Aromaticity and the Generalized Woodward–Hoffmann Rules for Pericyclic Reactions

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Abstract: The relationship between the generalized Woodward–Hoffmann rules for pericyclic reactions and the Hückel–Möbius rules of aromaticity is discussed, and it is pointed out that, since no formal analysis of the relationship is to be found in the literature, the commonly made assumption of equivalence requires detailed examination. It is shown that any pericyclic reaction is characterized by a *connectivity cycle,* a construct that defines pericycle topology in terms of the nodal properties of the individual basis-set AO's. By use of this construct, it is demonstrated that the generalized Woodward–Hoffmann rules and the aromaticity-based rules for pericyclic reactions are essentially equivalent. No proof of equivalence can be more rigorous than the available definitions of the topological terms "suprafacial" and "antarafacial", and appropriate formal definitions of these terms, more general and more precise than any that have previously been given, are therefore presented and illustrated. Applied to polycyclic transition states, the Woodward–Hoffmann rules and the Hückel–Möbius rules have exactly the same scope and limitations. By means of the connectivity cycle, compact new topological rules equivalent to the Hückel–Möbius rules are deduced for thermal and photochemical pericyclic reactions.

In a pericyclic reaction, by definition,[1] a concerted reorganization of bonds occurs around a ring of atoms. At any point along the reaction coordinate (except, usually, the initial and final points), a set of electrons (the *mobile* electrons) are cyclically delocalized over the reacting centers (and in many cases, over other rings as well). Current generalized treatments of pericyclic reactions isolate the mobile electrons and the ring, or network, of atoms over which they are delocalized (the *pericycle*) and are concerned, basically, with the dual control exercised over the process by (i) the number of mobile electrons and (ii) the topology of the pericycle. Thus, a pericyclic reaction is categorized as *allowed* or *forbidden* in terms of a special twofold condition, irrespective of classical effects (steric, inductive, angle strain, etc.) that can (and probably do in certain cases) prevent the "allowed" reaction or facilitate the "forbidden" one. Ultimately, then, any rules for pericyclic reactions are simply a means of probing qualitatively (and therefore with some assurance of generality) the effect of this electron-number-cum-topology duality upon the shapes of potential-energy surfaces in the region of possible reaction paths, a process being allowed thermally if this factor imposes no energy barrier upon the ground-state surface, and allowed photochemically if the effect is to create an energy well[2] or funnel[3] in the excited-state surface. Since a necessary concomitant of the excited-state funnel (or well) is a ground-state energy barrier,[2-5] it is easy to understand why the rules for thermal and photochemical pericyclic reactions should be antithetical. There is a simple and natural connection between such ideas and those of aromaticity and antiaromaticity, especially now that the latter concepts have acquired a topological content through Heilbronner's discussion of Möbius annulenes[7] and the subsequently formulated $4n$ rule for aromaticity in Möbius,[8] or anti-Hückel,[9] arrays. Reflecting this connection, which now has strong support from both MO[4,8,9] and VB[10] theory, various treatments exist based upon the idea (termed "Evans' principle" by Dewar)[9] that the theory of pericyclic reactions is simply the theory of aromaticity applied to transition states (an idea that has a very general appeal, bringing together, as it does, two considerable tracts of chemical theory). For such reasons, as well as for simplicity of application, perhaps the most satisfying of current generalized treatments of pericyclic reactions are those due to Zimmerman[8] and Dewar.[9] Each of these methods has its particular advantages: Zimmerman's, as an interface between the aromaticity approach and the use of correlation diagrams;[1,2b,8,11] Dewar's, in its applicability to pericycles containing more than one ring and therefore not necessarily subject to the Hückel–Möbius $(4n + 2)/4n$ rules of aromaticity.

Woodward and Hoffmann's generalization,[12] involving rules based on the parity of the total number of $(4q + 2)_s$ and $(4r)_a$ components, by contrast appears somewhat esoteric and *sui generis,* though it has the special attraction for the organic chemist that it fixes attention upon conventional chemical bonds and stereochemistry, rather than upon MO or VB theory. In a sense, this is its particular strength: it is not beyond conception that the generalized component rules (WH rules), being formulated in classical terms, might survive any drastic future revolution in bonding theory.[13] Almost, their very success ensures as much; any theory of bonding must necessarily accommodate, if not the WH rules themselves, then at least something very like them. Yet, at the present time, when an essential unity might justifiably be sought behind all the various approaches, the exact status of the WH rules remains obscure. Woodward and Hoffmann remark[12] that the generalized rules may be proved by induction from the rules for two-component cycloadditions.[14] Given rigorous and appropriately generalized definitions of the topological terms "antarafacial" and "suprafacial" this is indeed so, but no such definitions have yet been advanced in the literature. Moreover, an inductive proof of this type leaves unanswered various questions. Are the WH rules fundamentally equivalent to the aromaticity-based rules for pericyclic reactions? Or do the latter imply some similar, but not identical, set of "classical" rules? And if not identical, which set has the wider scope? The proposition that they are equivalent (tacitly accepted, it appears, by most authors) might be defended on the grounds that the two kinds of approach seem to agree well in their predictions. However, current agreement does not constitute formal proof.

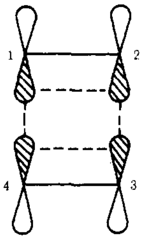
It is demonstrated formally in this paper that Woodward and Hoffmann's generalization and the theory of aromatic transition states are essentially equivalent (which strengthens one's faith in the former and ensures the potential "survival-value" of a classical base to the latter). Several novel points of interest arise therefrom.

Nodal Patterns and the Connectivity Cycle

The theory of aromatic transition states is based on the assumption that the rules for thermally and photochemically allowed pericyclic reactions are identical with the rules for aromaticity and antiaromaticity, respectively.[15] The practical value of this approach depends upon the existence of simple criteria for aromaticity in transition states. These criteria have been given with particular elegance by both Zimmerman[8] and Dewar[9] in terms of the topology of the AO-overlap connections in the pericycle. Since the relevant AO's (the *basis set*, over which the mobile electrons are delocalized) may form one or more closed cycles of overlap connections, it is evident that pericycles exist at various levels of complexity. Initially, we confine discussion to cases in which the basis-set AO's overlap in a *single* closed cycle, the immediate aim being to deduce the WH rules from the rules for aromaticity in monocycles. More complex pericycles are considered in the final section.

