

Disjoint Molecular Orbitals in Nonalternant Conjugated Diradical Hydrocarbons<sup>†</sup>

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The concept of disjoint NBMOs in diradical alternant hydrocarbons (AHs) is reviewed and extended to diradical nonalternant hydrocarbons (nonAHs). A valence-bond (VB) method for recognizing disjoint versus nondisjoint NBMOs (nonbonding molecular orbitals) in diradicals is presented. When circumscribed with hexagonal rings, disjoint diradicals produce nonradical polycyclic successors and nondisjoint diradicals produce diradical polycyclic successors. The interconnection between the topological VB terms of cross-conjugated, disjoint NBMOs, and essentially disconnected polycyclic hydrocarbons is delineated.

## INTRODUCTION

The study of diradicals is important for two primary reasons. First, understanding the structural prerequisites necessary for formation of diradicals bears on the fundamentals of bonding itself. Second, understanding the structural factors leading to high spin (triplets) versus low spin (singlets) diradicals is essential in the design of organic ferromagnetic materials which must be made of high spin systems<sup>1</sup> and in the design materials for bistable devices in which the lowest singlet and triplet states need to be nearly degenerate.<sup>2</sup>

Conjugated diradicals can be classified into two types according to whether their Hückel NBMOs (nonbonding molecular orbitals) can be confined to disjoint sets of atoms or not.<sup>3</sup> If the Hückel NBMOs can be confined to disjoint sets of atoms, then the lowest singlet and triplet states have been found to be nearly degenerate at the SCF calculation level. If the Hückel NBMOs cannot be localized to disjoint sets of atoms, then the diradical has a triplet ground state (gs) that lies well below the corresponding open-shell singlet state at the SCF level and higher, i.e., it is compliant with Hund's rule. For example, bisallyl diradical was shown both computationally and experimentally to be disjoint with nearly degenerate singlet and triplet ground states (gs),<sup>3–5</sup> and trimethylenemethane diradical was shown to be nondisjoint with a triplet gs well separated from the lowest singlet state.<sup>6</sup> This classification provides a useful basis for predicting the important differences in the effects of electron repulsion in these two classes of diradicals. The origin of this classification<sup>3</sup> and subsequent studies<sup>7</sup> of disjoint versus nondisjoint diradicals was with alternant hydrocarbon (AH) systems. Herein, we will study how this disjoint/nondisjoint concept can be extended to nonAHs.

In continuation of our prior work,<sup>8</sup> we will be concerned with the consequence of the AH versus nonAH paradigm and simple topological methodologies that can be extended to larger systems for the purpose of predicting potential ferromagnetic and bistable molecular substances.<sup>1–2,7</sup> Our analysis will use both HMO (Hückel MO) and valence-bond (VB) techniques to show how molecular connectivity can be exploited in the design of substances with these specific properties.

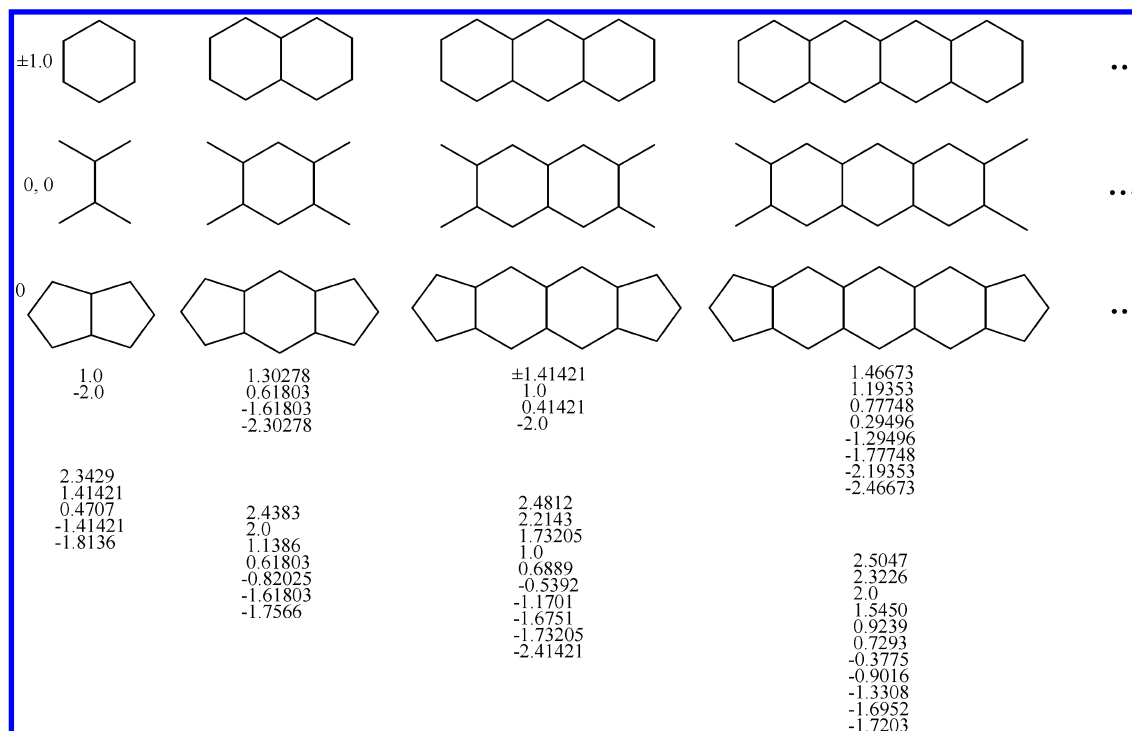
## RESULTS AND DISCUSSION

**Alternant Hydrocarbon Background.** Alternant hydrocarbons (AHs) have no odd size rings and can be represented by (bipartite) molecular graphs. Throughout this paper molecular graph representations, which can be regarded as C–C  $\sigma$ -bond skeletons of planar conjugated systems, will be used unless additional clarity is needed. The vertices of a molecular graph are  $p\pi$ -electronic carbon centers, and the reader will have to fill-in as many lines representing conjugated  $p\pi$ -bonds as possible and dots for the remaining unpaired electrons. A  $p\pi$ -conjugated radical system is maximally starred such that no two starred sites are adjacent and no two unstarred sites are adjacent and the larger of the two sets possess stars. An AH molecular graph can have either an even carbon (EAH) or odd carbon (OAH) conjugated  $p\pi$ -electronic system. An OAH can be a monoradical or higher odd-degree radical, and an EAH can be a nonradical, diradical, or higher even-degree radical. The pairing theorem applies to AHs but not to nonAHs. Herein, the chemical terms energy level and wave function are equivalent to the mathematical terms of eigenvalue and eigenvector, respectively.

