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In The Classroom

Pitfalls in the Application of Hückel's Rule

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A semicircular mnemonic is described which permits one to anticipate the Hückel eigenvalue patterns for symmetrical contiguous nonfused bicycles (e.g., biphenyl). The mnemonic constitutes a new technique that is complementary to the existing Frost circle mnemonic for hydrocarbon monocycles. Pedagogically, the development of this semicircular mnemonic in class will serve to establish that the widespread practice of applying Hückel's rule to polycycles is unsound.

It is now clear that Hückel's rule, along with Breslow's extension of it, which were designed to describe annulenes, should not be applied to polycycles, even those as simple as bicycles.

Introduction

For some time now, students of Hückel theory have been able to anticipate the relative energies of the π molecular orbitals of the annulenes by employing the Frost circle mnemonic.[1]. To anticipate the relative energies of the π molecular orbitals (i.e., their eigenvalues) for an annulene: (1) draw a circle whose center represents the nonbonding (or α) level and (2) inscribe the appropriate polygon in the circle with a corner down. Each point at which a corner of the polygon touches the

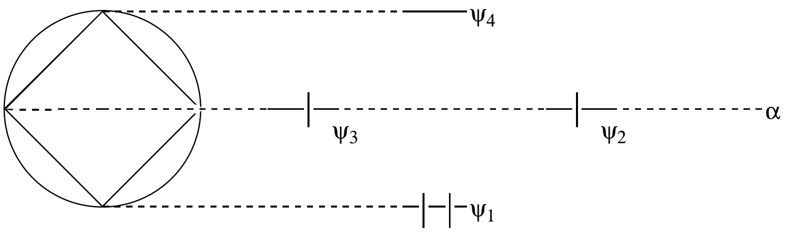

FIGURE 1. APPLICATION OF THE FROST CIRCLE MNEMONIC TO ANTICIPATING THE RELATIVE ENERGIES OF THE π-ELECTONS IN CYCLOBUTADIENE. NOTE THAT THE ELECTON SPIN CANNOT BE DEDUCED AT THE HÜCKEL LEVEL.

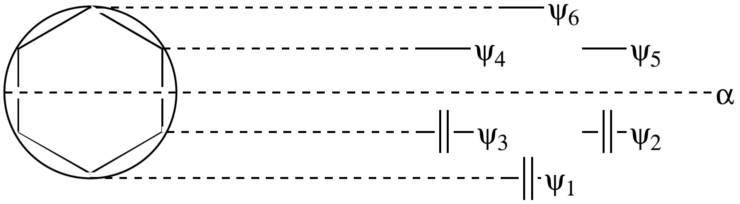

FIGURE 2. APPLICATION OF THE FROST CIRCLE MNEMONIC TO ANTICIPATING THE RELATIVE ENERGIES OF THE π-ELECTONS IN BENZENE

circumference of the circle represents the relative eigenvalue of a molecular orbital of the annulene. Figure 1 depicts the application of the “Frost-circle trick” to cyclobutadiene.

Quite apart from introductory Hückel theory, the Frost circle trick is often given in lectures which focus on aromaticity in hydrocarbons [2].

The Frost circle mnemonic provides a convenient basis for classroom generalizations about $4n + 2$ (aromatic) hydrocarbon monocycles and $4n$ (antiaromatic) hydrocarbon monocycles which are collectively covered under the rubric of Hückel’s rule (notwithstanding the fact that Breslow coined the term antiaromatic [3]). The prototypical $4n$ system, cyclobutadiene (Figure 1), has two nonbonding electrons while the prototypical $4n + 2$ system, benzene (Figure 2), has bonding electrons exclusively.

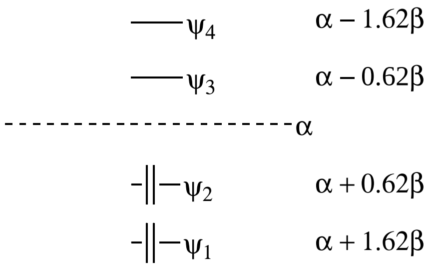

FIGURE 3. HÜCKEL π-ORBITAL ENERGIES FOR BUTADIENE.