As there is general agreement upon the rules for aromaticity in monocycles, it is immaterial which method is taken as starting point. However, in view of the form of argument to be employed here, it will be most convenient to adopt Zimmerman's treatment.[8] In this, one considers the sign of the overlap integral between adjacent members of the basis set of AO's. The AO phases can be assigned arbitrarily, but the parity (oddness or evenness) of the total number Z of negative overlaps in the basis set is invariant for a given pericycle topology. Systems with Z even and Z odd are described as Hückel and Möbius systems, respectively. The significance of these terms has been discussed fully by Heilbronner[7] and Zimmerman,[8] and it will suffice here to say that the parity of Z allows one to infer the HMO energy-level pattern of the pericycle and so to determine whether a given pericycle is aromatic or antiaromatic. Zimmerman's rules for allowed pericyclic reactions are given in Table I, in which $2m$ is the total number of mobile electrons, and n is any positive integer (or additionally zero in the $4n + 2$ case).

To exemplify Zimmerman's procedure for analyzing pericyclic reactions, a $[_{\pi}2_s + {_{\pi}2_s}]$ cycloaddition is illustrated in formula **1**, in which the shaded and unshaded lobes represent positive and negative regions, respectively, of the four basis-set AO's, and the dashed lines indicate the overlaps within the pericycle. All overlapping lobes have the same sign, Z (=0) is therefore even, and the system has Hückel topology. Since $2m = 4$, the reaction is photochemically allowed (and, of course, thermally forbidden). Alternative, but completely equivalent, ways of considering the system are shown in **2** and **3**. In **2**, Z is again zero; in **3**, where the basis set is chosen differently, $Z = 2$. In either case, Z is even, and we reach exactly the same conclusion as in the first analysis.



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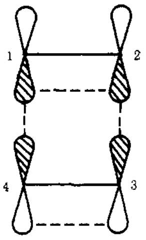

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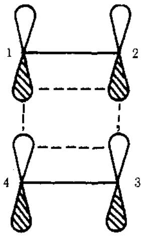

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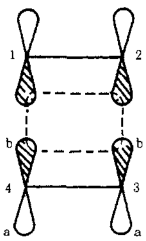

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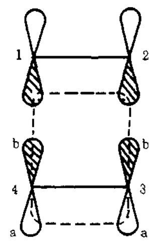

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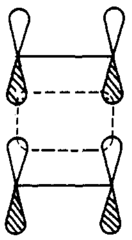

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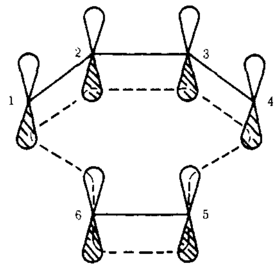

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Table I. Zimmerman's Rules for Allowed Pericyclic Reactions

Z	Topology	$2m$ Thermal	$2m$ Photochemical
Even	Hückel	$4n + 2$	$4n$
Odd	Möbius	$4n$	$4n + 2$

We now define a *connectivity cycle* as a continuous closed curve that passes through one or more lobes (or, more precisely, regions of nonzero wave function) of each basis-set AO in the pericycle, makes a single direct connection between each pair of adjacent overlapping AO's, and does not directly connect any nonoverlapping pair of lobes.

Connectivity cycles are easily obtained for a $[_{\pi}2_s + {_{\pi}2_s}]$ cycloaddition by joining up adjacent ends of the dashed lines indicating the overlaps in **1**, **2**, and **3**. The resulting connectivity cycles are shown in **4**, **5**, and **6**, respectively. All three are equally valid connectivity cycles for the $[_{\pi}2_s + {_{\pi}2_s}]$ process. There exist several other possibilities, which are easily constructed. In fact, connectivity cycles can be chosen with considerable freedom. To avoid a possible confusion, however, it should be pointed out that, for pericyclic reactions in which there is a single closed cycle of AO's, the connectivity cycle, too, must be monocyclic. We do not, for example, simultaneously make the connections 3a-4a and 3b-4b in **4** and **5**. An extra connection here would lead to a *bicyclic* connectivity cycle, which is not equivalent topologically to the monocyclic AO set. Hence the necessity for the word "single" in the definition of a connectivity cycle.

The parity of Z may be determined from diagrams such as **4**-**6** exactly as before, but note that, though essentially a purely mathematical construct, the connectivity cycle does draw our attention to a feature that does not enter explicitly into Zimmerman's treatment, namely, the nodal characteristics of the individual basis-set AO's: in **5**, the connectivity cycle is intersected by the node of AO-3 in passing from lobe b to lobe a, and likewise at atom 4; in **4** and **6**, on the other hand, the connectivity cycle is intersected by no AO nodes. A further example is shown in **7**, which illustrates one possible basis set and connectivity cycle (not the simplest!) for the thermally allowed Diels-Alder reaction. Here the cycle crosses two AO nodes (atoms 5 and 6) and two regions of negative overlap (overlaps 1-6 and 4-5). With these points in mind, we now turn to the generalized pericyclic reaction.

To any pericyclic reaction, assign a basis set and a connectivity cycle. As will be appreciated from **5** and **7**, the connectivity cycle will in general pass through both positive and negative AO regions. A sign inversion occurs upon the connectivity cycle whenever the latter passes (i) across a region of negative overlap or (ii) across the local[16] nodal surface of an AO. Let Z be the number of negative overlaps in the basis set, as before, and N the number of local nodal intersections of the connectivity cycle. The total number of sign inversions upon the connectivity cycle is thus $N + Z$. Now make a complete circuit round the connectivity cycle, starting with a given AO lobe. The sign of this lobe is of course fixed by one's prior assignment of the basis set. Con-

Table II. Connectivity Rules for Allowed Pericyclic Reactions

N	Topology	$2m$	
		Thermal	Photochemical
Even	Hückel	$4n + 2$	$4n$
Odd	Möbius	$4n$	$4n + 2$

sequently, between leaving and reentering this lobe to complete the circuit, one will of necessity encounter an *even number* of sign inversions. Hence $N + Z$ is even. Always, then, N and Z are either both even or both odd. Thus, it follows that, *for any cycle, the number of negative overlaps* (Z) *and the number of local nodal intersections* (N) *must have the same parity.*

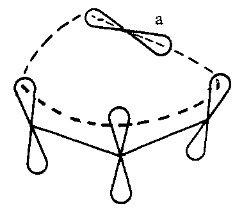
Having established this connection between N and Z, we may choose either as topological invariant for the pericycle. If we choose N, we are led to a new set of rules for allowed pericyclic reactions, as summarized in Table II. These rules can be applied without reference to the relative phases of the different AO's in the basis-set diagram; we merely count the number of times an arbitrarily chosen connectivity cycle is intersected by an AO node. Since $4n + 2$ and $4n$ represent opposite parities of m, the connectivity rules of Table II can obviously be summarized in the compact form of (1) and (2), which bring out well the twofold nature of

Thermally allowed
(aromatic transition state): $m + N$ is odd (1)

Photochemically allowed
(antiaromatic transition state): $m + N$ is even (2)

the conditions for allowed pericyclic reactions. Analogous statements in terms of m and Z are easily derivable from Table I.[17]

Formulas **8** and **9** illustrate the application of the connectivity rules to a [1,3] sigmatropic shift in which the atom at a migrates with inversion of configuration along the face of the lower three-center system. **8** and **9** are equivalent, simply representing alternative choices of connectivity cycle. In **8,** there is one nodal crossing (at a), and in **9** there are three (at a, b, and c). In both cases, N is odd and, as a four-electron process ($m = 2$), the reaction is allowed thermally. Analogously, $[_{\pi}2_s + {}_{\pi}2_s]$ and Diels-Alder cycloaddition can be analyzed readily by reference to formulas **4-7**.