The very existence of conjugated hydrocarbon diradicals and disjoint versus nondisjoint is the result of molecular connectivity. Our previous work<sup>8</sup> showed that a one-to-one topological relationship existed between essentially disconnected benzenoid hydrocarbon members belonging a two-dimensional array and disjoint diradical members belonging to another two-dimensional array. It was shown that selecting any member of one of these two-dimensional arrays and its matching partner in the other array that they were strongly subspectral in that all but one pair of eigenvalues between the two of them were identical. The members of these two arrays were generated by starting with two different strongly subspectral seed structures, benzene and bisallyl diradical, and successively connecting the same aufbau units in reverse. Figure 1 gives the molecular graphs corresponding to the conjugated hydrocarbon members belonging to the first rows of these two two-dimensional arrays. To illustrate this generation process consider benzene (C<sub>6</sub>H<sub>6</sub>, first hexagon molecular graph in the first row of Figure 1), naphthalene (C<sub>10</sub>H<sub>8</sub>, the second molecular graph in the first row of Figure 1), bisallyl (C<sub>6</sub>H<sub>8</sub>, first molecular graph in the second row of Figure 1), 1,2,4,5-tetramethylenebenzene (C<sub>10</sub>H<sub>10</sub>, second molecular graph in the second row of Figure 1), and the 1,3-butadiene-1,2,3,4-tetrayl (C<sub>4</sub>H<sub>2</sub>) aufbau unit. By transferring

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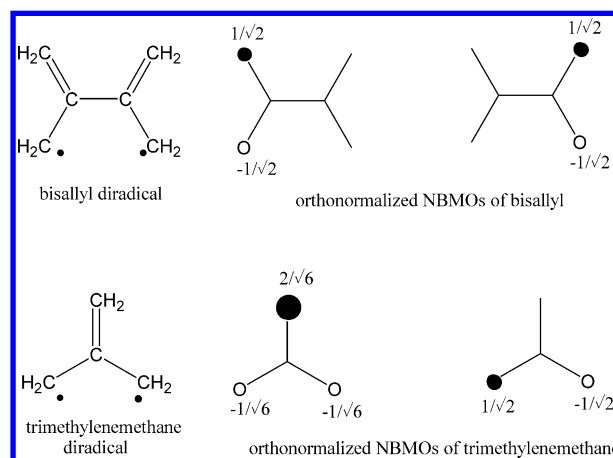
<sup>†</sup> Dedicated to Professor William Cecil Herndon on the occasion of his 70th birthday.



**Figure 1.** Strongly subspectra molecular graphs. The eigenvalues indicated at the onset of each row of molecular graphs are present in all members of that row. The first set of eigenvalues listed beneath each column is present in all three respective molecular graphs, and the second set of eigenvalues only belongs to the respective molecular graphs of the bottom row. The remaining eigenvalues for the alternant molecular graphs can be obtained from the pairing theorem.

two adjacent Hs from benzene to the 2,3-positions of the aufbau unit and attaching the 1,4-positions this augmented aufbau to the positions vacated on benzene generates naphthalene. Similarly, by transferring the 1,4 Hs from bisallyl to the 1,4-positions of the aufbau unit and attaching the 2,3-positions this augmented aufbau to the positions vacated on bisallyl generates 1,2,4,5-tetramethylenebenzene. Successive repetition of this process generates the first two rows shown in Figure 1. The essential point here is that a whole class of (essentially disconnected) nonradicals starting with a nonradical (benzene) and a whole class of related disjoint diradicals starting with a disjoint diradical (bisallyl) could be generated by attaching the same aufbau unit but using a different connectivity mode.

When two electrons have the same spin, the Pauli exclusion principle does not allow the electrons to simultaneously occupy the same region of space (orbitals). Electrons of opposite spin can occupy the same region of space causing them to have higher mutual Coulombic repulsion energy because they spend more time together. As shown in Figure 2 the degenerate NMBOs for bisallyl are disjoint. In both the lowest singlet and lowest triplet states of bisallyl one electron occupies each of these NMBOs. Because these MOs are disjoint, regardless of whether the electrons have the same or opposite spin, there is no probability that both electrons will simultaneously occupy the same AO. Thus, to a first approximation, the lowest singlet and lowest triplet states of bisallyl have the same energy at the HMO level.<sup>3</sup> In the lowest singlet state the two electrons in the NMBOs have opposite spin, and it is possible for each of the electrons in the bonding MO to localize partially at the same pair of carbons as the nonbonding electron that has the same spin. This type of correlation between electrons in the bonding and nonbonding MOs is energetically favorable because the two electrons of



**Figure 2.** Top view of the pairs of NMBOs of bisallyl diradical and trimethylenemethane diradical with their orthonormalized eigenvector coefficients.

the same spin cannot appear simultaneously in the same AO.<sup>3</sup> This type of correlation is not possible in the triplet state because the two electrons in the NMBOs have the same spin. Consequently, including correlation in higher level calculations between the bonding and nonbonding electrons drops the energy of the singlet below that of the triplet in bisallyl. When the NMBOs of the diradical are nondisjoint a triplet ground state is expected because in this state the Pauli principle prevents the two electrons in the NMBOs from simultaneously appearing in the AOs that the NMBOs have in common.<sup>3</sup>