It is seductively convenient to apply Hückel’s rule (monocyclic hydrocarbons which have $4n+2$ π electrons will be aromatic) and Breslow’s extension (monocyclic hydrocarbons which have $4n$ π electrons will be antiaromatic) to any molecule which has a cyclic π system. Nonetheless, it is instructive to examine the validity of conclusions reached by those who apply Hückel’s rule to non-monocycles. In this report I consider a subset of hydrocarbon bicycles (at the Hückel level) to see whether it is possible to enunciate meaningful generalizations about aromatic/antiaromatic bicycles.

Results and Discussion

Underlying qualitative analyses, like the Frost-circle trick, is the quantitative side of Hückel theory. Quantitative treatments [4] of hydrocarbon π systems begin with the topological information implicit in their Lewis structures and proceed using simple linear algebra to produce a polynomial called the secular equation; for example, the secular equation for butadiene is $x^4 - 3x^2 + 1 = 0$. The roots of the secular equation (in this case –1.62, –0.62, 0.62, 1.62) lead to the eigenvalues (energies) for the molecular orbitals (see Figure 3 for butadiene orbital energies).

Let’s consider relationships between an annulene, **A**, the corresponding acyclic polyene with one less carbon atom, **A-c** and the symmetrical contiguous nonfused bicycle, **A-A**. As an example, for **A** representing benzene, **A-c** would be pentadienyl and **A-A** would be biphenyl. Some time ago, Heilbronner [5] published a theorem which relates the secular equation of **A** (i.e., $S^A(x)$) and the secular equation of **A-c** (i.e.

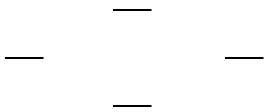

FIGURE 4. A QUARTET OF HÜCKEL EIGENVALUES FOR STRUCTURES **A-A**.

$S^{A\text{-}c}(x)$) to the secular equation of the corresponding symmetrical nonfused bicycle **A-A** (see equation 1).

$$S^{A-A}(x)=S^{A}(x)S^{A}(x)-S^{A-c}(x)S^{A-c}(x) \tag{1}$$

From equation 1, it follows that any eigenvalue that **A** and **A-c** have in common, will occur as a degenerate pair for **A-A**. But, as can be deduced from a symmetry argument and the Frost-circle mnemonic, the eigenvalues that **A** and **A-c** have in common are those that repeat as degenerate pairs in the set of eigenvalues for **A**. Thus, any degenerate pair of eigenvalues that **A** has will occur as a degenerate pair for **A-A** as well. As would be expected from a simple perturbational argument [6], Hückel calculations on the bicycles consistently give degenerate pairs of eigenvalues "sandwiched" between a pair of nondegenerate orbital energies, producing a quartet of eigenvalues as shown in Figure 4. Unique eigenvalues for **A** lead to a unique pair of eigenvalues for **A-A**.

One can now use the foregoing generalizations to deduce the relative orbital energies for any symmetrical contiguous nonfused bicycle. Figure 5 presents the procedure as it applies to biscyclobutadiene.

Application of this new semi-circular mnemonic to the smallest bicycles **A-A** (i.e., C_6, C_8, C_{10}, C_{12}) produces four different occupancy patterns for the π orbitals. Biscyclobutadiene **1** results are shown in Figure 5 and the other bicycles **2, 3** and **4** are shown in Figure 6.

The basic patterns repeat as the bicycles grow so that the C_{14} bicycle shows the same pattern as the C_6 bicycle, C_{16} shows the same pattern as C_8, and so on. In general, there is one pattern for all 8*n* bicycles, one for all 8*n* + 2 bicycles, one for all 8*n* + 4 bicycles and one for all 8*n* + 6 bicycles.