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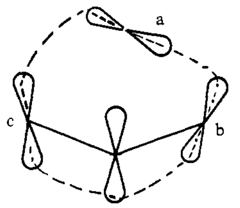

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The idea of a connectivity cycle is, of course, not restricted to pericycles, but can, with an obvious slight modification of wording in the definition, be applied to the static overlap situation in a stable molecule. Thus, rule 1 can also be regarded as a general rule for aromaticity in stable molecules, combining the original Hückel $4n + 2$ rule and the $4n$ rule for Möbius annulenes. In fact, just about the simplest possible statement of the aromaticity rules for monocycles in terms of topology and number of mobile electrons is that a monocyclically conjugated system will be aromatic if $m + N$ is odd.

Components and the Component Rules for Allowed Pericyclic Reactions

The basis set of AO's can be arbitrarily dissected into subsets, each containing one or more AO's. If we specify that no AO shall belong to more than one subset and that, in any subset containing more than one AO, the AO's shall be linearly connected (i.e., form an unbroken chain of nearest neighbor overlap connections in the pericycle), we can make a transition to a more "chemical" way of treating pericyclic reactions.

Accordingly, we choose each subset, defined as above, as the group of AO's corresponding to some chemical grouping (C=C, C=C—C=C, C—C, etc.) that is present in the reactant(s) and directly involved in the pericyclic process (i.e., undergoes a first-order change in bonding relationships in the reaction).[12] Occasionally, one or more subsets will be single AO units (if, for example, a lone pair is involved). We term these chemically discrete (or putatively discrete) units *components*. There is no loss of generality if we restrict consideration to *even-electron* components, for aromaticity and antiaromaticity are associated with even-electron systems, and any even-electron system can always be dissected into a set of components none of which contains an odd number of electrons. The number of electrons in a component must therefore be of the form $4q + 2$ or $4r$, where q and r are nonnegative integers.

Let an integer m_i be associated with the ith component in a pericyclic reaction such that $2m_i$ is the number of mobile electrons that this component contributes to the pericycle. m_i is thus odd or even, respectively, according as the number of electrons contributed is of the form $4q + 2$ or $4r$. Also, let N_i be the number of local nodal intersections of the connectivity cycle occurring within the ith component. N_i, like m_i, may be odd or even. Clearly, if the total number of components is ν

$$m = \sum_{i=1}^{\nu} m_i \text{ and } N = \sum_{i=1}^{\nu} N_i$$

and therefore

$$m + N = \sum_{i=1}^{\nu} (m_i + N_i) \qquad (3)$$

We are now concerned to deduce from rules 1 and 2, which were formulated in terms of the properties of the entire pericycle, equivalent rules formulated in terms of the properties of individual components. Since the argument involves parities rather than the absolute values of integers, it is convenient to divide the terms in the summation on the rhs of (3) into two groups, according as $m_i + N_i$ is even or odd. Correspondingly, we recognize two classes of component:

Class-0 components: $m_i + N_i$ even; total number $\nu(0)$
Class-1 components: $m_i + N_i$ odd; total number $\nu(1)$

the 0,1 notation being adopted simply because 0 and 1 are the least nonnegative residues of $m_i + N_i$ to modulus 2 for the two classes[19] (i.e., the smallest nonnegative integers having the same parity as $m_i + N_i$). Equation 3 may now be expanded to give 4,

$$m + N = \sum_{j=1}^{\nu(0)} (m_j + N_j) + \sum_{k=1}^{\nu(1)} (m_k + N_k) \qquad (4)$$

the new suffixes j and k being introduced because the even terms (j) and the odd terms (k) are now to be enumerated separately, rather than by a single sequence of integers. Now, since any even number is congruent (mod 2) to zero and to any other even number, and any odd number to 1 and to any other odd number,[19] we have, by definition

$$m_j + N_j \equiv 0 \pmod 2 \qquad (5)$$

and

$$m_k + N_k \equiv 1 \qquad (6)$$

and eq 4 therefore reduces to the congruence

$$m + N \equiv \sum_{k=1}^{\nu(1)} 1$$

the first summation on the rhs of eq 4 having vanished and the second collapsed to the number 1 taken $\nu(1)$ times. Hence

$$m + N \equiv \nu(1)$$

or, in words, *in any pericyclic reaction, $m + N$ and $\nu(1)$ must have the same parity.*[20] Combining this statement with the connectivity rules, 1 and 2, we obtain (7) and (8)

$$\text{Aromatic transition state (thermally allowed):} \quad \nu(1) \text{ is odd} \tag{7}$$

$$\text{Antiaromatic transition state (photochemically allowed):} \quad \nu(1) \text{ is even} \tag{8}$$

as the necessary conditions for transition-state aromaticity and antiaromaticity in terms of the parity of $\nu(1)$. To show that these conditions are also sufficient, suppose that a pericyclic reaction exists having $\nu(1)$ odd and a transition state that is not aromatic. Not being aromatic, the transition state must be either antiaromatic or noncyclically delocalized. The latter possibility was excluded at the outset by the definition of a pericyclic reaction, and consequently the transition state must be antiaromatic. But, by (8), it then follows that $\nu(1)$ must be *even*, which conclusion is absurd since it contradicts the original assumption. Hence, *every* pericyclic transition state having $\nu(1)$ odd must be aromatic. Likewise, every one with $\nu(1)$ even must be antiaromatic. Sufficiency is therefore established. Thus, viewed as component rules for allowed pericyclic reactions, (7) and (8) are coextensive with (1) and (2), respectively; they hold for all single closed cycles of overlap and, strictly, *only* for single cycles.

