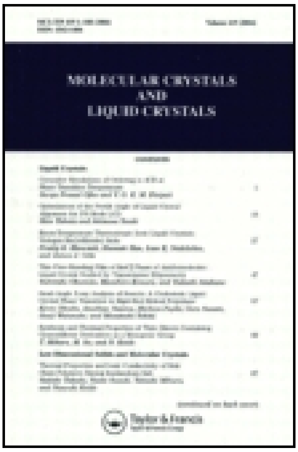

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# Qualitative Methods for Predicting the Ground States of Non-Kekule Hydrocarbons and the Effects of Heteroatom Substitution on the Ordering of the Electronic States

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# QUALITATIVE METHODS FOR PREDICTING THE GROUND STATES OF NON-KEKULE HYDROCARBONS AND THE EFFECTS OF HETEROATOM SUBSTITUTION ON THE ORDERING OF THE ELECTRONIC STATES

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**Abstract** Classification of the NBMOs of a non-Kekulé hydrocarbon as being disjoint or non-disjoint can be used to predict the spin of the ground state and the magnitude of the energy difference between it and the lowest excited state. If the NBMOs are non-disjoint, the bonding in the lowest excited states will be more localized than that in the ground state. The nature of the localized pi bonding in the lowest excited states allows one to predict qualitatively which will be most stabilized by heteroatom substitution and whether it is possible that the attendant stabilization, relative to the ground state, is capable of giving the substituted molecule a ground state of different spin multiplicity. The same predictions can also be made using VB theory.

## INTRODUCTION

Non-Kekulé molecules are conjugated molecules for which no classical Kekulé structures can be written.[1] Non-Kekulé hydrocarbons have been of great interest to both theoreticians and experimentalists during the past 25 years because, like carbenes, but unlike almost all other organic molecules with even numbers of electrons, non-Kekulé hydrocarbons can have high-spin ground states.[2] Some examples of such hydrocarbons, which have been investigated both computationally and experimentally, are trimethylenemethane (**TMM**), 2,4-dimethylenecyclobutane-1,3-diyl (**DMCBD**), *m*-benzoquinodimethane (**MBQDM**), tetramethyleneethane (**TME**), and 1,2,4,5-tetramethylenebenzene (**TMB**). These five non-Kekulé hydrocarbons are depicted in Figure 1.

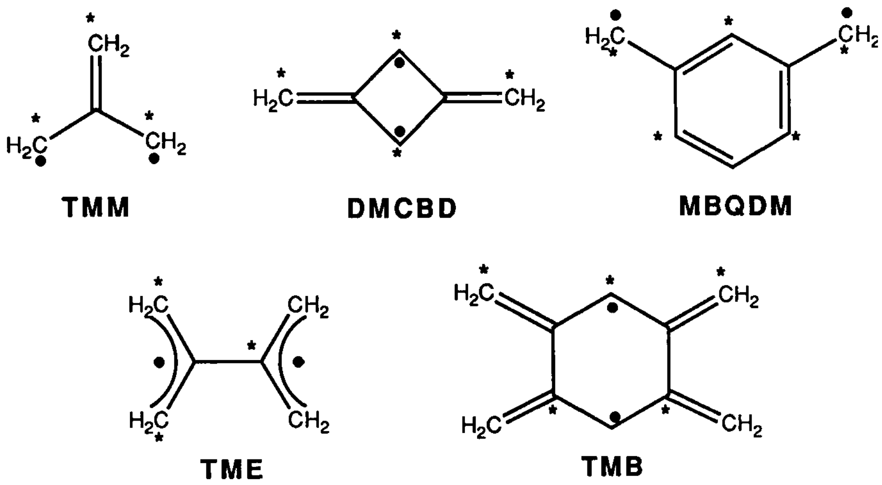


FIGURE 1 Some non-Kekulé alternant hydrocarbon (AH) diradicals. Starred and unstarred atoms are shown.

In a non-Kekulé hydrocarbon that contains no 4n-membered rings, the number of electrons that do not form bonds in any Kekulé structure is equal to both the number of non-bonding molecular orbitals (NBMOs) and the number of electrons that must be accomodated in them.[1] Combining this fact with Hund's rule,[3] Longuet-Higgins predicted that the spin quantum number, S, of the ground state of a non-Kekulé hydrocarbon with n non-bonding electrons ($S = 1/2$ for each) would be $S = n/2$.[1] Using this rule, all the molecules in Figure 1, each of which has two non-bonding electrons (whence the name "diradicals"[4] to describe them), would be predicted to have $S = 1$.

In 1977-78 two theoretical papers appeared, both of which pointed out that violations of Hund's rule might be found in non-Kekulé hydrocarbons. The paper by Borden and Davidson[5] arrived at this prediction by use of molecular orbital (MO) theory. The paper by Ovchinnikov[6] employed a Heisenberg Hamiltonian in what chemists term a valence-bond (VB) approach. Either MO or VB theory can lead to the same set of qualitative predictions regarding the ground states of non-Kekulé hydrocarbons.