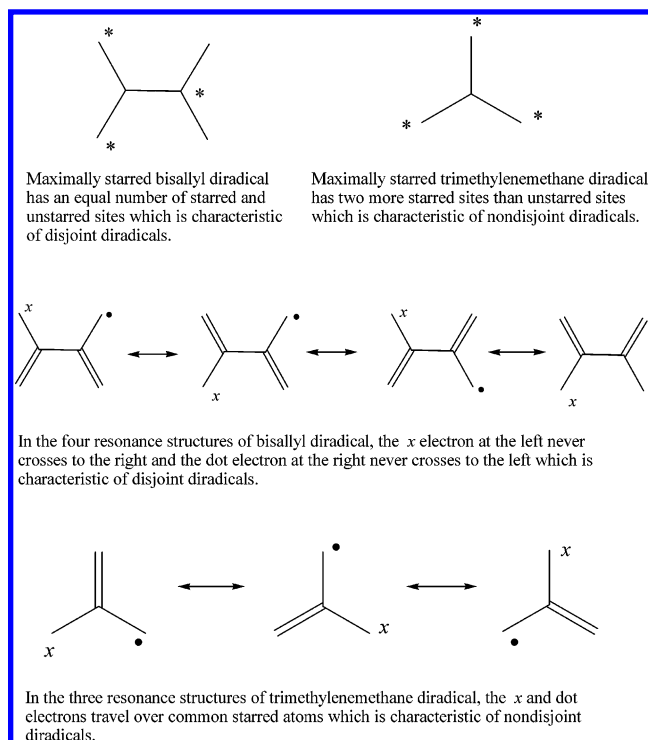
The singlet/triplet properties of bisallyl form the focal point of an intense conflict between theory and experiments.<sup>4</sup> By two different experiments bisallyl was first concluded to be a triplet and then a singlet, but by several different levels of ab initio calculations, it was first concluded to be a singlet

and then a triplet.<sup>3,4</sup> A related conflict between experimental results using two different techniques and ab initio calculations of a more conformationally constrained analogue of bisallyl, 2,3-dimethylenecyclohexane-1,4-diyl, also ensued with the final paper showing that the singlet and triplet states were degenerate.<sup>5</sup> This controversy between experiment and theory has led full circle back to the generalization that disjoint diradicals, like bisallyl which can be formed by joining two allyl monoradicals through their NBMO zero node positions, will have nearly degenerate singlet/triplet ground states, whereas nondisjoint diradicals, like trimethylenemethane, will invariably have triplet ground states.<sup>3</sup>

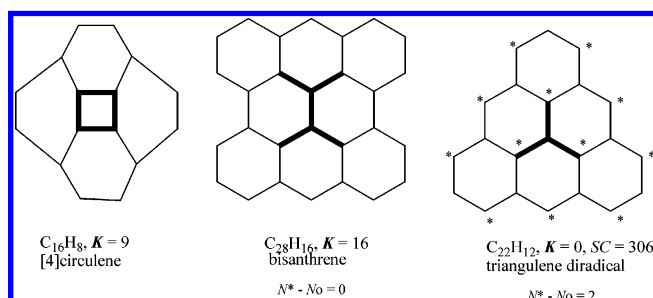
We have shown that Clar's Goblet, a  $C_{38}H_{18}$  hourglass-shaped benzenoid "concealed" diradical, could be constructed by joining two benzo[*cd*]pyrenyl monoradicals ( $C_{19}H_{11}$ ,  $SC = 52$ ) through their 1,11 unstarred positions and, therefore, is a disjoint diradical with a  $SC = 52 \times 52 = 2704$  predicted to have a singlet or nearly degenerate singlet/triplet gs.<sup>9</sup> This prediction was subsequently confirmed by B3LYP/6-31G\* calculations which determined that the singlet state was more stable than the triplet state by only 3.4 kJ/mol.<sup>10</sup>

**Relationship between Disjoint, Essentially Disconnected, and Cross-Conjugated.** Bisallyl diradical (tetramethyleneethane) is a doubly cross-conjugated species with two adjacent  $p\pi$ -orbitals each overlapping with three  $p\pi$ -orbitals. Disjoint, essentially disconnected, and cross-conjugated are molecular connectivity dependent terms. Bisallyl diradical ( $C_6H_8$ ) is isomeric to the nonradicals, 1,3,5-hexatriene ( $E\pi = 6.988 \beta$ ) and 3-methylene-1,4-pentadiene ( $E\pi = 6.899 \beta$ ); the former has all its  $p\pi$ -orbitals in linear-conjugation (all  $p\pi$ -orbitals overlapping with two or less other  $p\pi$ -orbitals) and the latter has its middle  $p\pi$ -orbital in cross-conjugation (overlapping with three  $p\pi$ -orbitals). Bisallyl is a diradical because of its connectivity. Also isomeric to bisallyl diradical ( $E\pi = 6.0 \beta$ ) is 2-methylenepentadienyl diradical ( $E\pi = 6.155 \beta$ ), the latter which is nondisjoint. Cross-conjugated systems are generally less stable than linear-conjugated systems. In the two-dimensional array mentioned above, benzene and the acenes in Figure 1 are the only members that are not essentially disconnected benzenoid hydrocarbons. The first, second, and third members of the second row in this aforementioned two-dimensional array<sup>8</sup> are biphenyl ( $C_{12}H_{10}$ ), perylene ( $C_{20}H_{12}$ ), and bisanthrene ( $C_{28}H_{14}$ ). Biphenyl ( $K = 4$ ), perylene ( $K = 9$ ), and bisanthrene ( $K = 16$ ) comprise of two benzene ( $K = 2$ ), naphthalene ( $K = 3$ ), and anthracene ( $K = 4$ ) units, respectively, joined together by one, two, and three bridging bonds, respectively, that are essentially single bonds since no Kekule' resonance structure can be drawn with a  $p\pi$ -bond crossing from one unit to the other. The number of Kekule' structures ( $K$ ) for each is given by the simple product of the number of Kekule' structures of the joined units.<sup>11</sup>

There are two distinct types of disjoint diradicals. Bisallyl is the prototype for one and square cyclobutadiene is the prototype for the other. Each type has two NBMOs that can be confined to different sets of atoms as shown in Figure 2 for bisallyl and can be circumscribed by hexagonal rings to give nonradical polycyclic successors, but the bisallyl type can additionally be determined by examination of the associated VB (valence-bond) structures as shown in Figure 3. Disjoint diradicals may or may not have an equal number of starred and unstarred sites.