For the class-1 components, to which (7) and (8) refer, $m_i + N_i$ is odd, which means that m_i and N_i have opposite parities. These components are therefore of two types: $(4q + 2)$-electron components with N_i even, and $(4r)$-electron components with N_i odd. If a component is denoted

$$\text{A if } N_i \text{ is odd and S if } N_i \text{ is even} \tag{9}$$

and these symbols are suffixed to $(4q + 2)$ and $(4r)$, representing the number of electrons in the component, we obtain the component notation that is shown in Table III (q, r, A, S column) along with the m_i,N_i parity equivalents. The component rules may now be given a more "Woodward-Hoffmann" appearance, as in statement 10 for the thermal case.

A thermal pericyclic reaction is allowed if, and only if, the total number of $(4r)_A$ and $(4q + 2)_S$ components is odd (10)

The analogous photochemical condition follows obviously from (8). The relationship of A and S to the terms "antarafacial" and "suprafacial" of the actual WH rules is discussed in the next section.

There exist various methods (differing in degrees of elegance, conciseness, and instructiveness) of reaching this point from the basic aromaticity rules, but that above brings out better than most the complementariness of topology and number of electrons and perhaps also affords some insight into the nature of components. So far as determining the allowedness or forbiddenness of a pericyclic reaction is concerned, a component is fully defined by the parity of its sum $m_i + N_i$. In this respect, there are only two types of component, classes 0 and 1 in Table III, and we see clearly from congruences 5 and 6 why only the latter class has determinative significance. But chemistry demands a sharper distinction; it is usually necessary to specify the parities of m_i and N_i separately (m_i,N_i column of Table III). The chief reason for this is that, normally, we seek to predict permitted topologies of reaction for a particular set of chemical groupings, containing specified numbers of electrons; i.e., given a fixed set of m_i's, we seek to deduce permitted sets of N_i's. Chemical exigencies, then, necessitate four categories of component. What fourfold symbolism one selects will be largely a matter of taste and custom, but some advantage may attach to a numerical notation, e.g., (m_i,N_i) with m_i and N_i written as their least residues (mod 2).[19] The four sets of components then become (0,0), (0,1), (1,0), and (1,1), as shown in Table III, the two "pericyclically" distinct categories ($m_i + N_i$ odd and even) being distinguished by the least residue sum of the two numbers within the brackets. This notation is presented here not with any real hope that it will supplant existing symbolisms, but rather with the idea that, in an essentially topological problem, it is instructive to identify numerical invariants.

Table III. Classification of Components

	Least residues of (m_i,N_i)	$m_i + N_i$	m_i,N_i	q, r, A, S notation
Class 0	(0,0)	0	Even, even	$(4r)_S$
	(1,1)	0	Odd, odd	$(4q + 2)_A$
Class 1	(0,1)	1	Even, odd	$(4r)_A$
	(1,0)	1	Odd, even	$(4q + 2)_S$

"Antarafacial", "Suprafacial", and the Generalized Woodward-Hoffmann Rules

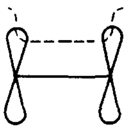
The generalized Woodward-Hoffmann rule for thermal reactions[12] is contained in (11), where $(4q + 2)$ and $(4r)$ have the same significance as in the foregoing discussion, and s and a denote *suprafacial* and *antarafacial*, respectively.

A ground-state pericyclic change is symmetry allowed when the total number of $(4q + 2)_s$ and $(4r)_a$ components is odd (11)

The term "symmetry-allowed" effectively means no more than "will proceed easily", as does our term "allowed". (Except in certain special cases, symmetry, in the strict sense, is irrelevant to pericyclic reactions.) Rules 10 and 11 for thermal (i.e., ground-state) pericyclic reactions are therefore equivalent provided that (and this is no trivial point) our terms A and S are equivalent to the Woodward-Hoffmann terms "antarafacial" and "suprafacial", respectively. Similar comments, of course, apply to the corresponding photochemical rules. It therefore remains to establish a relationship between A and S, on the one hand, and "antarafacial" and "suprafacial" on the other.

By definition 9, a component is A if the total number of local nodal intersections of the connectivity cycle within that component is odd, and S if the total number is even. The idea, which is clearly apparent throughout Woodward and Hoffmann's work,[1] that bonds are made or broken upon the same side of a nodal surface in a suprafacial process and upon opposite sides in an antarafacial process is strongly suggestive of equivalence, and this equivalence is, in fact, readily demonstrated for most ordinary types of component.

Consider a planar π system participating as an S component. The connectivity cycle undergoes an even number of AO nodal intersections within the component, i.e., crosses the molecular (π-nodal) plane an even number of times, and must therefore enter at and leave from the same face of the π system. Bonding interactions therefore develop during reaction at two AO lobes situated upon the same face of the π system. Diagrams **10-13** illustrate the situation for C=C


$S(N_i = 0)$
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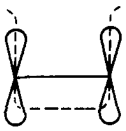
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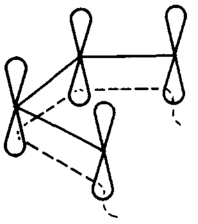
$S(N_i = 0)$
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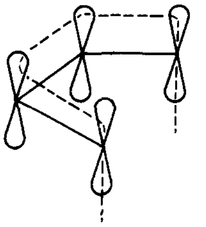
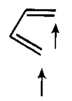
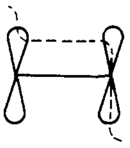
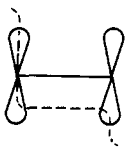

$S(N_i = 2)$
13


suprafacial
14


suprafacial
15

and C=C—C=C acting as S components; **10** and **11** are of course equivalent, merely corresponding to different choices of connectivity cycle, as is also the case with **12** and **13.** In an A-type π component, on the other hand, the connectivity cycle crosses the molecular plane an odd number of times (N_i odd) and must therefore enter at and leave from opposite faces of the π system; i.e., the two new bonding interactions develop upon opposite faces of the π system (cf. **16**–**19**). For any planar π component, then, S necessarily implies the formation of bonds to the same side of the molecular plane, and A the formation of bonds to opposite sides. Hence, applied to π components, S and A correspond exactly to "suprafacial" and "antarafacial", respectively, as defined and illustrated by Woodward and Hoffmann[21] (cf. **14, 15, 20,** and **21** in which the new bonds are formed in the senses indicated by the arrows).