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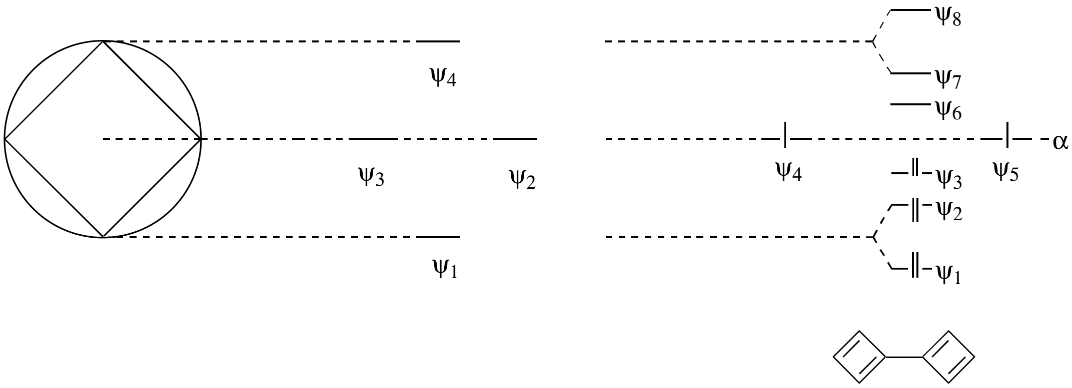

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FIGURE 5. THE SEMICIRCULAR MNEMONIC FOR BISCYCLOBUTADIENE 1.

If the words aromatic and antiaromatic are to imply similar things for both monocycles and bicycles, then the $8n$ bicycle pattern (triplet ground state), which best matches the 4N monocycle pattern (triplet ground state - see Figures 1 and 5), should be appropriate for antiaromatic symmetric contiguous nonfused bicycles. Like the $4n + 2$ monocycles, the $8n + 2$ bicycle pattern exhibits degenerate, fully filled, highest-occupied bonding molecular orbitals (see Figure 2 and compound **3**, Figure 6). Thus the $8n + 2$ bicycles should be appropriate for aromatic, symmetric, contiguous nonfused bicycles. Unlike the monocycles, the bicycles produce two other patterns (one for $8n + 4$ and one for $8n + 6$ systems), which can simply be classed as nonaromatic.

A simple, established measure of aromaticity (at the Hückel level) for the annulenes is the Dewar resonance energy [6, 7]. A plot of annulene carbon content versus Dewar resonance energy (DRE) looks like a picket fence with large DREs for the $4n + 2$ annulenes and small DREs for the $4n$ annulenes (see Figure 7). The corresponding plot for $8n$ and $8n + 2$ contiguous symmetric nonfused bicycles gives a similar picture (see Figure 8).

While the generalizations regarding aromatic ($8n + 2$) and antiaromatic ($8n$) contiguous nonfused bicycles are nicely supported at the Hückel level, there is a surprising feature. Planar biphenyl **4** (Figure 6) is classified as nonaromatic ($8n + 4$ system) by these rules. Of course biphenyl **4** is widely discussed as an aromatic molecule. In the gas phase, however, biphenyl **4** is **not flat**. The two phenyl rings

