How to Recognize Disjoint Hydrocarbons: A Hückel Theory Topic

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Abstract: Categorizing even alternant hydrocarbons as joint or disjoint serves as the basis for differentiating between antiaromatic, Y-antiaromatic and very Y-antiaromatic structures. Both previously proposed methods for categorizing even alternant hydrocarbons as joint or disjoint are unreliable. A new approach is presented and shown to be both conveniently applicable and reliable. Because this topic bridges Hückel theory and modern structural concerns, it is suitable for inclusion in undergraduate Hückel theory courses.

Introduction

One of the best-known results to come out of Hückel theory is the generalization known as Hückel's rule, that is $4N + 2$ annulenes are aromatic. A simple quantitative presentation of Hückel results for the annulenes is provided by the Frost circle mnemonic [1]. Higher-level theory and experimental work have each offered full substantiation for the Hückel view of benzene which is the $4N + 2$ prototype.

In sharp contrast, the Hückel description of cyclobutadiene is not supported either by higher-level theoretical treatments or by experimental work. While Hückel theory predicts that cyclobutadiene is a square, ground-state triplet (resonance energy = 0β), both higher-level theory and experiment show it to be a rectangular, ground-state singlet [2, 3].

Because Hückel theory is so widely disseminated, there have been some attempts [4, 5] to provide a simple method for correcting errant Hückel predictions about ground-state multiplicity. Because this topic links Hückel theory and structural problems of current interest to researchers, I include it in my Hückel theory course. I elected to cover the Borden and Davidson approach [5], which will be presented and modified herein.

Discussion is restricted to even, alternant hydrocarbons (i.e.. no structures have odd-membered rings) as was the case for earlier reports [5, 6]. Alternant, even hydrocarbons, which have two nonbonding Hückel molecular orbitals, can be divided into two types, those which are disjoint and those which are not [5]. In accord with my earlier suggestion [6], even alternant hydrocarbons that have two nonbonding molecular orbitals (NBMOs) and are not disjoint will be called joint hydrocarbons. Borden and Davidson used cyclobutadiene **1** and trimethylenemethane **2** to exemplify disjoint and joint systems (see Figure 1).

When a pair of molecular orbitals is degenerate, the coefficients for those molecular orbitals cannot be chosen uniquely [7]. Consequently, there are two commonly used representations for the degenerate pair of NBMOs for cyclobutadiene **1** (see Figure 2).

In Figure 2, the **A** pair of representations for the NBMOs of **1** has the following feature: a nonzero coefficient for a given vertex in one NBMO is always paired with a zero coefficient for that same vertex in the other NBMO. These orbitals are said to be disjoint as is the structure they describe (cyclobutadiene **1**), the possibility of nondisjoint representations notwithstanding. When there is no nondisjoint representation for the NBMOSs that satisfies the homogeneous linear equations for the structure of interest, both the NBMOs and the structure are joint. Trimethylenemethane **2** has joint NBMOs and is a joint hydrocarbon (see Figure 3).

According to Borden and Davidson [5], the wave function for the lowest-lying singlet of the disjoint hydrocarbon **1** has "no high-energy ionic terms corresponding to the simultaneous occupancy of the same AO by these two electrons." Hence, **1** and other disjoint hydrocarbons should have nearly degenerate, lowest-lying singlet and triplet states. In contrast, **2** and other joint hydrocarbons have destabilized singlet states and should invariably be ground-state triplets.

Borden and Davidson classified tetramethyleneethane **3** as disjoint on the basis of the representations for its NBMOs, which are shown in Figure 4. On this basis, **3** is expected to have nearly degenerate lowest-lying singlet and triplet states. Full π-space CI calculations found **3** to be a ground-state singlet [5]. Subsequently, Dowd et al. [8–12] showed that a family of tetramethylenethanes are all ground-state triplets whether their geometry is planar or not. Other experimental results show that nonclassical hydrocarbons (those which, like **2** and **3**, must show two nonbonding electrons in their Lewis structures) are invariably ground-state triplets regardless of their status as joint or disjoint structures [13]. A recent PM3 study [6], predicts that (i) fully π-bonded, even, alternant, disjoint hydrocarbons have nearly degenerate lowest-lying singlet and triplet states, (ii) nonclassical, even, alternant, joint hydrocarbons are ground-state triplets with a relatively large energy difference between the lowest-lying triplet and singlet states, and (iii) nonclassical, even, alternant disjoint hydrocarbons are ground-state triplets with an even larger energy difference between lowest-lying triplet and singlet states. The first two findings conform with the Borden and Davidson proposals, while the third is diametrically opposed to their proposal.