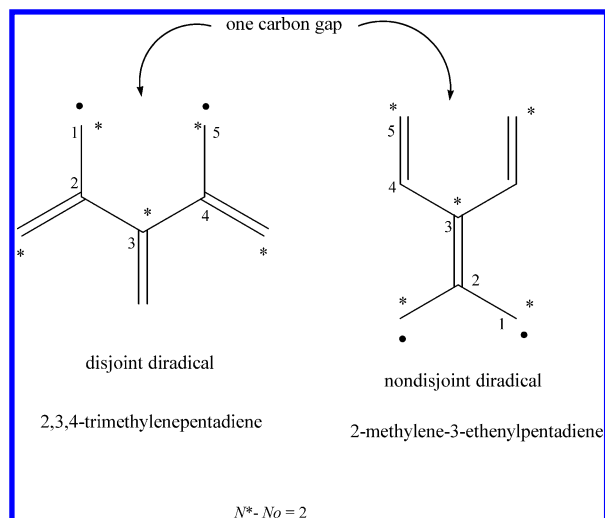
**Figure 3.** Summary of VB characteristics of disjoint versus nondisjoint diradicals.



**Figure 4.** Circumscribing square cyclobutadiene and bisallyl disjoint diradicals (shown in bold) with hexagonal rings gives the nonradicals, [4]circulene and bisanthrene, respectively. Similarly circumscribing trimethylenemethane, a nondisjoint diradical (shown in bold), with hexagonal rings gives the nondisjoint diradical, triangulene.

Circumscribing square cyclobutadiene with hexagonal rings gives [4]circulene ( $C_{16}H_8$ ), and circumscribing bisallyl gives bisanthrene (Figure 4) which is one of 8  $C_{28}H_{14}$  benzenoid hydrocarbon isomers; square cyclobutadiene is the excised internal structure of [4]circulene and bisallyl is the excised internal structure of bisanthrene.<sup>12</sup> In general, circumscribing the bisallyl type of disjoint diradical with hexagonal rings leads to essentially disconnected polycyclic conjugated hydrocarbons that are nonradical, like circumscribing bisallyl gives bisanthrene (Figure 4).

Trimethylenemethane diradical is the prototype for non-disjoint NBMOs. The two nondisjoint NBMOs overlap onto common atoms which also can be discerned by examination of the VB structures (Figure 3). Nondisjoint AHs have an excess of starred sites. If one examines all the resonance structures of a maximally starred monoradical, nondisjoint diradical, or nondisjoint higher degree polyradical, it will be observed that the unpaired electrons will only be found on the starred sites and the corresponding NBMOs will have zero nodes at the unstarred sites. When a nondisjoint diradical



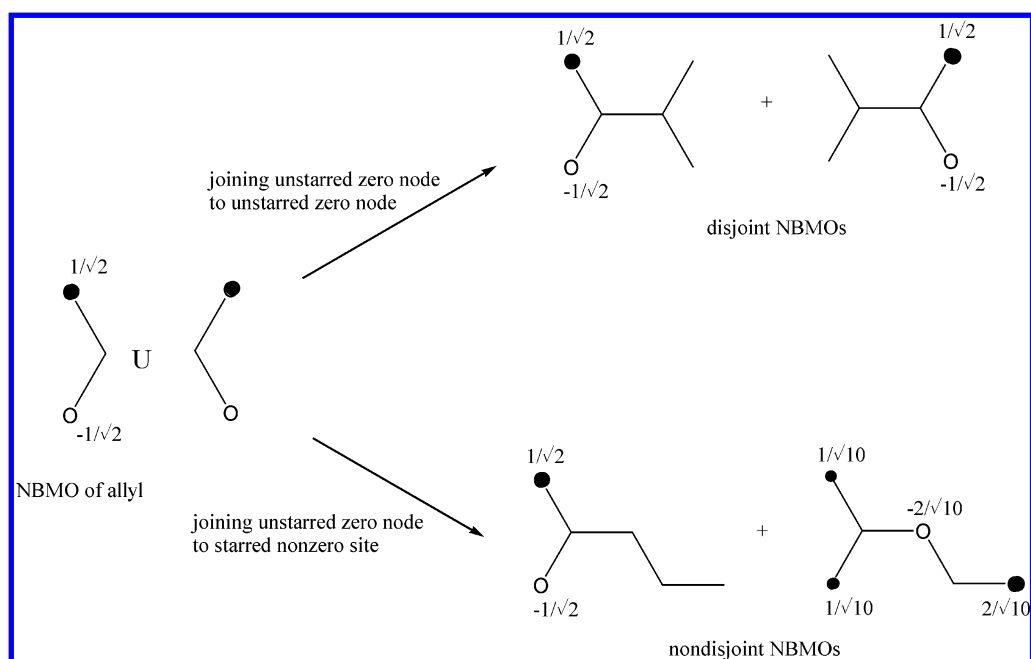
**Figure 5.** Two diradicals that are incapable of being circumscribed with hexagonal rings.

is circumscribed by hexagonal rings, its polycyclic successor is also a nondisjoint diradical. Circumscribing trimethylenemethane diradical with hexagonal rings gives triangulene diradical (Figure 4) which is one of 3  $C_{22}H_{12}$  benzenoid hydrocarbons, the others being (nonradical) benzo[ghi]perylene and anthanthrene; trimethylenemethane diradical is the excised internal structure of triangulene.<sup>13</sup> In general, it has been shown that circumscribing all nondisjoint polyradicals with hexagonal rings leads to polycyclic (benzenoid) successors that are also nondisjoint polyradicals in which the radical degree is preserved.<sup>14</sup>