## OVCHINNIKOV'S EQUATION

In the VB model, used by Ochinnikov, electrons are initially assumed to be perfectly correlated. For example, in the non-Kekulé hydrocarbons shown in Figure 1, one electron occupies the p-π atomic orbital (AO) on each carbon. A π bond can form between adjacent carbons only if the π electrons on each have opposite spin. Thus, in a VB model the ground state of any molecule is determined by which set of possible distributions of α and β electron spins allows the formation of the maximum number of bonds.

Ovchinnikov derived a simple mathematical expression for predicting the ground state of any alternate hydrocarbon (AH), whether or not it is a non-Kekulé molecule. An AH is a conjugated hydrocarbon in which the carbons can be divided into two sets, traditionally called the starred and unstarred, such that no atoms belonging to the same set are nearest neighbors.[7] This division is possible for all the molecules in Figure 1, so that they are all AHs.

The problem of determining the spin distribution that gives the most bonding in an AH has a simple solution -- put a π electron of one spin, for instance α, at each starred atom and one of opposite spin at each unstarred atom, thus ensuring that each carbon will be able to form π bonds to each of its nearest neighbors. If the number of starred atoms, $N^*$, is equal to the number of unstarred atoms, $N$, as is the case in most AHs (e.g. ethylene, cyclobutadiene, benzene), the number of α and β spin electrons will also be the same, and the ground state will be a singlet. However, if there are more starred than unstarred atoms in an AH, in the ground state the number of α spin electrons will exceed the number of β spin electrons by $N^* - N$. Ovchininikov presented a proof that the excess of α spin is equal to the spin quantum number, $S$. It then follows that

$$S = (N^* - N)/2 \tag{1}$$

for the ground state of any AH.

Application of this formula to predicting the spin of the ground states of the non-Kekulé hydrocarbons in Figure 1 simply involves counting starred and unstarred atoms. Noting that in **TMM**, **DMCBD**, and **MBQDM** N* - N = 2, these molecules are all predicted to have ground states with S = 1. *Ab initio* calculations on these three non-Kekulé hydrocarbons also predict that each of them will have a triplet ground state;[8-10] and experimental results are in agreement with this theoretical expectation.[11-13]

**TME** and **TMB** are diradicals too. Nevertheless, when eq. 1 is applied to predicting the ground state of each, since N* - N = 0, both diradicals are predicted to have a singlet ground state and thus to violate Hund's rule. Once again *ab initio* calculations make the same prediction.[14,15]

Experiment indicates that the prediction of both low-tech (eq. 1) and high-tech (*ab initio* calculations) theory, that **TME** has a singlet ground state, is incorrect.[16] However, eq. 1 really applies only to the planar diradical, where the p-π AOs at the central carbons can interact most strongly. The *ab initio* calculations on **TME** uniformly predict that the lowest singlet does, in fact, lie furthest below the triplet at a planar geometry; but that both states prefer non-planar geometries. Thus, the experimental finding of a triplet ground state for **TME** does not really contradict the prediction of eq. 1, that the lowest electronic state of fully-conjugated, *planar* TME is a singlet.

Since **TMB** almost certainly has a planar geometry, it provides a better test of the validity of eq. 1 and of its prediction that violations of Hund's rule may be found among non-Kekulé hydrocarbons. However, the first experiments on **TMB** by Roth and co-workers indicated that it too has a triplet ground state.[17] Nevertheless, subsequent studies by Berson's group have provided strong evidence for a singlet that is either the ground state or that has very long-term kinetic stability toward relaxation to a lower-lying triplet.[18]

Klein and co-workers have provided a mathematically more rigorous derivation of eq. 1[19] and shown how it can be extended to predicting the ground states of conjugated polycarbenes.[20] Since conjugated mono-carbenes have triplet ground states, the preferred spin of an electron in the σ orbital of such a carbene is the same as that of an electron in the π orbital. Thus, eq. 1 remains valid for predicting the ground state of a conjugated polycarbene if each carbenic center is given a value of 2 in summing up N* and N.