In accord with experiment and the PM3 study, I propose that molecules be categorized in the following way: (i) even, alternant, classical, disjoint hydrocarbons are antiaromatic, (ii) even, alternant, nonclassical, joint hydrocarbons are

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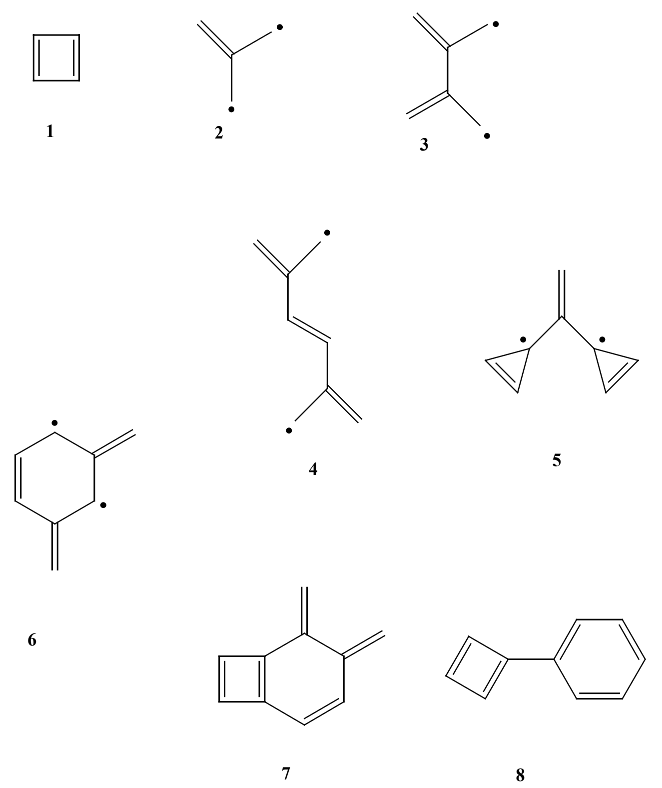


Figure 1.

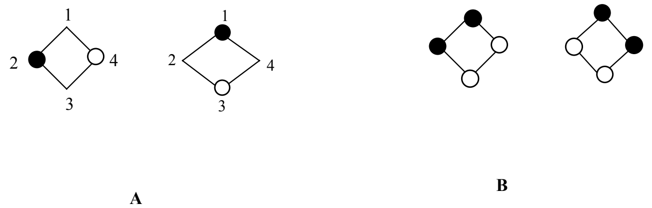


Figure 2. Two pairs of representations for the nonbonding molecular orbitals of cyclobutadiene.

Figure 3. Non-disjoint NBMO's for the joint hydrocarbon trimethylenemethane **2**.

Figure 4. Disjoint representation for the NBMOs tetramethylenethane **3**.

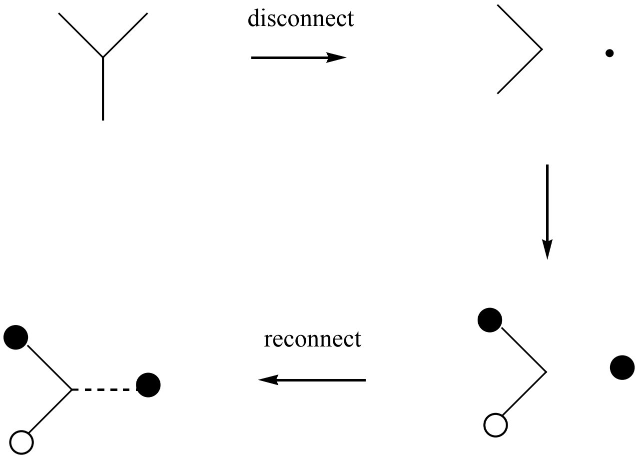


Figure 5. Skeletal disassembly and reassembly to carry out a PMO analysis of trimethylenemethane **2**.

Y-antiaromatic [14], and (iii) even, alternant, nonclassical, disjoint hydrocarbons are very Y-antiaromatic. Note that "antiaromatic" is used to describe classical Lewis structures that are ground-state triplets at the Hückel level and "Y-antiaromatic" is used to describe Lewis structures which must show two dots and are ground-state triplets at the Hückel level. With an overview in hand, one can now turn to the Hückel-level mechanics of classifying structures as joint or disjoint.