$A(N_i = 1)$
16


$A(N_i = 1)$
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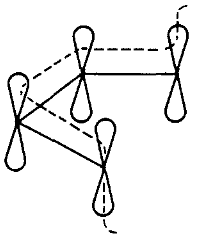
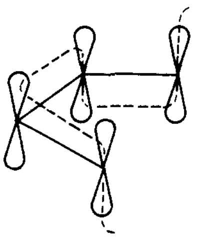
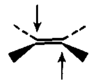
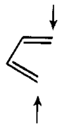

$A(N_i = 1)$
18


$A(N_i = 3)$
19


antarafacial
20


antarafacial
21

For σ bonds derived from two sp^3-type AO's, there are two separate nodes, one at each atom, and so N_i is 0, 1, or 2. Passage of the connectivity cycle through a node at one of the termini implies that, as the original σ bond breaks, that terminus forms a new bond via its rear lobe, i.e., with inversion of configuration. On the other hand, a terminus at which there is no nodal intersection forms a new bond with retention of configuration. The possibilities are shown in **22**–**24,** in which r and i indicate retention and inversion of

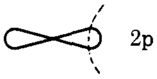
$S(N_i = 0)$
22

$A(N_i = 1)$
23

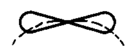
$S(N_i = 2)$
24

configuration, respectively. The stereochemical consequences of the modes A and S are thus: A, ir or ri; S, rr or ii. Here again, there is precise agreement with the antarafacial (ir, ri)–suprafacial (rr, ii) terminology.[14]

An isolated 2p or sp^3 AO presents no difficulty; **25** and **27** are clearly both S and suprafacial, and **26** and **28** both A and antarafacial.



25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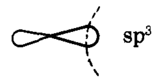

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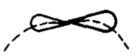
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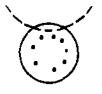
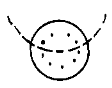
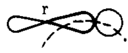
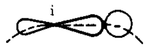

$N_i = 0$
29


$N_i = 2$
30



$N_i = 0$
31



$N_i = 1$
32

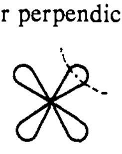
The equivalence of the A–S and the antarafacial–suprafacial terminology thus holds for all the cases that Woodward and Hoffmann have discussed explicitly. It is not possible to give formal proof of equivalence in the general case, the reason being simply that no formal general definitions of the terms "antarafacial" and "suprafacial" exist in the literature. However, precisely because such definitions do not exist, it is justifiable at this point to invent them. Accordingly, we shall now assert the identity of "antarafacial" and "suprafacial" with, respectively, A and S. Since A and S are already defined in connectivity terms by virtue of (9), our proposed definitions of the Woodward–Hoffmann terms can be stated as in (12). This statement is exact and

A component is antarafacial if the total number of
local nodal intersections of the connectivity cycle
occurring within that component is odd,
and suprafacial if the total number is even (12)

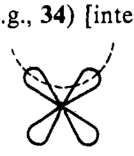
completely general, and it contravenes no valid statement existing or implied in the literature as to the meaning of "antarafacial" and "suprafacial". Rules 10 and 11 now become exactly equivalent, as do the corresponding photochemical rules. Therefore, if (12) is accepted, the generalized WH rules follow directly from rules 1 and 2 and have precisely the same scope; they hold wherever the Hückel–Heilbronner rules of aromaticity are valid. Hence, for *monocyclic* transition states, the WH rules and the theory of aromatic transition states will invariably make identical predictions. In this sense, the two kinds of approach are equivalent.

The connectivity-cycle approach affords a simple, general, and rigorous method of categorizing any conceivable type of component. For example, an isolated 1s orbital is invariably S (no nodes), as is an isolated 2s orbital, whether or not the connectivity cycle passes through the spherical node (shown as a dotted circle in **29** and **30**); a C–H bond is S if the configuration of the carbon atom is retained (**31**), and A if the configuration is inverted (**32**); the treatment of an isolated d orbital is straightforward (cf. **33**–**35**).

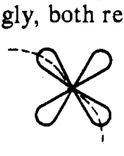
It will be appreciated that A and S, as determined for any given component by the connectivity procedure, can always then be redefined for that particular component in purely geometric, or stereochemical terms. Consider, for example, the statement above on the C–H bond. Also, consider two d-orbital examples. A single-atom component participating through a d orbital can be classified according as the bonds being made and broken are collinear (e.g., **33** and **35**) or perpendicular (e.g., **34**) [interestingly, both retention



S(N_i = 0)
33

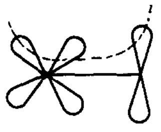


A(N_i = 1)
34

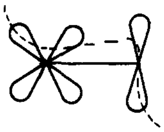


S(N_i = 2)
35

(**33**) and inversion (**35**) are suprafacial, in contrast to the p or sp^3 orbital case (**25–28**)]. For a d_π–p_π bond participating as in **36** or **37**, antarafacial is cis and suprafacial trans (the reverse of the situation for a p_π–p_π bond, e.g., **10** and **16**).[22] We could draw up a set of such "chemical" definitions, thereby preserving any advantage that the generalized Woodward–Hoffmann rules may possess by virtue of their purely geometric formalism.



A(N_i = 1)
36



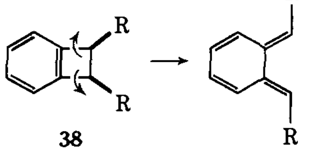
S(N_i = 2)
37

Polycyclic Transition States

Whilst the Hückel-Möbius rules of aromaticity are strictly applicable only to monocycles, their extension to individual rings within a polycyclic network is now strongly justified by several different theoretical approaches, including the PMO[9] and VB[10b] methods and graph theory.[24] Indeed, it appears in general more fruitful to employ this piecemeal, or analytic, approach to aromaticity in polycycles [and, for instance, to relate the properties of biphenylene to the presence in the molecule of two aromatic (benzenoid) rings and an antiaromatic (cyclobutadienoid) ring] than to treat aromaticity and antiaromaticity as unitary qualities characterizing a polycyclic system as a whole, for which treatment there exist no obvious generally applicable criteria.[25] As regards polycyclic transition states, the power of the analytic approach is amply demonstrated in Dewar's discussions[9] of pericyclic reactions from the standpoint of the PMO method.

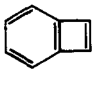
Given this approach of isolating individual rings, together with the fact, established in the foregoing, that the generalized WH rules and the Hückel-Möbius rules are merely alternative statements of the same basic idea concerning monocyclic systems, it is readily understandable that the WH rules should normally be successful when applied to a pericyclic shift of bonds round a particular ring embedded in a more complex network.

Thus, to describe the disrotatory electrocyclic ring opening of benzocyclobutenes (eq 13) as a [$_\pi2_s$ + $_\sigma2_s$] process,



38 (13)

and therefore as thermally forbidden by the WH rules, has exactly the same status as the alternative description in terms of a transition state isoconjugate with planar benzocyclobutadiene (**39**) and therefore destabilized by the presence of an antiaromatic, four-membered Hückel ring. In both descriptions, the process is reduced to an analog of the electrocyclic ring opening of cyclobutene. We might, instead, reduce it to an analog of cycloocta-1,3,5-triene ring opening by focusing attention upon the entire periphery of the reacting system, which corresponds to the eight-membered Hückel ring of **39**. On this basis, we can describe disrotatory ring opening in WH terms as a thermally forbidden [$_\pi2_s$ + $_\pi2_s$ + $_\pi2_s$ + $_\sigma2_s$] process (a representation appropriate to the other Kekulé structure of **38**) and, in doing so, we are simply translating into the language of components the statement that the outer eight-membered ring of the isoconjugate system (**39**) is antiaromatic.