**VB Recognition of Disjoint versus Nondisjoint Diradicals.** It needs to be emphasized here that VB can distinguish between the bisallyl type of disjoint diradicals and nondisjoint diradicals (Figure 3). For disjoint diradicals the number of starred ( $N^*$ ) and unstarred ( $N_o$ ) sites may be equal ( $N^* = N_o$ ) or they may not; when inequality does occur, the VB approach will show that the unpaired electrons are unable

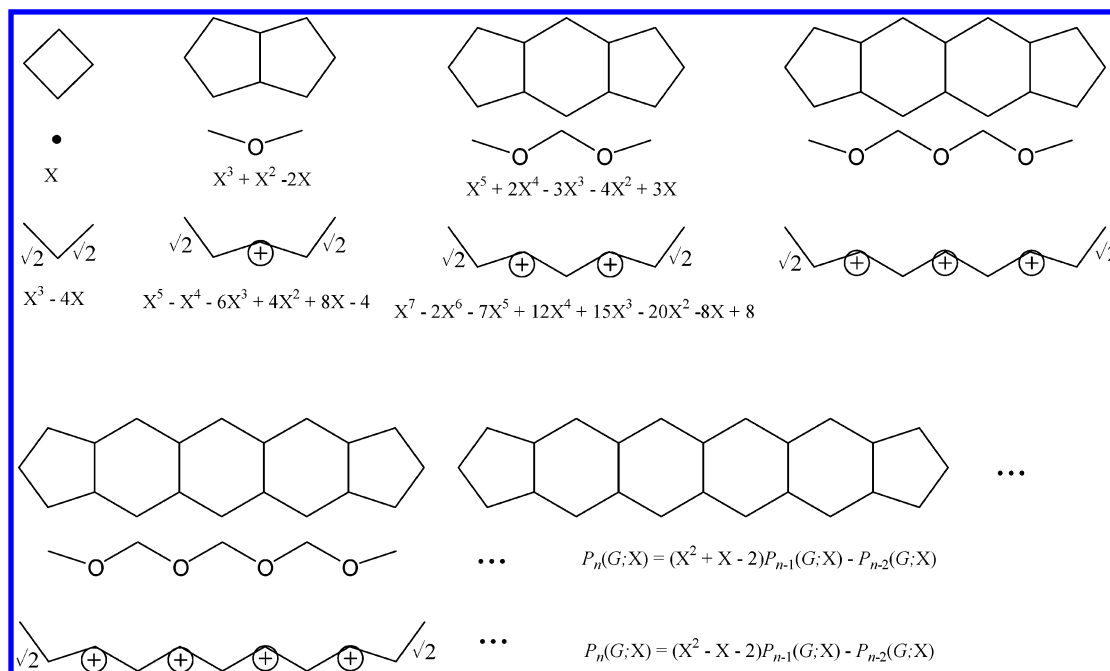
to travel to all of the starred sites (Figure 5). For example, maximally starred 2,3,4-trimethylenepentadiene diradical ( $C_8H_{10}$ ) gives  $N^* - N_o = 2 = N_o$ . VB shows that neither radical electron can be delocalized to the 3-position which is zero node in the disjoint NBMOs. For nondisjoint polyradicals the difference between the number of starred ( $N^*$ ) and unstarred ( $N_o$ ) sites is equal to the radical degree ( $N^* - N_o = \text{No. of NBMOs}$ ). Also for maximally starred AHs, the starring pattern characteristics of mono-radicals and nondisjoint polyradicals identifies the unstarred sites as having zero nodes for the corresponding NBMOs and that the unpaired electrons can only be found on the starred sites in any resonance structure. Circumscribing disjoint diradicals with hexagonal rings generates a Kekulean polycyclic successor, whereas circumscribing a nondisjoint polyradical with hexagonal rings generates a polycyclic successor with the same radical degree (Figure 4). Note that some diradicals cannot be circumscribed because they have less than two carbon gaps.<sup>12</sup> For example, 2,3,4-trimethylenepentadiene disjoint diradical and 2-methylene-3-ethenylpentadiene nondisjoint diradical ( $C_8H_{10}$ ) in Figure 5 cannot be circumscribed with hexagonal rings. In other words, when circumscribing is possible, successive circumscribing with hexagonal rings preserves symmetry and, for AHs without  $4n$  antiaromatic rings, the difference in the number of starred and unstarred sites ( $N^* - N_o = \text{constant}$ ). These properties are important in the evaluation of disjoint versus nondisjoint radicals.

**PMO Construction of AH Diradicals.** Using a PMO (perturbation molecular orbital) approach,<sup>15</sup> one can construct diradicals by the union of two OAH fragments at a node in the NBMO of at least one of them.<sup>3</sup> Joining two OAH fragments through the node of each gives a disjoint diradical and through a node of one and a star site on the other gives a nondisjoint diradical. To illustrate the various PMO combinations consider the union of two allyl monoradicals (Figure 6).<sup>7</sup> If two allyl radicals are joined together at their



**Figure 6.** PMO union of two allyl monoradicals to generate diradicals. Joining the unstarred zero node of one allyl fragment to the unstarred zero node of another gives a diradical with a pair of disjoint NBMOs. Joining the unstarred zero node of one allyl fragment to the starred nonzero site of another gives a diradical with a pair of nondisjoint NBMOs.