Results and Discussion

Borden and Davidson [5] suggest two back-of-the-envelope approaches for differentiating between joint and disjoint hydrocarbons. In the first approach, one simply places stars on every other center of the structure, in the manner traditionally used to decide whether it is alternant or nonalternant. Conclusions based on whether the number of starred atoms is equal to the number of unstarred atoms are "not infallible" [5]; hence, this approach is doubly unsuitable for undergraduate students.

In the PMO approach [5], the even, alternant hydrocarbon is divided into two odd-alternant fragments, each of which may have one NBMO. The form of the NBMO may be deduced from alternant hydrocarbon theorems [15] or obtained from Hückel calculations. The fragments are then recombined and a conclusion drawn based on the magnitude of the coefficients in the NBMOs for the reacting centers. Figure 5 presents this approach as applied to trimethylenemethane **2**. When the reacting fragments reconnect a center with a zero coefficient to a center with a nonzero coefficient, the hydrocarbon is supposed to be joint. If the recombination connects centers that both have zero coefficients, the structure is supposed to be disjoint. The conclusions provided by different PMO disconnections are very sensitive to the odd, alternant fragments selected and often give different answers for a single compound. Figure 6 presents a simple example.

In Figure 6, the 7+1 disconnection leads to the conclusion that **4** should be joint, while the 5+3 disconnection leads to the conclusion that **4** should be disjoint. Related ambiguities plague the PMO approach to aromaticity estimates [16]. Because the PMO approach is unreliable, it too is unsuitable for undergraduate students.

It is possible to unambiguously categorize hydrocarbons as joint or disjoint in the following manner. First, one must decide whether the structure has a pair of singly occupied