For example, in each repeating unit of the oligomeric carbene **A**, shown in Figure 2, there is one more starred than unstarred atom. Therefore, the spin quantum number of the ground state of the oligomer with m repeating subunits should be given by the formula, S = m. Experimental confirmation of the predictions implicit in this expression for m > 1 have been provided by the research of Itoh and Wasserman for m = 2[21] and by Itoh, Iwamura and coworkers for m = 3, 4, and 5.[22] A branched variant of **A** with six carbenic centers has recently been prepared by Iwamura and co-workers and found, as expected, to have a high-spin ground state with S = 6.[23]

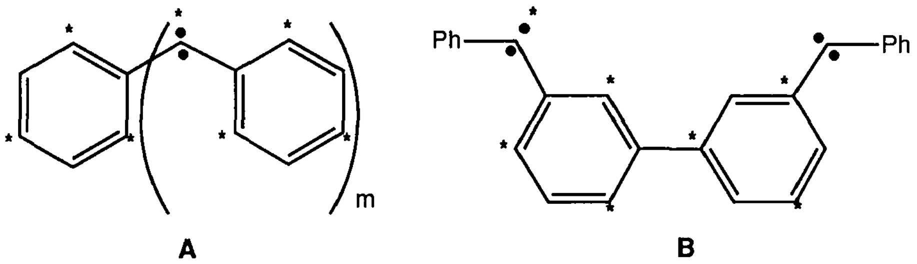


FIGURE 2 Non-Kekulé carbenes with N* ≠ N (**A**) and N* = N (**B**).

In contrast to **A**, bis-carbene **B** in Figure 2 has N* = N. Therefore, it should have S = 0, despite the fact that in the non-Kekulé $\pi$ system of **B**, two electrons occupy two NBMOs. In agreement with the expectation of S = 0 in **B**, Itoh and coworkers in 1978 found that **B** does, indeed, have a singlet ground state.[24] Subsequently, other examples of bis-carbenes[25]and bis-nitrenes[26] with N* = N and singlet ground states have been reported.

Itoh explained the difference between the ground states **A** and **B**, not on the basis of eq. 1 and the VB model that underlies it, but rather in terms of the topology of the $\pi$ NBMOs of these two carbenes. He pointed out that in **A** the two $\pi$ NBMOs both are confined to only the starred carbons; whereas, in **B** the two NBMOs are confined to disjoint sets of atoms, one to the starred set and the other to the unstarred set. In the previous year Borden and Davidson had anticipated Itoh's experimental result by predicting that non-Kekulé hydrocarbon diradicals with disjoint NBMOs might have singlet ground states and thus violate Hund's rule.[5,27]

## DISJOINT AND NON-DISJOINT NBMOS

Borden and Davidson chose as their starting point Hückel theory. As noted above, VB theory assumes that electrons are initially correlated perfectly, thus minimizing their coulomb repulsion energy; and bonding is conceived of as a pertubation on this distribution of electrons. In contrast, Hückel theory totally ignores Coulomb's law and focuses only on maximizing the buildup of electron density in the regions where the AOs on the atoms overlap most strongly.

Borden and Davidson considered how the topology of the two Hückel NBMOs of an AH diradical would affect the mutual coulomb repulsion energy of the two electrons that occupy these MOs. The Hückel NBMOs of any AH can easily be found, without actually doing a Hückel calculation, by using the rule that in the NBMOs of an AH the coefficients of the starred atoms must sum to zero about each unstarred atom.[1,7,28] The coefficients of the unstarred atoms may also sum to zero about each starred atom, or they may all be identically zero.

In the former case the NBMOs can be chosen so that one spans just the starred set of atoms, and the other spans just the unstarred set. Since NBMOs of this type have no atoms in common, they were described by Borden and Davidson as being disjoint. In the latter case, since the NBMOs must span only the starred atoms, the NBMOs *usually* have atoms in common; and, if this is the case, they are termed non-disjoint.

It is often possible to tell whether the NBMOs of an AH are disjoint, simply by counting the number of starred and unstarred atoms. It has been proven[1,5] that the difference, $N^* - N$, is equal to the difference between the number of NBMOs that span just the more numerous, starred set of atoms and the number that span just the unstarred set. Thus, $N^* - N = 0$ is a sufficient condition for showing that pairs of NBMOs (assuming there are some) are disjoint. However, as Borden and Davidson pointed out, $N^* - N \neq 0$ is not a sufficient condition for the existence of disjoint MOs; since, even if $N^* - N \geq 2$ NBMOs are confined to the starred set of atoms, they may still be disjoint (*vide infra*).

Whether the NBMOs are disjoint or non-disjoint has a profound effect on the energy difference between high- and low-spin states of a non-Kekulé molecule. In the state of highest spin, where all the electrons in the NBMOs have parallel spins, the Pauli principle (which is embodied mathematically in the anti-symmetrization of the electronic wavefunction) gives zero probability of finding any of these electrons in the same AO simultaneously. Consequently, even if the NBMOs are non-disjoint, the spatial wavefunction for the highest spin state does not contain ionic terms, corresponding to the simultaneous occupancy of the same AO by any of these electrons.

In contrast, since the Pauli principle does not apply to electrons of opposite spin, wavefunctions for lower spin states *may* contain such ionic terms. These terms are of high coulomb energy; since, when two electrons occupy the same AO, the distance between them is obviously smaller than when the electrons occupy different AOs. This is the physical reason why high-spin states usually have substantially lower energies than states of lower spin and why Hund's rule is generally successful.