**Figure 7.** The transition from AH to nonAH, the pairing theorem, and disjoint diradical character.

unstarred sites which have zero nodes in their NBMOs, one obtains bisallyl diradical in which the two precursor NBMOs remain unchanged because they neither interact with each other or other MOs. If the unstarred site of one allyl fragment is joined to a starred site of the another allyl fragment, one obtains 2-methylenepentadienyl diradical (vinyltrimethylenemethane diradical). In this case, the NBMO in the precursor allyl fragment that was joined through its zero node remains unchanged in the successor. The other successor NBMO arises from the interaction of the NBMO of the allyl fragment that was joined through its starred site with the bonding MO of the other allyl fragment (Figure 6).<sup>7</sup> The pairing theorem requires that the NBMOs occur in pairs for AHs with an even number of  $p\pi$ -electronic centers.<sup>16</sup>

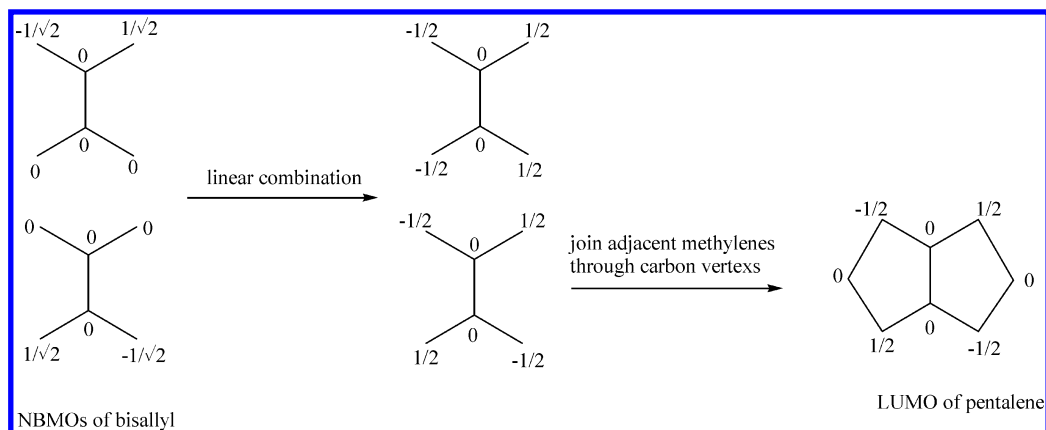
**Disjoint and Nondisjoint Nonalternant Diradicals.** Cyclopentadienyl cation is a nondisjoint diradical that has been calculated<sup>17</sup> and experimentally found<sup>18</sup> to have a triplet gs as predicted by Hund's rule. This nonAH diradical is an antiaromatic, odd carbon species with nonzero degenerate NBMOs. In comparison, square cyclobutadiene is an AH disjoint diradical that is an antiaromatic, even carbon species with degenerate zero NBMOs. We will show that while disjoint degenerate NBMOs are less prevalent in nonAHs, they nevertheless do exist in nonAHs.

Figure 7 gives a nonAH series generated by starting with cyclobutadiene, an AH, and successively splicing-in the 1,3-butadienetetrayl aufbau unit. The relationship of this series with the pair of strongly subspectral series previously studied by us<sup>8</sup> should be evident from Figure 1. The transition from alternant to nonalternant becomes "total" with *s*-indacene (third molecular graph in Figure 7); pentalene (second molecular graph in Figure 7) might be regarded as being partially alternant because it can be embedded or mirror-plane fragmented to allyl monoradical, an AH having the paired eigenvalues of  $\pm\sqrt{2}$ . All the molecular graphs in Figure 7 have both vertical and horizontal mirror-planes, the latter which gives the vertex weighted (upper) and edge-vertex weighted (lower) graph fragments shown; the vertex

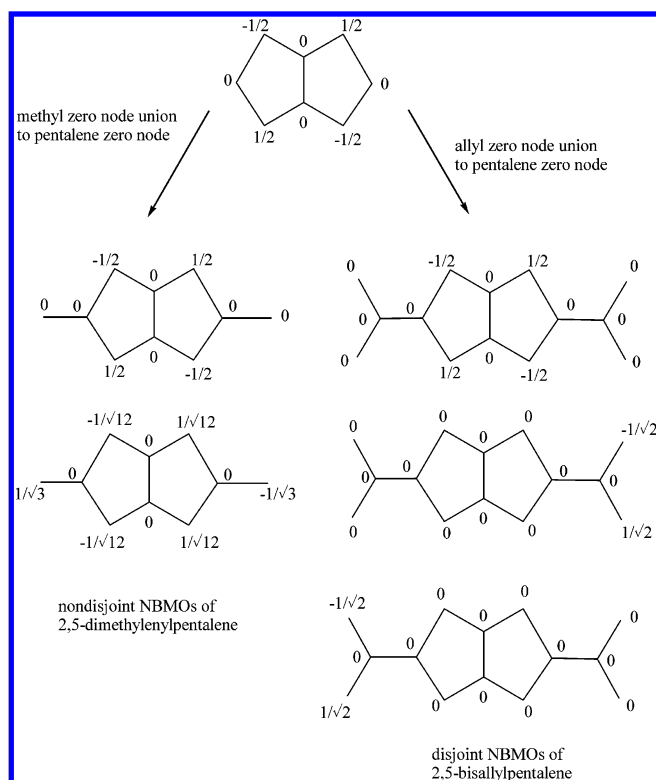
weight of  $-1$  is indicated by open circles and the vertex weight of  $+1$  by circles containing the plus symbol with the edges of weight  $\sqrt{2}$  explicitly noted. The characteristic polynomials for the first three vertex weighted and edge-vertex weighted graphs are given in Figure 7 and their roots (eigenvalues) can be found in Figure 1. From these characteristic polynomials and the respective recursion equations listed Figure 7, one can produce the characteristic polynomials of all other mirror-plane fragments.