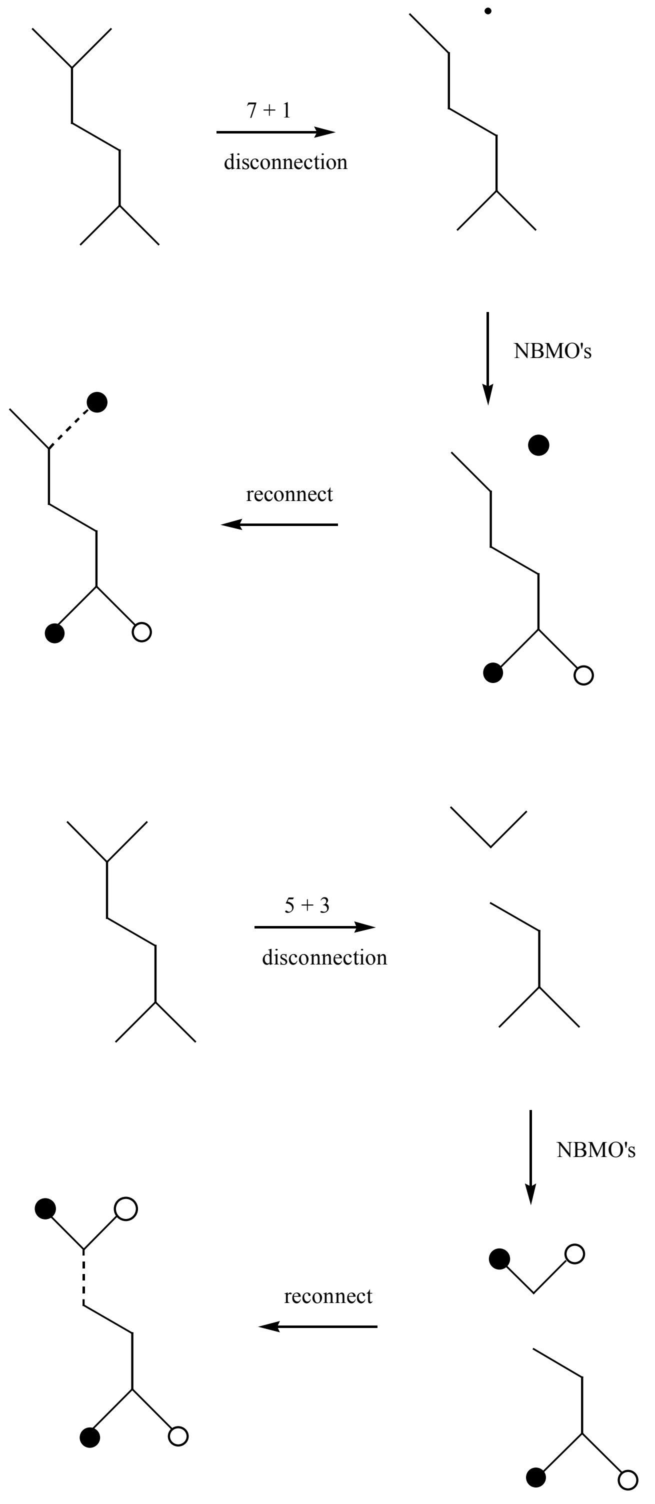


Figure 6. The PMO approach breaks down: proof that **4** is joint and also disjoint.

NBMOs. Neither the presence nor the absence of dots on the Lewis structure is sufficient to guarantee the presence of NBMOs at the Hückel level. For example, both cyclobutadiene and benzene have classical Lewis structures, but one has a pair of NBMOs and the other does not. Trimethylenemethane **2** has a pair of Hückel nonbonding MOs but 1,1-biscyclopropenyl ethene **5** has no NBMOs (see Figure 1), even though both have nonclassical Lewis structures.

To determine whether the structure has NBMOs, one can do traditional Hückel calculations, either manually or by computer. For each NBMO, Hückel calculations will provide a secular equation root of zero and an eigenvalue of α.

Chemical Graph Theory [17, 18] provides a simple back-of-the-envelope alternative. Each hydrocarbon of interest has a polynomial associated with it, which has the form:

$$a_0x^n + a_1x^{n-1} + a_2x^{n-2} + ... + a_{n-1}x^1 + a_n = 0 \qquad (1)$$

The number of nonbonding orbitals for the structure is equal to the number of polynomial coefficients which are equal to zero, beginning with a_n. If $a_n \neq 0$, there are no NBMOs. If only a_n = 0, there is one NBMO and if a_n and a_{n-1} are zero the structure has two NBMOs and so on. But, for an alternant hydrocarbon, the number of NBMOs must be even; therefore, a proof that a_n = 0 establishes that the structure has at least two NBMOs. One can determine a_n quickly and easily by counting Sachs' graphs using a new procedure recently outlined in detail [19]. The vast majority of small, even, alternant hydrocarbons with at least two NBMOs at the Hückel level are Hückel triplets; however, some are Hückel quintets and, therefore, one should confirm that a_{n-2} is not zero before proceeding.

In the second step, one must obtain the simplest possible representation for one of the NBMOs. Frequently, neither NBMO produced by computer calculations is in the required form. This is an example where a computer is unlikely to be helpful. Generally, nonbonding orbitals can be represented with nonzero coefficients on every other center (e.g., see the **A** pair of orbitals in Figure 2). Nonzero coefficients attached to a common zero must add up to zero; therefore, simple representations of the nodal properties will often have an open and a closed circle attached to a zero center. This assertion is known as the zero-sum rule [5].

A little thought will lead to the conclusion that penultimate centers (any center attached to a terminal carbon atom) must always have zero coefficients in NBMOs. Writing those zeros on the structure first will materially shorten the time required to produce a complete representation for the NBMO. Whenever the structure is symmetric with respect to a plane perpendicular to the molecular plane, an antisymmetric NBMO should be sought first. As an example, the antisymmetric NBMO for the *m*-quinodimethane **6** (see Figure 1) has zero coefficients at C_2, C_4, C_6 and C_8 (see Figure 7). C_2 and C_6 have zero coefficients because they are penultimate centers, while C_4 and C_8 have zero coefficients because the NBMO is antisymmetric. It is then straightforward to fill in the nonzero coefficients as shown in Figure 7. None of the nonzero coefficients can be removed from the NBMO in Figure 7 without violating the zero-sum rule.

Whenever one subset of nonzero coefficients is separated from another by two or more contiguous zero coefficients, the representation can be simplified by deleting one subset. An example is presented in Figure 8. Of course, the simplification, presented in Figure 8, does not violate the zero-sum rule.

Classification of hydrocarbons which have two NBMOs into the joint or disjoint categories constitutes a two-value logic system, that is, not disjoint equals joint. One way to complete the examination of structure **6,** begun in Figure 7, would set up the homogeneous linear equations for **6** as shown in eqs 2 through 9 (see the skeletal numbering system in Figure 7).