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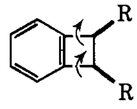
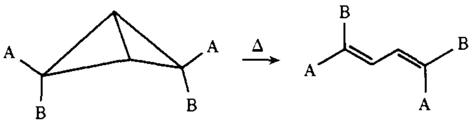


40

41

Analogous parallels are easily seen in the corresponding conrotatory case (**40**), which in a convenient notation may be represented by the connectivity network **41**, in which the sign ~ indicates the Möbius topology of the two 4*n* circuits.[27] There is an exact correspondence between the [$_\pi2_s$ + $_\sigma2_a$] formulation and the presence of a four-atom Möbius circuit or, to choose the outer path, between [$_\pi2_s$ + $_\pi2_s$ + $_\pi2_s$ + $_\sigma2_a$] and the presence of an eight-atom Möbius circuit. Examples of this thermally allowed conrotatory process are known.[28]

The stereospecific[29] thermal ring opening of bicyclobutanes (eq 14) illustrates another aspect of the isolated-ring approach. The reaction is categorized as a [$_\sigma2_s$ + $_\sigma2_a$] process (**42**),[30] which conforms to the generalized WH rule. Any possible influence that the "off-circuit" transannular 1,3 interaction might exert upon the process is neglected in this analysis, but the neglect is easily justified. The transition state is isoconjugate with Möbius bicyclobutadiene (connectivity network **43**) and, since there are good theoretical reasons[9,10b] for deleting the 1,3 link as an *essential single bond*,[9] the network is reducible to a Möbius cyclobutadiene cycle (**44**). The photochemical conversion of hexa-1,3,5-trienes into bicyclo[3.1.0]hexenes (eq 15) involves a similar "off-circuit" interaction. The two allowed modes, [$_\pi4_s$ + $_\pi2_a$] and [$_\pi4_a$ + $_\pi2_s$],[31] strictly have connectivity networks **45** and **46**, respectively, but these both reduce to Möbius benzene upon deletion of the transannular essential single bond.



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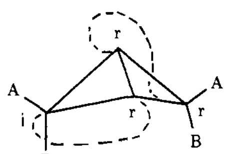

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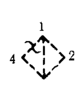

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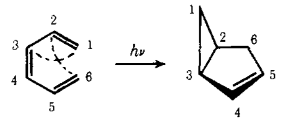

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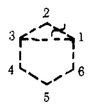

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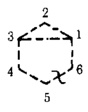
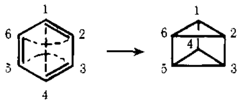


46

In the light of these parallels, it might be considered feasible to construct, in essentially classical chemical terms, a completely general treatment of pericyclic reactions resting upon the twofold base of the 4*n*/(4*n* + 2) rules and the isolated-ring approach to polycycles, but otherwise independent of current theories of bonding. Indeed, the essential single bond is effectively a classical concept, for the term refers to bonds that are single in all possible Kekulé (unexcited resonance) structures for a system (e.g., the central bonds in bicyclobutadiene, pentalene, and azulene).[9] However, there are serious obstacles in the way of a wholly satisfactory classical treatment of pericyclic reactions. It is not only that a classical formalism per se can reveal little of the inwardness of pericyclic reactions (well exemplified by the subtleties obligatory in the analysis of photochemical processes);[2-6,15] this conceded (and the concession is serious enough), there remain problems of internal consistency in connection with polycyclic transition states. "Off-circuit" interactions cannot always be ignored, as indeed is stressed by Woodward and Hoffmann in their discussion of the interconversion of prismane and benzene.[32] Superficially, this reaction in the benzene → prismane direction (eq 16) is a simple $[{}_{\pi}2_s + {}_{\pi}2_a + {}_{\pi}2_a]$ process, and therefore allowed thermally. But, as Woodward and Hoffmann show by means of an orbital correlation diagram, it is actually an instance where adverse "off-circuit" interactions render the process thermally forbidden. The obvious pericycle 1-2-6-5-3-4 is totally inadequate to define this system (cf. also ref 9b and 10b). One can imagine a wide variety of reactions showing related features (cf. ref 32) and, to enable the generalized WH method to cope independently with such complexities, it would be necessary to incorporate into it a very detailed set of subsidiary rules ad hoc. At the present time, one must surely conclude, any semblance of truly independent status is an illusion.



(16)

For polycycles, as for monocycles, the generalized component rules are simply a classical chemical statement of the Hückel-Möbius rules of aromaticity; they have the same scope, the same limitations.

Several discussions have appeared concerning overlap situations more complex topologically than those normally encountered amongst pericyclic reactions and polycyclic aromatic compounds as conventionally understood, viz., spiroconjugation,[33,34] bicycloaromaticity,[34,35] and laticyclic and longicyclic systems.[34] Conceivably, these analyses and graph-theoretic methods[24,36] together contain the germ of some more complete systematization of delocalized networks than those currently available.

Reflecting upon the classical stereochemical formalism of the generalized WH rules, Rassat [37] suggests that, as rules of parity, the WH rules may be aspects of a wider truth: "la chimie est impaire". Perhaps not surprisingly, considering its extent, this intriguing conjecture is not developed in detail, although different kinds of reaction (SN2, SN2′, etc.) are cited as supporting examples, and an attempt is made to subsume photochemical pericyclic reactions under this surmised general chemical rule of parity.

Acknowledgments. I am indebted to Drs. J. R. Knowles and G. H. Whitham and the late Professor C. A. Coulson for their helpful comments and criticism and to Dr. J. A. Barltrop for many stimulating discussions of "orbital symmetry". It is a pleasure also to thank Mr. D. K. Stout for his hospitality at Gardda, Gwynedd, where this study first took shape.

References and Notes

(1) (a) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Verlag Chemie-Academic Press, Weinheim/Bergstr., Germany, 1970; (b) *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(2) (a) W. Th. A. M. van der Lugt and L. J. Oosterhoff, *Chem. Commun.*, 1235 (1968); *J. Am. Chem. Soc.*, **91**, 6042 (1969); (b) H. E. Zimmerman, *ibid.*, **88**, 1566 (1966); *Acc. Chem. Res.*, **5**, 393 (1972).