However, Borden and Davidson pointed out that in an AH diradical with $N^* - N = 0$, since the NBMOs are disjoint, the nonbonding electrons will, *regardless of spin*, be confined to different sets of atoms (starred for one electron, unstarred for the other). Therefore, in diradicals with disjoint NBMOs, to a first approximation, the singlet and triplet will have the same energy.

## NON-KEKULE AHS THAT HAVE DISJOINT NBMOS AND N* = N

That **TME** and **TMB** are non-Kekulé AHs with disjoint NBMOs is easily deduced from the fact that in both $N^* - N = 0$. The disjoint NBMOs in **TME** are the localized NBMOs for each of the two allyl moieties; one NBMO spans the two starred methylene groups and the other NBMO the two methylene groups that are unstarred. In **TMB** the disjoint NBMOs are the localized NBMOs for each of the two pentadienyl moieties.

Because **TME** and **TMB** are disjoint diradicals, in both diradicals the lowest singlet and triplet are expected to have comparable energies. In fact, this is found to be the case by *ab initio* calculations.[14,15] As discussed above, in both **TME** and **TMB** the singlet is actually computed to lie slightly below the triplet, so that both diradicals are predicted to violate Hund's rule.

The lower energy that is calculated for the singlet can be attributed to two types of bonding that are not included in simple Hückel theory.[5] The first of these is that non-nearest neighbor interactions between AOs allow weak bonding to occur between the two localized NBMOs. These interactions cause $\psi_S$ -- the in-phase combination of the localized, allylic, NBMOs in **TME** and of the localized, pentadienylic, NBMOs in **TMB** -- to have a lower energy than $\psi_A$ -- the out-of-phase combination.

Since the wavefunction ~~for~~ the lowest triplet

$$\Psi(T) = |\ldots\psi_S{}^{\alpha}\psi_A{}^{\alpha}> \qquad (2)$$

places one electron in $\psi_S$ and one electron in $\psi_A$, it cannot profit maximally from the lower energy of the former NBMO. However, since the wavefunction for the lowest singlet state

$$\Psi(S) = c_S|\ldots\psi_S{}^{\alpha}\psi_S{}^{\beta}> - c_A|\ldots\psi_A{}^{\alpha}\psi_A{}^{\beta}> \qquad (3)$$

allows more electron density to be placed in $\psi_S$ than in $\psi_A$ ($c_S > c_A$), the singlet can be stabilized by long-range bonding, involving non-nearest neighbor interactions between the AOs of the localized NBMOs.

The second effect that selectively stabilizes the singlet involves $\pi$ bonding between the carbons where the two localized radical fragments are joined by single bonds in **TME** and **TMB**. The NBMOs have nodes at these carbons; so one might anticipate that the spins of the electrons in the NBMOs would not have any effect on the $\pi$ bonding between these pairs of carbons. However, when electron correlation is included, the spins in the NBMOs cause an uneven distribution of the α and β spin electrons in the bonding π orbitals; and this spin polarization results in some unpaired spin density appearing at the nodal carbons.

In the triplet the spins that are induced at the nodal carbons in each of the radical fragments are parallel, since the spins that induce them are parallel. However, in the lowest singlet, the spins that are induced at the nodal carbons in each of the radical fragments are paired since the spins that induce them are paired. Consequently, the spins induced at the nodal carbons in planar **TME**[5,14] and in **TMB**[15] selectively stabilize the singlet over the triplet and thus contribute to the violation of Hund's rule that is predicted computationally for both fully-conjugated, non-Kekulé, AH diradicals.[29]

A visual representation of the reasons why **TME** and **TMB** are expected to have singlet ground states may be obtained by following the VB prescription for maximum bonding in these two diradicals. This involves placing an α spin electron at each starred atom and a β spin electron at each unstarred atom, as shown for **TME** in structure **A** of Figure 3. It can then be easily seen that this spin distribution allows π bonding to occur across the C-C single bond that connects the two allylic fragments, as well as between the terminal methylene groups of the two fragments. In contrast, in the lowest triplet state of **TME**, which is depicted in structure **B** of Figure 3, the parallel spins at these pairs of carbons prevent π bonding between them.

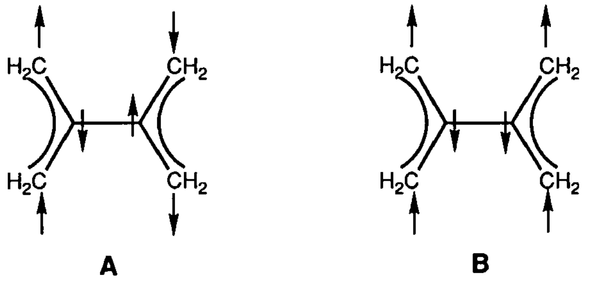


Figure 3 VB depictions of the lowest singlet (**A**) and triplet (**B**) state of **TME**.