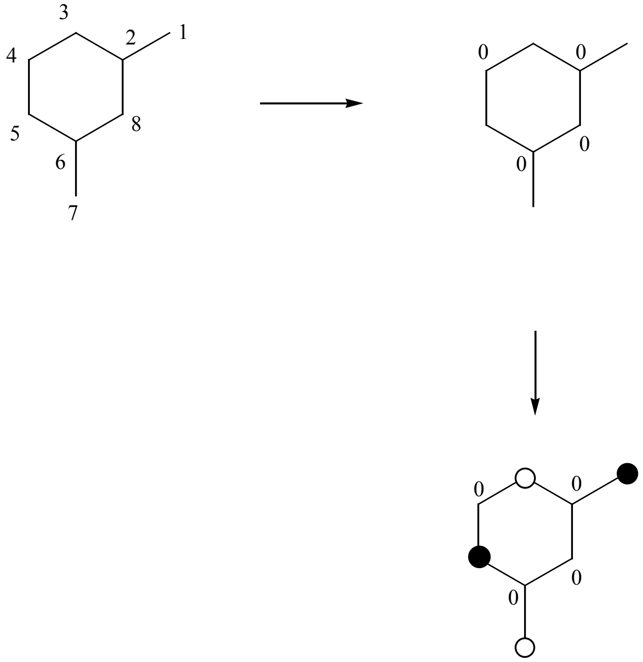


Figure 7. Deducing the simplest representation for an NBMO of **6**.

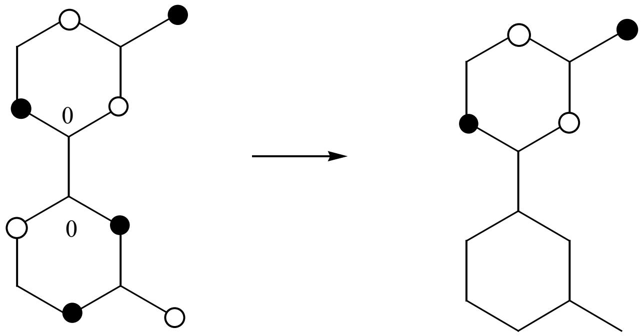


Figure 8. Simpifying the representation of an NBMO.

$$a_1x + a_2 + 0 + 0 + 0 + 0 + 0 + 0 = 0 \qquad (2)$$

$$a_1 + a_2x + a_3 + 0 + 0 + 0 + 0 + a_8 = 0 \qquad (3)$$

$$0 + a_2 + a_3x + a_4 + 0 + 0 + 0 + 0 = 0 \qquad (4)$$

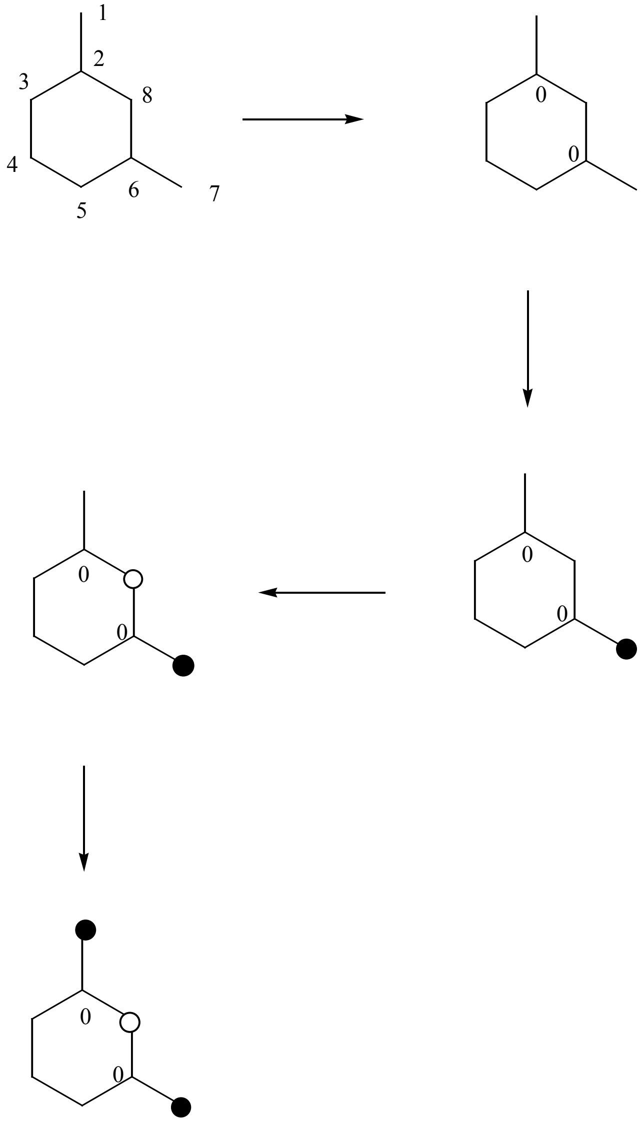
$$0 + 0 + a_3 + a_4x + a_5 + 0 + 0 + 0 = 0 \qquad (5)$$