(3) J. Michl, *Mol. Photochem.*, **4**, 243, 257, 287 (1972).

(4) R. C. Dougherty, *J. Am. Chem. Soc.*, **93**, 7187 (1971).

(5) In view of recent discussion of chemiluminescent processes,[6] "volcano" (to pursue further Michl's funnel analogy)[3] might well seem particularly apt as a description of the ground-state energy barrier.

(6) F. McCapra, *Chem. Commun.*, 155 (1968); *Pure Appl. Chem.*, **24**, 611 (1970); cf. also ref 3, p 243, and ref 4.

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

(8) H. E. Zimmerman, *J. Am. Chem. Soc.*, **88**, 1564 (1966); *Angew. Chem., Int. Ed. Engl.*, **8**, 1 (1969); *Acc. Chem. Res.*, **4**, 272 (1971).

(9) (a) M. J. S. Dewar, *Tetrahedron, Suppl.*, **8** (I), 75 (1966); "Aromaticity", *Chem. Soc., Spec. Publ.*, **No. 21**, 177 (1967); "The Molecular Orbital Theory of Organic Chemistry", McGraw-Hill, New York, N.Y., 1969, Chapters 6 and 8; (b) *Angew. Chem., Int. Ed. Engl.*, **10**, 761 (1971).

(10) (a) J. J. C. Mulder and L. J. Oosterhoff, *Chem. Commun.*, 305, 307 (1970); (b) W. J. van der Hart, J. J. C. Mulder, and L. J. Oosterhoff, *J. Am. Chem. Soc.*, **94**, 5724 (1972).

(11) H. C. Longuet-Higgins and E. W. Abrahamson, *J. Am. Chem. Soc.*, **87**, 2045 (1965); ref 3, p 287.

(12) Reference 1a, p 169.

(13) A related comment was made by Professor R. B. Woodward in a lecture at the Chemical Society Symposium on Orbital Symmetry Correlations in Organic Reactions, Cambridge, January 9, 1969.

(14) Reference 1a, p 70.

(15) From the complex of ideas associated with the controversial terms "aromatic" and "antiaromatic", one or other of two aspects has normally been selected in justification of this assumption, namely, (1) stabilization or destabilization of the cyclically delocalized system relative to some acyclic model, and (2) the presence or absence of low-lying electronically excited states in the cyclic system. While these two aspects are by no means mutually exclusive, the latter is probably the more useful and instructive if it is desired to gain a unified view of thermal and photochemical pericyclic reactions. In these terms, if the transition state is aromatic, there will be a wide gap between the ground-state and the excited-state potential-energy surface and therefore no special ground-state energy barrier to reaction, whereas, if the transition state is antiaromatic, the corresponding gap will be very narrow and there will therefore be a high ground-state barrier coupled with a low-lying well (or funnel) in the excited-state surface through which an electronically excited reactant molecule can undergo easy radiationless deactivation to ground-state product[2,3,4,10b] (hence the comments in the opening paragraph). The stabilization–destabilization aspect, however, has the merit of affording a basis for comparing the energies of cyclic transition states with the energies of open-chain analogs, thereby rationalizing the general experience that an allowed pericyclic reaction is normally more favorable than the corresponding nonconcerted stepwise reaction, which in turn is normally more favorable than the corresponding forbidden pericyclic reaction.[9]

(16) The word "local" is inserted here to indicate that we only consider intersections made by a node in the immediate vicinity of the atom to which that node belongs, i.e., intersections occurring when the connectivity cycle is closer to that particular atom than to any other atom in the pericycle. The argument in the text is a mathematical one rather than a physical one, and so the fact that, strictly, nodal surfaces are infinite in extent is irrelevant.

(17) Zimmerman and Iwamura[18] have defined a reactivity index r, which is, effectively, $m - Z$. This, of course, has the same parity as $m + Z$. Our proof that $N + Z$ is even shows that $m \pm Z$ and $m \pm N$ formulations of the parity of rules for pericyclic reactions are all exactly equivalent.

(18) H. E. Zimmerman and H. Iwamura, *J. Am. Chem. Soc.*, **92**, 2015 (1970), ref 19.

(19) G. H. Hardy and E. M. Wright, "An Introduction to the Theory of Numbers", 4th ed, Oxford, England, 1960, pp 49–50. If a, b, and x are integers (not necessarily positive) and $(a - b)$ is exactly divisible by x, we say that a is congruent to b to modulus x, and write

$$a \equiv b (\mathrm{mod}\ x)$$

The sense of "exactly divisible" is that there exists an integer p (not necessarily positive) such that $(a - b) = px$. Elementary properties of congruences, having obvious parallels in ordinary algebra, are as follows.

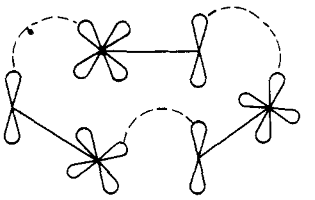
$a \equiv b$ implies $b \equiv a$. If $a \equiv b$ and $b \equiv c$, then $a \equiv c$. If $a \equiv (b + d) \pmod{x}$ and two further integers b' and d' exist, satisfying the congruences $b \equiv b'$ and $d \equiv d'$ to modulus x, then $a \equiv (b' + d') \pmod{x}$.

If $a \equiv \alpha \pmod{x}$ and $0 \leq \alpha \leq (x - 1)$, then α is the *least residue* (strictly, least nonnegative residue) of a to modulus x. To modulus 2, $\alpha = 0$ or 1 (even or odd integer, respectively).

(20) *Aliter.* We note that the first summation on the rhs of eq 4, comprising only even terms, must be an even number irrespective of $\nu(0)$. The second summation comprises $\nu(1)$ terms, each of which is odd, and consequently this summation is even if $\nu(1)$ is even and odd if $\nu(1)$ is odd. Hence, $m + N$ is the sum of an even number and a number having the same parity as $\nu(1)$. Consequently, $m + N$ is odd if $\nu(1)$ is odd, and even if $\nu(1)$ is even, which is equivalent to the statement in the text.

(21) Reference 1a, p 65.

(22) In absence of suitable pericyclic examples, the treatment of d-orbital systems is perhaps best illustrated by reference to planar heteromorphic monocycles of alternating $2p_{\pi}$ and $3d_{\pi}$ (xz) orbitals.[23a] A heteromorphic system $(AB)_n$ can be regarded as a ring of n two-electron d_{π}–p_{π} components interacting antarafacially (cf. **36**), as shown for the $n = 3$ case in formula i. The generalized WH rule (11) (which can clearly be applied to stable molecules as well as to transition states) cannot be satisfied by a ring consisting solely of $(4q + 2)_a$ components, irrespec-



i

tive of *n*. In these terms, no planar heteromorphic $2p_\pi$–$3d_\pi$ (*xz*) system can be aromatic. Therefore, no alternation effect analogous to the Hückel 4*n* + 2 rule for planar p_π–p_π systems is to be expected. The argument is perhaps naive, but the conclusion is identical with that reached in Craig's more rigorous analysis.[23a] For detailed discussions and leading references on the possibility (or otherwise) of aromaticity in systems containing d orbitals see ref 23.