Unlike Figure 1, Figure 3 by itself does not indicate the relative strengths of the π bonds in **TME**. Without this additional information, it is not obvious why the selective stabilization of the singlet over the triplet in planar **TME** is calculated to be small (2-4 kcal/mol).[14] Indeed, experimental evidence indicates that the selective stabilization of the planar singlet is so small that, at its equilibrium geometry, the triplet lies below the planar (or any other) singlet geometry.[16] Even the *ab initio* calculations that predict a singlet ground state for **TME** find that π bonding across the C-C single bond that connects the two allylic fragments is so weak in the lowest singlet state that this state prefers a geometry in which the p orbitals on these two carbons are orthogonal and do not interact.[14]

The specific example of **TME** highlights a general problem with eq. 1, whose derivation is based on the same type of VB argument that leads to the prediction that structure **A** in Figure 3 is lower in energy than structure **B**. By itself, eq. 1 gives no indication of whether the energy separation between the predicted ground state and the first excited state in a molecule is expected to be large or small. This prediction requires some information about the relative strengths of the π bonds in the molecule, which could be obtained from either a VB or MO calculation or, more simply, by just drawing resonance structures.

On the other hand, using the MO approach of Borden and Davidson, if a molecule has disjoint NBMOs, the prediction of a small energy separation between the lowest singlet and states of higher spin is easily made. However, the prediction of which state is actually lowest in energy requires additional considerations of the effects of long-range bonding and spin polarization.

In diradicals like **TME** and **TMB**, with $N^* - N = 0$, long-range bonding between non-nearest neighbor atoms and spin polarization are both expected to favor the singlet. Therefore, Borden and Davidson suggested that diradicals with disjoint NBMOs are likely candidates to have singlet ground states.[5] Thus, a non-Kekulé AH in which $N^* - N = 0$ can be predicted to be a molecule in which a violation of Hund's rule is likely to be found, either by using VB theory, from which eq. 1 is derived, or by using the fact that the Hückel NBMOs in such a molecule can be chosen to be disjoint.

As discussed above, support for the correctness of this prediction comes from subsequent experimental studies of **TMB**[18] and of bis-carbenes[24,25] and bis-nitrenes.[26] A singlet ground state has also been reported for a derivative of another AH diradical in which $N^* - N = 0$;[30] and Iwamura and co-workers have found that a conjugated bis-nitroxide, in which the NBMOs are disjoint, has a singlet ground state too.[31]

## NON-KEKULE AHS THAT HAVE DISJOINT NBMOS AND $N^* \neq N$

If $N^* - N \geq 2$, at least two of the NBMOs will span just the starred atoms. However, it is still possible that the NMBOs may, nevertheless, be disjoint.[5] As an example, Borden and Davidson cited pentamethylenepentane (**PMP**), whose structure is depicted in Figure 4. In **PMP** $N^* - N = 2$; and, hence, both NBMOs in this diradical are confined to just the starred atoms. However, it is clear from inspection of the structure of **PMP** that the NBMOs of **PMP** are the NBMOs of the two allyl moities that **PMP** contains. These NBMOs are disjoint; and, moreover, unlike the disjoint NBMOs in **TME**, those in **PMP** are separated by a vinylidene group. Iwamura has suggested the term "doubly disjoint" to describe this type of connectivity.[31]

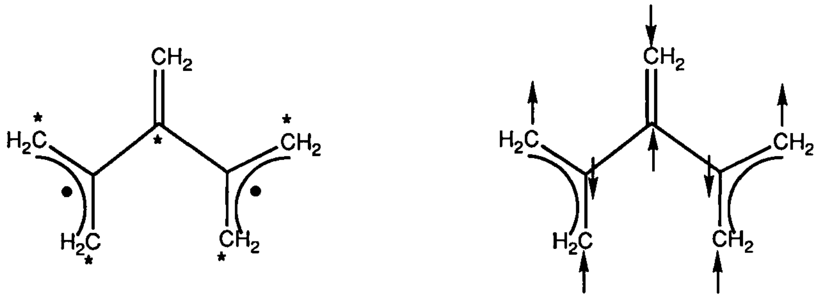


Figure 4 Bonding in **PMP** and VB depiction of the triplet state.

As a result of the interposition of a vinylidene group between the allyl moieties in **PMP**, one might anticipate that the amount of interaction between the small spin density at the central carbons of the allyl moieties would be less in **PMP** than in **TME**. This is indicated by comparison of the VB structure for triplet **PMP**, which eq. 1 predicts to be the ground state and which is shown in Figure 4, with that for the singlet ground state of **TME**, which is shown in Figure 3.