$$0 + 0 + 0 + a_4 + a_5x + a_6 + 0 + 0 = 0 \qquad (6)$$

$$0 + 0 + 0 + 0 + a_5 + a_6x + a_7 + a_8 = 0 \qquad (7)$$

$$0 + 0 + 0 + 0 + 0 + a_6 + a_7x + 0 = 0 \qquad (8)$$

$$0 + a_2 + 0 + 0 + 0 + a_6 + 0 + a_8x = 0 \qquad (9)$$



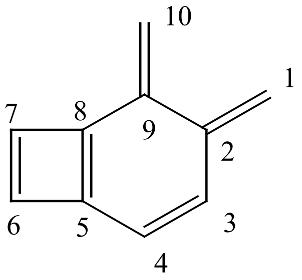
C

Figure 9. Deducing the simplest representation for the NMBO of **6**.

6 has a second NBMO. Furthermore, $a_2 = a_6 = 0$ in that NBMO, because C_2 and C_6 are penultimate carbons. If the new NBMO is disjoint with respect to the representation shown in Figure 7, then $a_1 = a_3 = a_5 = a_7 = 0$. When these values are substituted into eqs 2 through 9, eq 4 requires a_4 to be zero, and equation 7 requires that a_8 be zero. Because all of the coefficients are zero, no such orbital exists and **6** must be a joint hydrocarbon. Thus, as a nonclassical joint hydrocarbon, it should be very Y-antiaromatic.

To obtain an acceptable form of the second NBMO for **6**, draw the structure and fill in zeros for the penultimate centers (see Figure 9). Start with terminal carbons and follow the shortest path between them, filling in nonzero coefficients with opposite signs as you move through the structure. The simplest representation that does not violate the zero-sum rule is the goal, that is, **C** in Figure 9. The zero-sum rule does not require or forbid the assignment of NBMO nonzero coefficients for C_3, C_5. It is the goal of maximum simplicity that makes **C** the proper representation.

Next, the C_{10} structure **7** (Figure 1) will be analyzed completely. Hückel calculations by computer will show **7** (classical, alternant) has only two NBMOs. Alternatively, the chemical graph theory approach described elsewhere [19], can be set up (see Figure 10) and executed to show that a_{10} is zero but a_8 is not (see Figure 11) establishing manually that **7** has only two NBMOs.



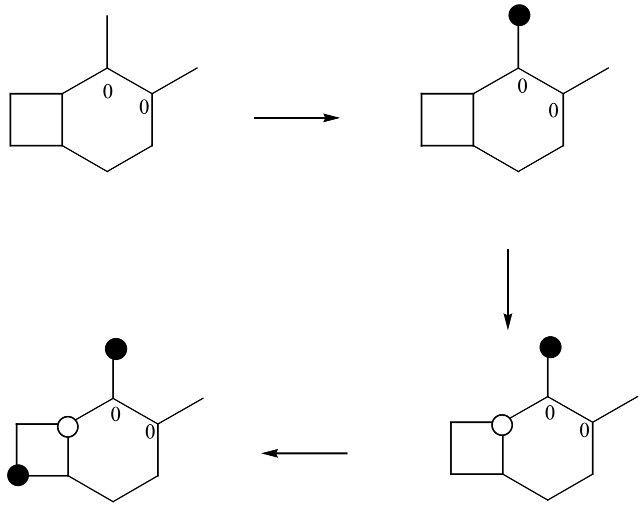
7

Edges	Rings
(1,2)	(5,6,7,8)
(2,3) (2,4)	(2,3,4,5,8,9)
(3,4)	(2,3,4,5,6,7,8,9)
(4,5)	
(5,6) (5,8)	
(6,7)	
(7,8)	
(8,9)	
(9,10)	

Figure 10. Complete listing for edges and rings for **7**.