The series of vertex weighted graphs listed in Figure 7 are right-hand mirror-plane fragments and are identical to those obtained by horizontal mirror-plane fragmentation of the molecular graph members belonging to the second series given in Figure 1, the first three which have been previously listed.<sup>16</sup> This series of right-hand mirror-plane fragments ( $G_1$ ) have eigenvalues ( $X$ ) that are complimentary [ $X(G_1) + X(G_2) = -1$ ]<sup>19</sup> to the eigenvalues of the series of right-hand mirror-plane fragments ( $G_2$ ) that are generated by horizontal mirror-plane fragmentation of the acene series (top molecular graph series) in Figure 1. Thus the two upper AH series in Figure 1 are both strongly subspectral and complementary in their eigenvalues.<sup>19</sup>

**PMO Construction of Disjoint and Nondisjoint NonAH Diradicals.** In regard to the NBMOs, the second series in Figure 1 can be converted to the third series which is also the same series in Figure 7. Take the linear combination of the disjoint NBMOs of the members in the second series as illustrated with bisallyl in Figure 8 to obtain an alternative but equivalent set of NBMOs. The adjacent methylene groups have identical magnitude but opposite sign eigenvector coefficients which can be joined through a carbons with each corresponding to a zero-sum node for one of the original NBMOs. In this way bisallyl can be converted to pentalene where one the NBMO in bisallyl becomes the zero eigenvalue LUMO (lowest unoccupied molecular orbital) of pentalene both having the identical eigenvector. Thus, all the indacenoids in Figure 7 have one zero eigenvalue ( $X =$



**Figure 8.** Construction of the LUMO of pentalene from the NBMOs of bisallyl.

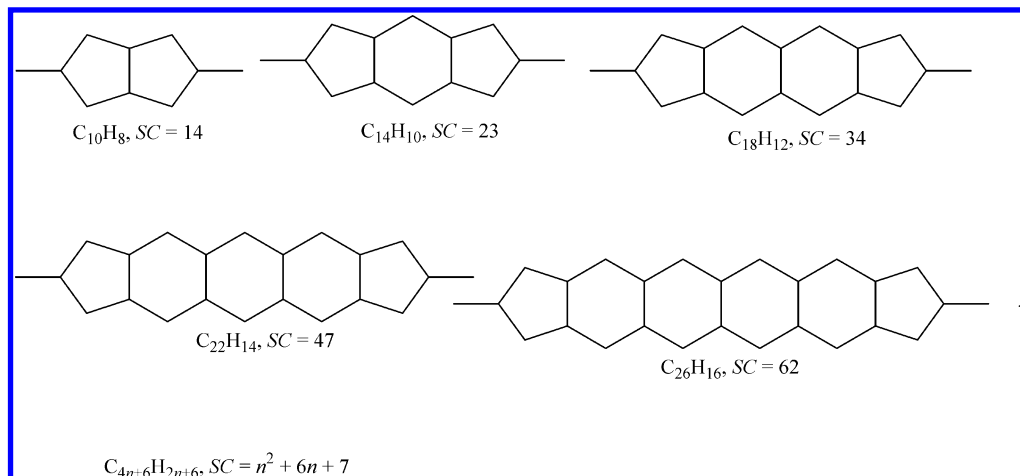


**Figure 9.** Normalized and orthogonal NBMO eigenvectors derived from pentalene union with two methyl and allyl radicals.

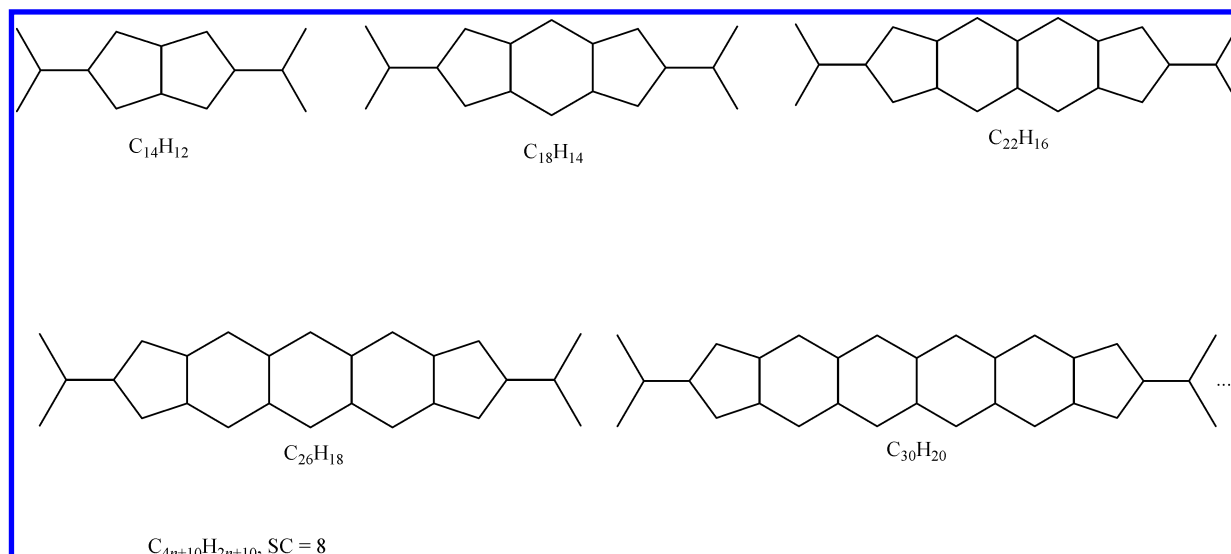
0 for LUMO) which have zero nodes at the central vertex of the trio belonging to the two end pentagonal rings.

Figure 9 gives the PMO union of pentalene with methyl and allyl radicals to generate the nondisjoint NBMOs of 2,5-dimethylenypentalene diradical and the disjoint NBMOs of 2,5-bisallylpentalene diradical, respectively. These PMO unions can be performed on all members of the indacenoid series in Figure 7 to give the two series given in Figures 10 and 11. Corresponding members (same generation) of the series in Figures 10 and 11 have the same right-hand mirror-plane fragments as those given in Figure 7. Thus corresponding members of the second and third series in Figure 1 and Figures 10 and 11 have the same right-hand mirror-plane fragment and have the same set of corresponding eigenvalues. It is interesting to note that 2,5-bisallylpentalene and all other members of the series in Figure 11 have three mutually disjoint NBMOs. One can obtain the NBMO eigenvectors of 2,5-dimethylenypentalene by embedding trimethylenemethane diradical on it.<sup>16</sup> Since bisallyl diradical can be embedded on 2,5-bisallylpentalene, the latter has the eigenvalues of bisallyl. One can take the linear combination of the last two NBMO eigenvectors of 2,5-bisallylpentalene as done for bisallyl diradical in Figure 8 and obtain another equivalent set.