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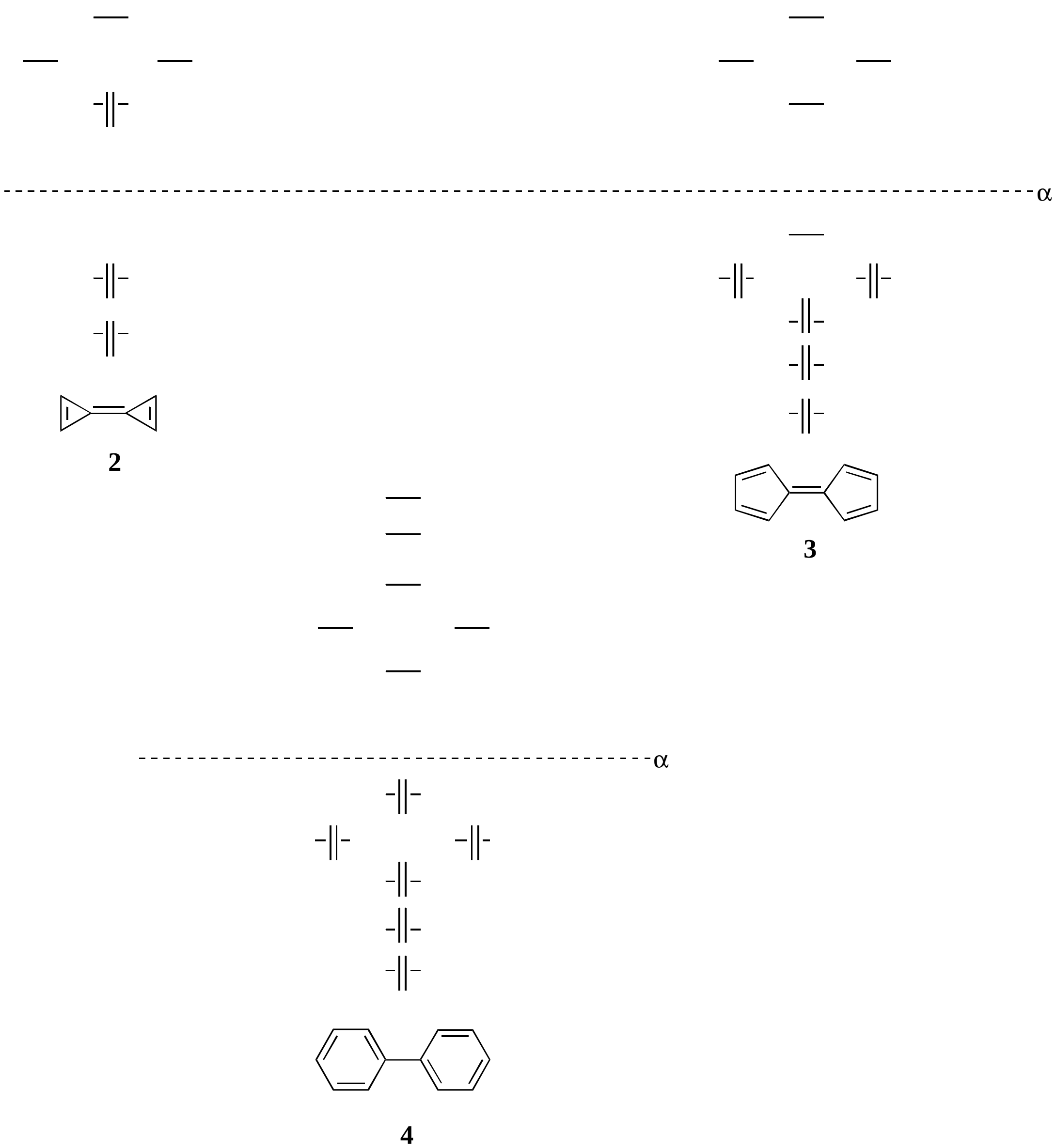

2 **3** **4**

FIGURE 6. π-ORBITAL OCCUPANCY PATTERNS FOR SOME SYMMETRIC CONTIGUOUS NONFUSED BICYCLES.

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occupy separate planes which are tilted about 45° with respect to each other [8] (see Figure 9).

Furthermore, the C–C bond linking the biphenyl rings is about 1.48 Å long [8] indicating that it has a weaker resonance interaction than styrene, which has a corresponding bond length of 1.44 Å [8]. Nonplanarity for biphenyl is usually explained in terms of crowding between the ortho hydrogens in the flat structure [8, 9].

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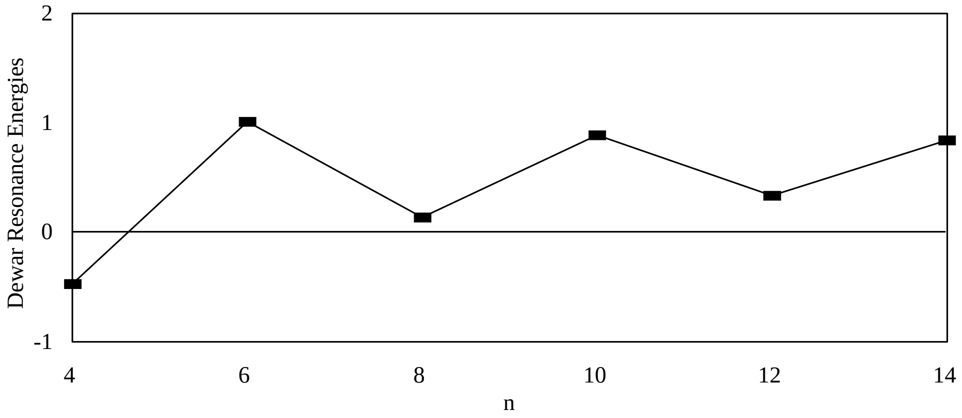