S_x Graphs	Contribution to a_x (polynomial)
x = 10	
(1,2) (3,4) (5,6) (7,8) + e = 1	$2\,(-1)^5\,(2)^0 = -2$
(1,2) (3,4) (5,8) (6,7) + e = 1	
(1,2) (3,4) (5,6,7,8) + e = 1	$1\,(-1)^4\,(2)^1 = +2$
$a_{10} = +2 - 2 = 0$	
x = 8	
(1,2) (3,4) (5,6) + e = 3	
(1,2) (3,4) (5,8) + e = 2	
(1,2) (3,4) (6,7) + e = 2	
(1,2) (3,4) (7,8) + e = 1	
(1,2) (4,5) (6,7) + e = 2	
(1,2) (4,5) (7,8) + e = 1	
(1,2) (5,6) (7,8) + e = 1	
(1,2) (5,8) (6,7) + e = 1	
(2,3) (4,5) (6,7) + e = 2	$22\,(-1)^4\,(2)^0 = +22$
(2,3) (4,5) (7,8) + e = 1	
(2,3) (5,6) (7,8) + e = 1	
(2,3) (5,8) (6,7) + e = 1	
(2,9) (3,4) (5,6) + e = 1	
(2,9) (3,4) (5,8) + e = 1	
(3,4) (5,6) (7,8) + e = 1	
(3,4) (5,8) (6,7) + e = 1	
(1,2) (5,6,7,8) + e = 2	
(2,3) (5,6,7,8) + e = 1	
(2,4) (5,6,7,8) + e = 1	$5\,(-1)^3\,(2)^1 = -10$
(3,4) (5,6,7,8) + e = 1	
(2,3,4,5,8,9) + e = 1	$1\,(-1)^2\,(2)^1 = +2$
(2,3,4,5,6,7,8,9) = 1	$1\,(-1)^1\,(2)^1 = -2$
$a_8 = 22 - 10 + 2 - 2 = 12$	

Figure 11. Graph theory proof that 7 has two and only 2 NBMOs.



D

Figure 12. Deduction of the simplest form of one NBMO for **7**.

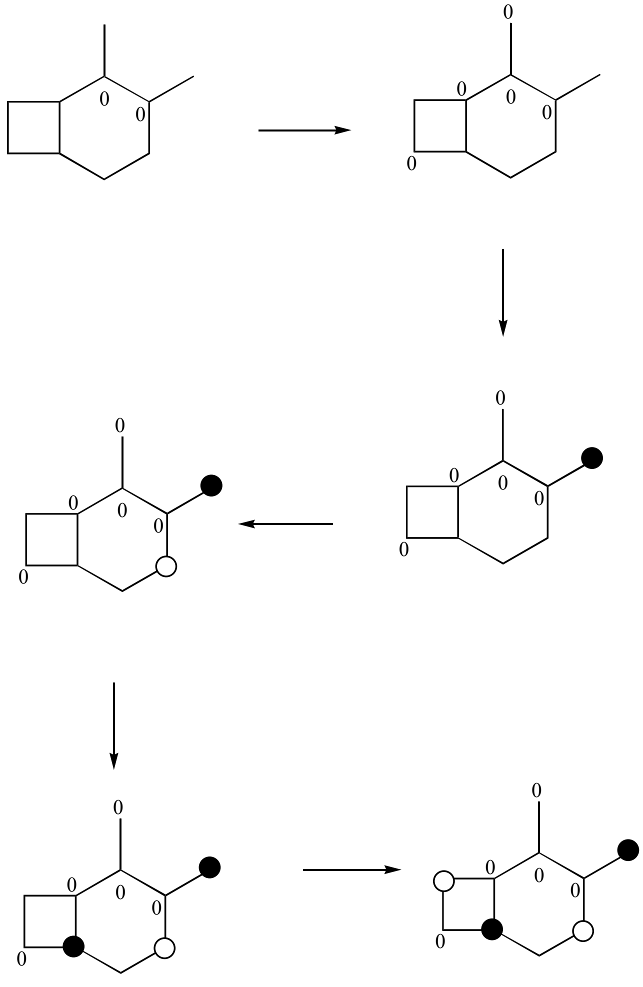


Figure 13. Deduction of the simplest form of the second NBMO of **7**.