Figure 3 suggests that in **TME** the energy difference, resulting from the interaction of electrons on the two central carbons, between the singlet and triplet states might be approximated by the singlet-triplet energy difference in ethylene, scaled by some factor involving the amount of unpaired spin density at the central carbons of the two allyl moieties. Figure 4 indicates that, using the same type of approximation, the energy difference between the singlet and triplet states of **PMP** should be no greater than the singlet-triplet energy difference in **TMM** times the same scaling factor. This comparison suggests that in **PMP** there should be a factor of 4-5 reduction in the calculated singlet-triplet energy difference of 2-4 kcal/mol in **TME**,[14] which, in turn, is expected to be substantially smaller than the singlet-triplet energy difference in a non-disjoint diradical, such as **TMM**[8] (*vide infra*).

EPR studies by Iwamura and co-workers of isomeric, conjugated bis-nitroxides provide support for the qualitative predictions of the size of singlet-triplet energy gaps, based on whether NBMOs are non-disjoint (as in **TMM**), disjoint (as in **TME**), or doubly disjoint, as in **PMP**.[31] The EPR studies found that the energy difference between the triplet ground state and singlet excited state in the non-disjoint isomer was about three times that between the singlet ground state and the triplet excited state in the disjoint isomer. The magnitude of the singlet-triplet splitting in the "doubly disjoint" isomer was found to be the smallest of all; and, moreover, in contrast to the prediction of eq. 1, the ground state was actually found to be a singlet.

## CONSEQUENCES OF NON-DISJOINT NBMOS

Non-Kekulé AHs have at least $N^* - N$ Hückel NBMOs that are confined to only the starred set of atoms.[1,5] Thus, $N^* - N$ of the NBMO's have the possibility (*vide supra*) of being non-disjoint. In a molecule which has $N^* - N \geq 2$ NBMOs that actually are non-disjoint, Hund's rule is expected to apply to the $N^* - N$ electrons in them. Consequently, the ground state of a non-Kekulé AH with N* - N non-disjoint NBMOs is expected to have this number of electrons with parallel spins. Thus, its spin quantum number is predicted to be S = (N* - N)/2, in agreement with eq. 1.

However, as noted in the previous section, eq. 1 only predicts the multiplicity of the ground state, not the size of the energy difference between it and the lowest excited state. In contrast, if a molecule is found to have non-disjoint Hückel NBMOs, because the wavefunction for a high-spin ground state avoids the ionic terms that are present in the wavefunctions for excited states of lower spin, a substantial energy difference between the ground state and the first excited state is expected. Thus, in such a molecule the splitting between the ground and first excited state is expected to be considerably larger than in a non-Kekulé molecule with disjoint or "doubly disjoint" NBMOs. This qualitative prediction is supported by the results of *ab initio* calculations[8-10,14,15] on the diradicals in Figure 1 and by the recent experiments of Iwamura and co-workers.[31]

A second prediction, made possible by the finding that a non-Kekulé AH has non-disjoint Hückel NBMOs, is that the low-spin states will use a different set of MOs than the state of highest spin; and, hence, these excited states will have very different equilibrium geometries from that of the high-spin ground state.[5] This prediction is based on the fact that, when the Hückel NBMOs are non-disjoint, the very large coulombic repulsion between the non-bonding electrons in low-spin states can be reduced by confining the NBMOs to different sets of atoms. This requires that the low-spin excited states use a different and more localized set of MOs, which provide less bonding than the Hückel orbitals that are utilized by the high-spin ground state.

A well-studied example is provided by **TMM**.[5,8] The bonding in each of the three lowest electronic states of **TMM** is depicted in Figure 5. The bonding in the triplet is fully delocalized, with $\pi$ bonds of equal strength between the central carbon and each of the three methylene groups and equal spin densities on all three.

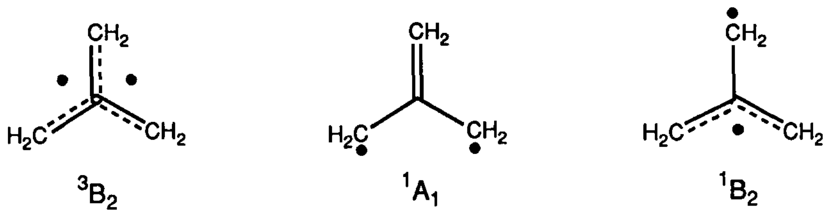


Figure 5 Bonding in the three lowest electronic states of **TMM**.

However, as shown in Figure 6, the Hückel NBMOs that are utilized by the $^3A_2$ state are non-disjoint. Consequently, singlet wavefunctions, either two-configuration,

$$^1A_1 = |...2b_1^{\alpha}2b_1^{\beta}> - |...1a_2^{\alpha}1a_2^{\beta}> \qquad (4)$$

or open-shell

$$^1B_2 = |...2b_1 1a_2(\alpha\beta - \beta\alpha> \qquad (5)$$

that utilize the Hückel NBMOs contain high-energy, ionic terms, corresponding to the simultaneous occupancy of the same AO by both non-bonding electrons.