(23) (a) D. P. Craig in "Theoretical Organic Chemistry", Kekulé Symposium, Butterworth, London, 1959, p 20; D. P. Craig and N. L. Paddock in "Nonbenzenoid Aromatics", Vol. 2, J. P. Snyder, Ed., Academic Press, New York, N.Y., 1971, p 273; (b) L. Salem, "The Molecular Orbital Theory of Conjugated Systems", W. A. Benjamin, New York, N.Y., 1966, p 158; M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry", McGraw-Hill, New York, N.Y., 1969, p 430.

(24) I. Gutman and N. Trinajstić, *Top. Curr. Chem.*, **42**, 49 (1973), and references cited therein. The graph–theoretic demonstration (the "loop rule") is, however, still restricted to Hückel topologies. It is difficult to see what graph–theoretic significance can be attached to the negative off-diagonal elements that necessarily occur in the topological matrix of a Möbius system.

(25) For instance, Craig's rules,[23a,26] which test for a totally symmetric VB ground state, are restricted to systems possessing a twofold axis that passes through at least two π centers. Many polycycles of interest, e.g., benzocyclobutadiene, are thereby excluded. Moreover, the rules refer only to Hückel topology.

(26) D. P. Craig, *J. Chem. Soc.*, 3175 (1951); "Non-Benzenoid Aromatic Compounds", D. Ginsburg, Ed., Interscience, New York, N.Y., 1959, p 1.

(27) The sign ~ is placed in the two-atom bridge of **41**, because this is common to the two Möbius circuits of the network but outside the six-atom Hückel circuit. Correct usage of the sign ~ is generally self-evident if it is thought of as denoting a nodal intersection or a negative overlap in the basis set of AO's.

(28) E.g., R. Huisgen and H. Seidel, *Tetrahedron Lett.*, 3381 (1964); G. Quinkert, K. Opitz, W. W. Wiersdorff, and M. Finke, *ibid.*, 3009 (1965).

(29) G. L. Closs and P. E. Pfeffer, *J. Am. Chem. Soc.*, **90**, 2452 (1968).

(30) Reference 1a, p 76.

(31) Reference 1a, p 79.

(32) Reference 1a, p 107 ff.

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

(34) M. J. Goldstein and R. Hoffmann, *J. Am. Chem. Soc.*, **93**, 6193 (1971).

(35) M. J. Goldstein, *J. Am. Chem. Soc.*, **89**, 6357 (1967).

(36) D. H. Rouvray, *Chem. Br.*, **10**, 11 (1974); *R. Inst. Chem. Rev.*, **4**, 173 (1971); A. T. Balaban, Ed., "Chemical Applications of Graph Theory", Academic Press, London, England, 1974.

(37) A. Rassat, *C. R. Acad. Sci. Ser. C*, **274**, 730 (1972).

Perturbed [12]Annulenes. Derivatives of Dibenzo[*cd,gh*]pentalene[1]

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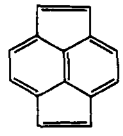
Abstract: The synthesis of 4,8-dihydrodibenzo[*cd,gh*]pentalene from 4,5-methylenephenanthrene is reported. The key step involves a ring contraction of the diazo ketone from 4,5-methylene-9,10-phenanthraquinone which is complicated by an unusual addition of the intermediate ketocarbene to the aromatic solvent. This dihydrodibenzopentalene derivative serves as the precursor of three derivatives of dibenzo[*cd,gh*]pentalene, dibenzo[*cd,gh*]pentaleno-4,8-quinone, dibenzo[*cd,gh*]pentaleno-4,8-semiquinone anion, and dilithium dibenzo[*cd,gh*]pentalenide. The properties of these derivatives support the utilization of the peripheral electronic model which describes the dibenzopentalene system as a perturbed [12]annulene. The use of pentafluorophenylcopper in a decarboxylation of a benzhydryl carboxylic acid is described.

The concept of antiaromaticity, founded in molecular orbital theory, remains an important challenge in organic chemistry.[4] While various monocyclic [4*n*]annulenes have been made, all the members except for *n* = 1 suffer from sufficiently gross molecular distortions from the required symmetrical planar structure to make them invalid tests of the model.[5] Studies on the cyclobutadiene system have been somewhat perplexing. Infrared studies suggest a square planar structure for the parent system,[6] while 1,2-diphenylcyclobutadiene[7a] and "push-pull" cyclobutadienes[7b] have been claimed to be rectangular structures that rapidly equilibrate by bond shift. A paramagnetic ring current has been claimed for tri-*tert*-butylcyclobutadiene.[8] Electrochemical studies of substituted derivatives suggest substantial electronic destabilization. The dehydro[12]annulenes,[9a] which should exhibit greater molecular planarity than the parent [12]annulene,[9b] do exhibit properties of a paramagnetic system. More pertinent work lies in the very recent reports of 1,3,5-tri-*tert*-butylpentalene and 1,6- and 1,7-bridged methano[12]annulenes for which NMR data suggest substantial paramagnetic contributions to the proton chemical shifts.[10] We initiated a series of studies directed toward the three isoelectronic hydrocarbons **1–3** since we felt that these would be unusually good models for the planar [12]annulene with minimum bond alternation (the structural requirements for antiaromaticity).[11] As a criterion for the success of our peripheral electronic model, we took the splitting between the HOMO and LUMO. For the antiaromatic [12]annulene system, these orbitals are degenerate, and the molecule is a ground-state triplet. Therefore, the success of these structures in serving as models for the antiaromatic [12]annulene system requires a minimum perturbation from the triplet ground state. Calculations support this contention. PPP-SCF calculations indicate the lowest lying triplet state of pyracylene **1** is approximately 2.05 eV above the ground state, while that for dibenzo[*cd,gh*]pentalene (**3**) is only 0.32 eV. Compound **2** falls in between. Indeed, the spectroscopic and chemical properties of pyracylene are quite abnormal and can be best interpreted in terms of a perturbed [12]annulene.[11] In this paper, we wish to report our studies directed toward the dibenzopentalene system **3**.



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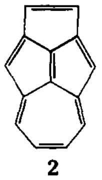

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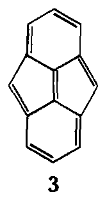

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