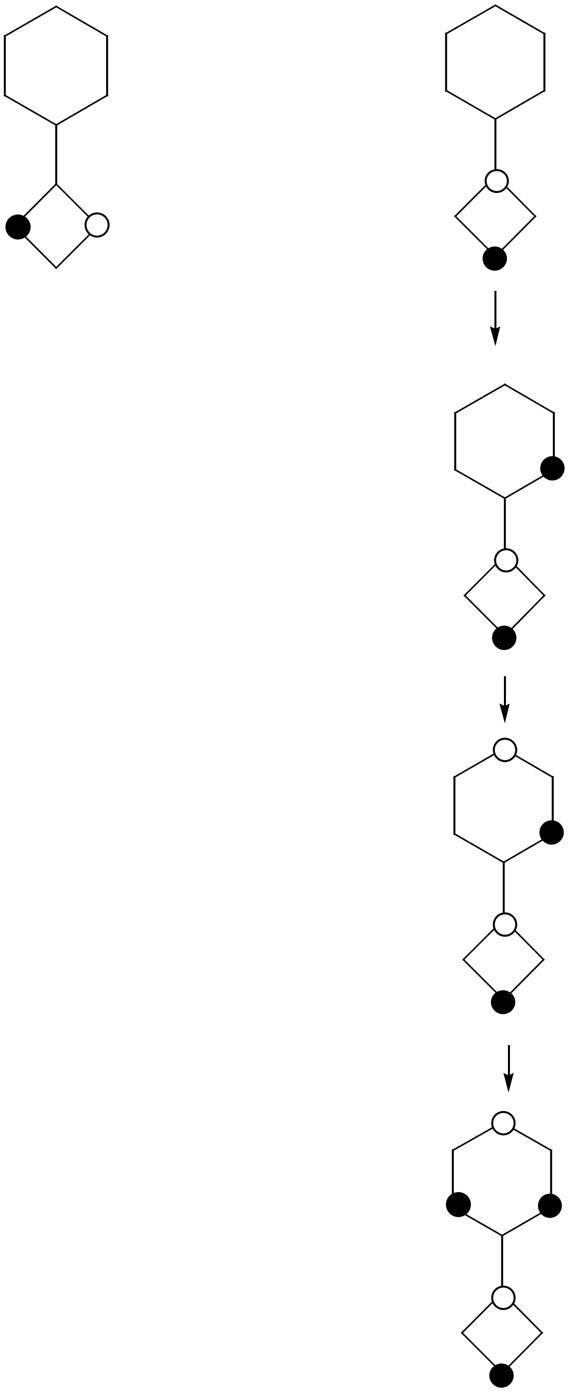


Figure 14. Deducing forms for the NBMO of **8**.

To deduce the simplest form of one NBMO for **7**, draw the skeleton and print zeros on penultimate centers (see Figure 12). Choose a terminal carbon, assign a nonzero coefficient to it, and proceed in accord with the zero-sum rule and the principle of maximum simplicity (see Figure 12).

To complete the classification of **7** as joint or disjoint one can set up the homogeneous linear equations and insert the appropriate coefficient values to test to see if **7** is disjoint (done earlier for **6**). Alternatively, one can draw the structure again and simply place the additional zero coefficients on it. The zero-sum rule will permit one to deduce the presence of additional zero coefficients. At that point, either all of the coefficients will be zero (structure is joint) or some will not be zero (structure is disjoint). Figure 13 presents this convenient process for obtaining the desired form of the second NBMO for **7**. The simple process shown in Figure 13 leads to the unambiguous conclusion that the classical, alternant structure **7** is disjoint and therefore antiaromatic.

Finally, when a classical structure like **8** (see Figure 1) has a pair of NBMOs but no penultimate carbon, one can begin to find the simplest form for an NBMO by placing nonzero coefficients on every other center around the perimeter of a 4*N* circuit. This procedure leads to two representations for the NBMOs of **8**, one of which must be extended to obey the zero-sum rule as shown in Figure 14.

Conclusions

The distinction between joint and disjoint alternant hydrocarbons is important to those who are interested in antiaromatic and Y-antiaromatic structures (see references 6 and 20 for recent examples). Classifying molecules into these categories requires one to obtain the simplest form for the pair of NBMOs associated with such structures. A perturbational approach is unsatisfactory. This report has shown that one can obtain the simplest form of one of the NBMOs using the zero-sum rule. Thereafter, appropriate substitutions in the homogeneous linear equations will lead to an unambiguous conclusion regarding the status of a structure as joint or disjoint.

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