Important interactions between one neutral ribbon and a second neutral (left), cationic (middle), or anionic (right) ribbon.

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 stabilization of ions should exceed those of neutral molecules, irrespective of topology.⁵²

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**).^{53,54} With two interruptions (**8**)



or three (**31**) no trace of the expected pericyclic stabilization is detected, whether measured by the heat of hydrogenation⁵⁵ or by the photoelectron spectroscopically determined position of the higher occupied levels.⁵⁶

By contrast, we have already encountered cations (**11**, **17**) and anions (**10**, **19**), both pericyclic and longicyclic, whose stability is manifest in spite of two interruptions. Still others may be cited.^{28d}

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 reaction



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 symmetry” 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. Consider, for example, the following closely analogous processes: the rearrangement of **32** to semibullvalene **12c**⁵

(52) Assuming, of course, that the ribbon lengths are roughly comparable. For the relationship between interaction energy and energy gap, see ref 14.

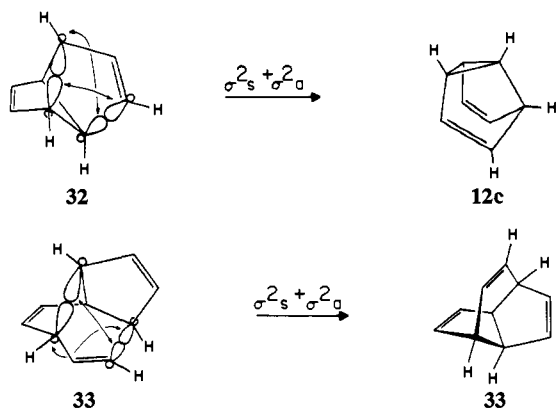
(53) J. B. Conn, G. B. Kistiakowsky, and E. A. Smith, *J. Amer. Chem. Soc.*, 61, 1868 (1939); R. B. Turner, W. R. Meador, W. E. Doering, L. H. Knox, J. R. Mayer, and D. W. Wiley, *ibid.*, 79, 4127 (1957).

(54) Perhaps appropriately, it was this hydrocarbon which first suggested the possibility of interrupted pericyclic stabilization, i.e., “homoaromaticity.” Cf. W. E. Doering, G. Laber, R. Vonderwahl, N. F. Chamberlain, and R. B. Williams, *ibid.*, 78, 5448 (1956).

(55) W. R. Roth, W. P. Bang, P. Goebel, R. L. Sass, R. B. Turner, and A. P. Yu, *ibid.*, 86, 3178 (1964).

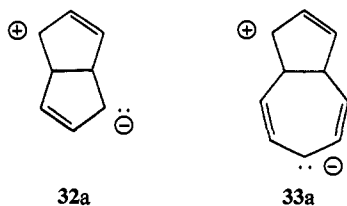
(56) P. Bischof, R. Gleiter, and E. Heilbronner, *Helv. Chim. Acta*, 53, 1425 (1970).

(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. Zimmerman, J. D. Robbins, and J. Schantl, *ibid.*, 91, 5878 (1969).



and the degenerate transformation of **33**.⁵⁸ 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⁻ pericyclics—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 .⁵⁹

The hitherto rarely explored laticyclic topology provides unusual opportunities to vary such parameters. We therefore emphasize that our choice of skeletal frameworks for **24**, **25**, and **26** was little better than arbitrary. Although these do optimize the favorable σ orientation of p orbitals and should be readily accessible, one must always watch out for the ultimate consequence of π -electron stabilization—the formation

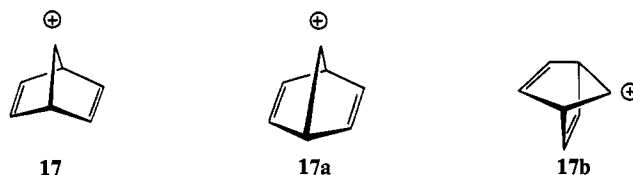
(58) T. J. Katz and J. T. Cheung, *J. Amer. Chem. Soc.*, **91**, 7772 (1969); S. Masamune, H. Zenda, M. Wiesel, N. Nakatsuka, and G. Bigam, *ibid.*, **90**, 2727 (1968).

(59) E. Heilbronner and H. Bock, “Das HMO-Modell und seine Anwendung,” Vol. 3, Verlag Chemie, Weinheim/Bergstr., Germany, 1970, p 247.

of new σ bonds.⁶⁰ The prudent investigator should therefore weigh the practical advantages to be gained from such alternate laticyclic frameworks as, for example, that of **34**.

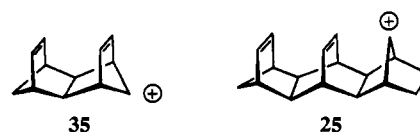


A less obvious geometric factor is the ability of most skeletal frameworks to adjust themselves so as to maximize opportunities for stabilization. The 7-norbornadienyl cation **17** provides a well-known, if unusually complicated example. Our previous discussion of



longicyclic stabilization noted that interactions between the two 2^o ribbons of **17** were destabilizing while those between the 1⁺ and either 2^o 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.^{16,23c,56}

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-



sponding longicyclic, *e.g.*, the 7-norbornadienyl cation **17**. In fact, the *p*-nitrobenzoate of **35** solvolyzes at about the same rate as does the 7-norbornadienyl, presumably because the more flexible tetracyclic **35** more easily accommodates stabilizing distortions.⁶²

Stabilization and Aromaticity

We have described our constructs as “stabilized” whenever interaction between ribbons lowered the consequent electronic energy. In practice, such a “standard state,” the set of isolated ribbons, is a moderately inaccessible one. If for no other reason then, it seems wise to introduce a second adjective. This should instead describe the advantage to be gained by assembling

(60) J. M. Brown, *J. Chem. Soc. B*, 868 (1969).

(61) R. K. Lustgarten, M. Brookhart, and S. Winstein, *J. Amer. Chem. Soc.*, **89**, 6350, 6352 (1967).

(62) E. L. Allred and J. C. Hinshaw, *Tetrahedron Lett.*, 1293 (1968).

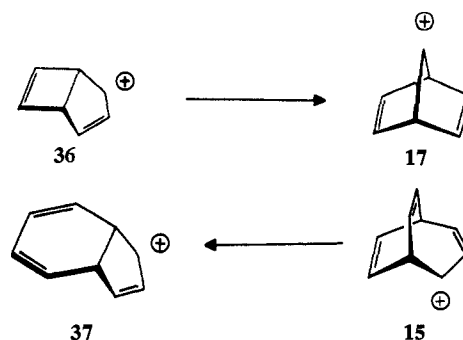
a set of ribbons into one experimentally realizable topology rather than into another.

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.^{14b} 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**,⁶¹ and the destabilized longicyclic **15** to the stabilized pericyclic **37**.^{29,63}

(63) M. J. Goldstein and B. G. Odell, *J. Amer. Chem. Soc.*, **89**, 6356 (1967).



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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