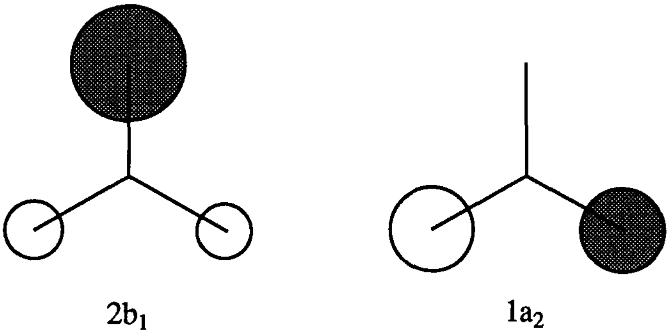


Figure 6 Hückel NBMOs for **TMM**. Only one lobe of each p-π AO is shown.

A lower energy is obtained for each singlet state with a set of MOs that are different from the Hückel orbitals and which confine the two electrons of opposite spin to different atoms. For example, in the $^1B_2$ state confining the $2b_1$ NBMO to the carbon where the $1a_2$ NBMO has a node prevents the electrons that occupy these orbitals from ever appearing in the same AO. However, the resulting reduction in coulomb repulsion energy in $^1B_2$ is achieved only at the expense of a reduction in $\pi$ bonding from that in $^3B_2$ . As shown in Figure 5, the $\pi$ bonding in$^1B_2$ resembles that in an allyl radical, with the second non-bonding electron localized at the remaining methylene group. Consequently, this singlet state prefers a different equilibrium geometry than the $D_{3h}$ geometry of the triplet.

The $^1B_2$ state prefers an equilibrium geometry with two medium-length and one long C-C bond. In contrast, the $^1A_1$ state has a strong $\pi$ bond to one methylene carbon and little or no $\pi$ bonding to the other two, so that it is calculated to prefer a geometry with one short and two long C-C bonds. These two states are calculated to have nearly the same energy, and both lie on the lowest singlet potential surface for **TMM**.[8]

The prediction of differences between the bonding in the triplet and in the two lowest singlet states of **TMM** can also be made from VB theory. VB structures for **TMM**, which assume that electrons of opposite spin are localized at different atoms, are shown in Figure 7. The first structure, which has $\alpha$ spin electrons at the three starred atoms and a $\beta$ spin electron at the central carbon, corresponds to the $S_z = 1$ component of the triplet ground state. In this state $\pi$ bonding occurs between the central carbon and all three methylene groups.

The next three structures, in which a second $\beta$ spin electron is located on one methylene group, obviously all have $S_z = 0$. The sum of all three represents the second of the three components of the triplet state. The combination of just the first two with the opposite sign represents $^1A_1$, with a strong $\pi$ bond to one methylene group and the two non-bonding electrons localized, one each, on the other two methylene groups. The third $S_z = 0$ structure, with a smaller contribution from the sum of the first two, represents $^1B_2$, in which the central carbon is $\pi$ bonded to two of the methylene groups, but not to the third.

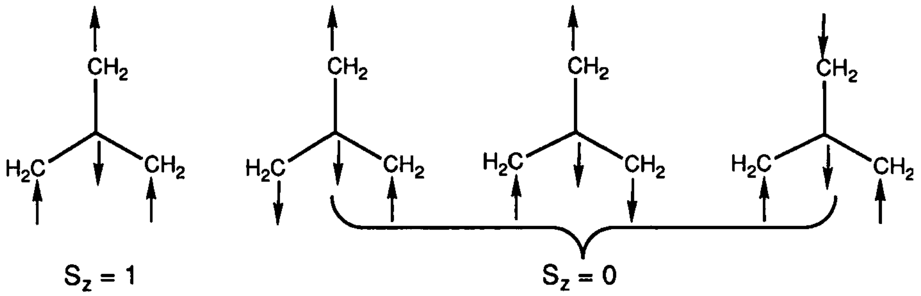


Figure 7 VB structures for **TMM**

Like **TMM**, **DMCBD** and **MBQDM** are also diradicals with non-disjoint NBMOs. Consequently, like the former, the latter two diradicals also have singlet states in which the bonding is much more localized than that in the triplet ground state. The type of localization that occurs in the lowest two singlet states of **DMCBD** and **MBQDM** is discussed in the next section, which deals with the effects of heteroatom substitution. As discussed in the following section, the nature of the localized $\pi$ bonding in each singlet state determines whether heteroatom substitution stabilizes it, relative to the more delocalized triplet state.