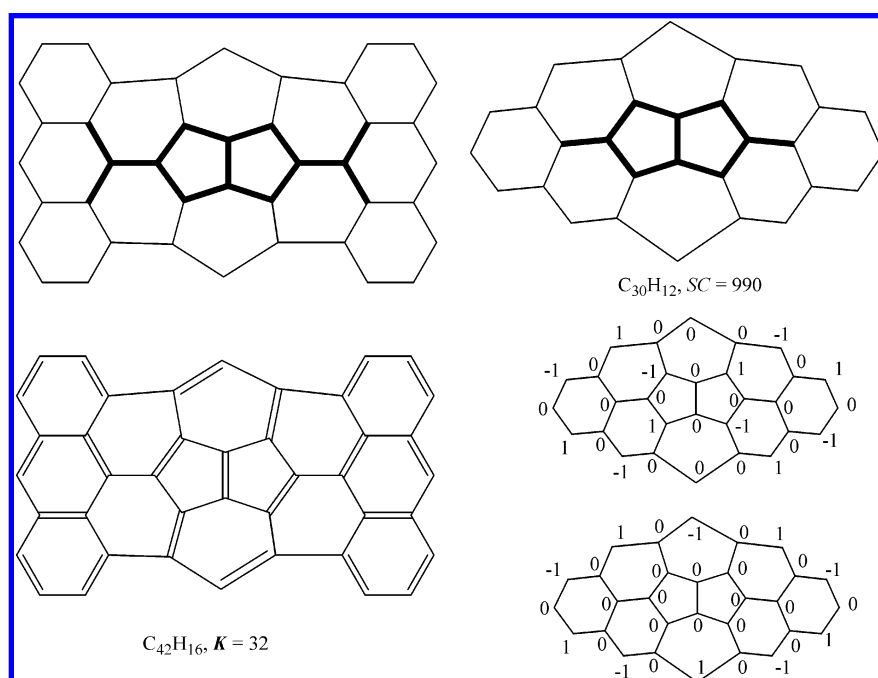
The number of resonance structures (or structure count) for members of the nondisjoint series in Figure 10 increases per  $SC = n^2 + 6n + 7$  ( $n$  = membership generation), whereas for the disjoint series in Figure 11, all members have exactly  $SC = 8$  resonance structures regardless of their size.  $SC = 8$  is the product of 2 for each of the two allyl components and for the polycyclic indacenoid component. For compari-



**Figure 10.** 2,5-Dimethylenypentalene nondisjoint diradical series.



**Figure 11.** 2,5-Bisallylpentadiene disjoint diradical series.



**Figure 12.** Circumscribing an indacenoid disjoint diradical gives a nonradical successor and a nondisjoint diradical gives a diradical successor. The unnormalized NBMO eigenvectors for the nondisjoint diradical successor are given.

son, the number of resonance structures for the acene series (first series), the disjoint series (second series), and the indacenoid series (third series) in Figure 1 are given by  $SC = K = n + 1$ ,  $SC = (n + 1)^2$ , and  $K = 2$ , respectively.

**Circumscribing with Hexagonal Rings as a Test for Disjoint versus Nondisjoint Diradicals.** The first generation members in Figures 10 and 11 are circumscribed with hexagonal rings in Figure 12. The circumscribed  $C_{30}H_{12}$  indacenoid successor of the nondisjoint diradical, 2,5-dimethylenepentadiene, is still a nondisjoint diradical<sup>20,21</sup> with the nondisjoint NBMOs shown in Figure 12. Vertical mirror-plane fragmentation of this  $C_{30}H_{12}$  indacenoid gives phenalenyl monoradical as a right-hand fragment having the NBMO (unnormalized eigenvector, see page 74 in ref 14) that is evident in the right side of the middle molecular graph shown in Figure 12. The circumscribed  $C_{42}H_{16}$  successor to the disjoint diradical, 2,5-bisallylpentadiene, is a Kekulean (nonradical), essentially disconnected polycyclic conjugated

indacenoid hydrocarbon with  $K = 32$  which is the simple product of the Kekulé structures of its two end anthracene ( $K = 4$ ) moieties and a central indeno[2,1,7:hia]indene ( $K = 2$ ) unit. Vertical mirror-plane fragmentation of the  $C_{42}H_{16}$  indacenoid in Figure 12 gives the monoradical, benzo[cd]pyrene, as its right-hand fragment which shows that the LUMO = 0 for this indacenoid.

We previously showed<sup>21</sup> that circumscribing 1,3-dimethylenepentadiene, a closed-shell biradical,<sup>22</sup> gives a nonradical  $C_{30}H_{12}$  indacenoid. Closed-shell biradicals are diradicals by VB and closed-shell  $p\pi$ -electronic systems by HMO calculations and have one zero energy level for a frontier orbital. Circumscribing closed-shell biradicals composed of an even number of odd size rings or disjoint diradicals with hexagonal rings leads to nonradical polycyclic conjugated successor hydrocarbons. In contrast, circumscribing nondisjoint diradicals with hexagonal rings leads to diradical polycyclic conjugated successors. Thus, in summary, the series of

nonAHs in Figure 11 have been shown to have disjoint NBMOs by three different methods: HMO, VB, and topologically by circumscribing with hexagonal rings.

## CONCLUSION

While reviewing the concept and applications of disjoint versus nondisjoint NBMOs which was derived for AHs, the first examples of disjoint NBMOs in nonAHs have been presented in continuation of our study of the consequence of the AH versus nonAH paradigm. A VB method has been shown to be capable of distinguishing between certain diradicals having disjoint and nondisjoint NBMOs. The radical degree of nondisjoint polyradicals is preserved when circumscribed with hexagonal rings in its successor polycyclic hydrocarbon but not preserved in disjoint polyradicals. The interrelationships between the VB terms of cross-conjugated, essentially disconnected, and disjoint have been illuminated. Compared to their isomers cross-conjugated, essentially disconnected, and disjoint species tend to be less stable. Connectivity is a strong determinant of spin multiplicity in polyradical molecules.

## REFERENCES AND NOTES

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