FIGURE 7. DEWAR RESONANCE ENERGIES (IN β UNITS) FOR C_n ANNULENES.

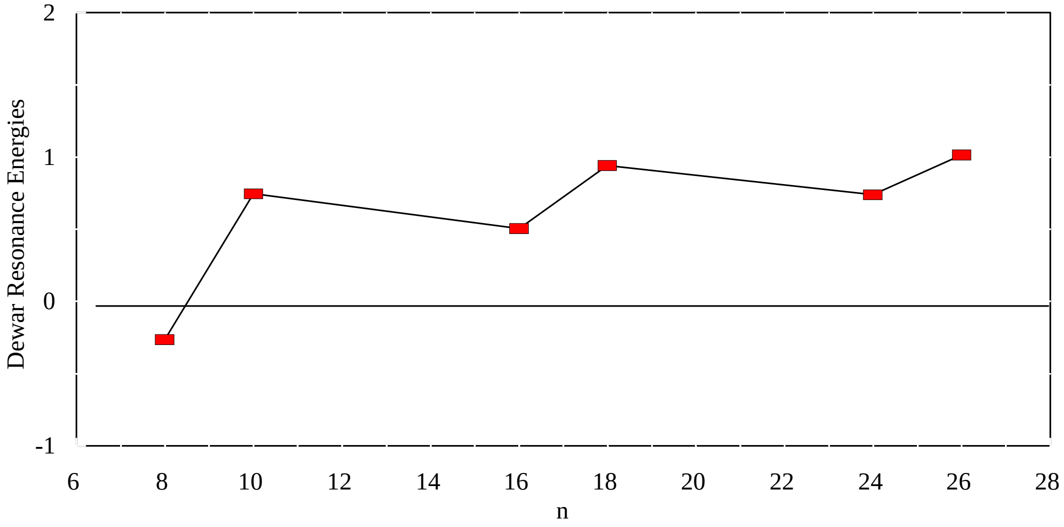

FIGURE 8. DEWAR RESONANCE ENERGIES (IN β UNITS) FOR C_n SYMMETRIC CONTIGUOUS NONFUSED BICYCLES, WHICH HAVE 8*n* AND 8*n*+2 π-ELECTONS.

Nonetheless, it may well be, in accord with the Hückel picture, that planar biphenyl is also destabilized by the relatively high-lying electrons in its HOMO, which would enjoy substantial stabilization in approximately perpendicular conformations. This

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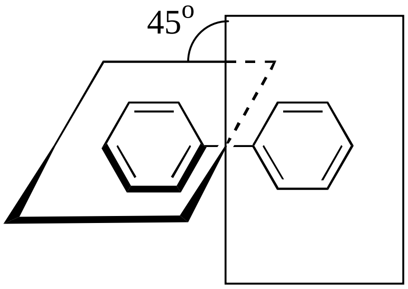

FIGURE 9. GAS PHASE GROUND STATE CONFORMATION FOR BIPHENYL 4.

would certainly be the conclusion if a kinetic based criterion for aromaticity were to be employed [10] (δE_{FMO} for planar biphenyl: 1.4β; for perpendicular biphenyl: 2β).

It is now clear that Hückel's rule, along with Breslow's extension of it, which were designed to describe annulenes, should not be applied to polycycles, even those as simple as bicycles. For example, a monocyclic structure which is antiaromatic ($4n$ π electrons) can easily have a planar nonaromatic bicyclic counterpart (e.g., 12 π electrons). It is for this reason that the usual approach to aromaticity in transition states [10] requires analysis in terms of monocyclic orbital arrays.

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