## EFFECTS OF HETEROATOM SUBSTITUTION

Ovchinnikov conjectured that heteroatom substitution would not invalidate the arguments that produced eq. 1.[6] However, heteroatom substitution has the possibility of lifting the approximate degeneracy of the NBMOs sufficiently that, in the ground state of the substituted molecule, two electrons occupy the MO that is most stabilized. Spin pairing of electrons will obviously have the most dramatic effect when the hydrocarbon, from which the substituted molecule is derived, has a high-spin ground state. Therefore, the most interesting non-Kekulé AHs in which to investigate the effect of heteroatom substitution are those which have non-disjoint NBMOs and, thus, are expected to have a high-spin ground state.

If it is assumed that the same NBMOs are used for both the lowest singlet and triplet in a diradical, it is easy to derive an equation for the circumstances under which a singlet wavefunction, like that in eq. 3, can fall below the triplet wavfunction.[32] However, as noted in the previous section, in diradicals with non-disjoint NBMOs the lowest singlets do not use the same MOs as the triplet, so that this expression is not applicable.[33] However, one can qualitatively understand the effects of heteroatom substitution on the triplet and two lowest singlet states in such diradicals by considering the bonding in these states and the effect of heteroatoms on it.

For example, if one methylene group in **TMM** is replaced by an oxygen atom, the bonding in the lowest three states of **TMM** (Figure 5) can be used to obtain the first-order description of the bonding in oxyallyl (**OA**) that is shown in Figure 8. Since C-O π bonds are considerably stronger than C-C π bonds, it is trivial to predict from Figure 8 the first-order effect of replacing a terminal methylene group by an oxygen.

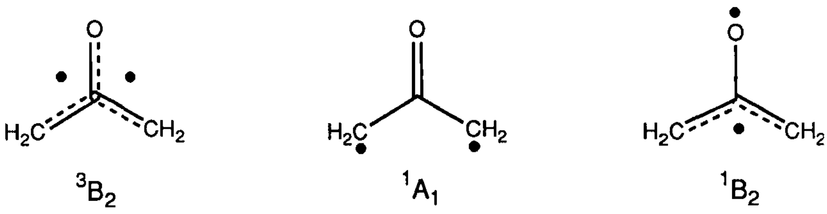


Figure 8 Bonding in **OA**

The $^1A_1$ state should be stabilized the most by this substitution, since it has the largest amount of C-O π bonding. Only one of the three resonance structures for the triplet ($^3B_2$) contains a π bond to oxygen; so $^3B_2$ should be stabilized less; and the $^1B_2$ state should not be stabilized at all, since it has no π bonding to oxygen. Therefore, on going from **TMM** to **OA**, the near degeneracy of $^1A_1$ and $^1B_2$ in **TMM**[8] should be strongly lifted, and $^1A_1$ should also be be stabilized with respect to $^3B_2$.

The predictions, based on this simple model, have been confirmed by the results of *ab initio* calculations.[34] The highest level *ab initio* calculations on **OA** predict that $^1A_1$ and $^3B_2$ have nearly the same energy and that substitution of methyl for one hydrogen on each methylene group[34] or incorporation of **OA** into a four- or five-membered ring[35] will make $^1A_1$ the ground state. The prediction of a singlet ground state for cyclic derivatives of **OA** appears to have found confirmation in recent experiments by Miyashi and co-workers.[36]

One might inquire how, based on Figure 8, $^1A_1$ could become the ground state of **OA** or a simple derivative, since the $^3B_2$ state could always use the same set of MOs as $^1A_1$ and thus have just as strong a $\pi$ bond to oxygen. There is, in fact, computational evidence that this does tend to occur in $^3B_2$.[34] Any delocalization in $^3B_2$, made possible by the correlation between the pair of electrons in its NBMOs, might then be anticipated to make the triplet the ground state.

What allows a $^1A_1$ ground state is the difference between the form of the wavefunction for this state (eq. 3) and that for the lowest triplet (eq. 2). In the triplet exactly one electron occupies $\psi_S$, in this case the $2b_1$ MO. This MO is stabilized, relative to $\psi_A$ ($1a_2$), because the in-phase ($b_1$) combination of p-$\pi$ AOs on the two methylene carbons is stabilized by mixing with the low-lying, unfilled $\pi^*$ orbital of the carbonyl group in $\psi_S$; whereas the out-of-phase ($a_2$) combination of p-$\pi$ methylene-carbon AOs in $\psi_A$ has the wrong symmetry to mix with $\pi^*$. However, because both $\psi_S$ and $\psi_A$ are each occupied by one electron in the triplet, the $^3B_2$ wavefunction is unable to take maximal advantage of the lower energy of $\psi_S$, compared to $\psi_A$.

In contrast, in the $^1A_1$ wavefunction the first configuration can have a much greater weight than the second, so that the occupation number, $2c_S^2$, of $\psi_S$ can be greater than that of $\psi_A$. In fact, the occupation number of about 1.4 for $\psi_S$ in the $^1A_1$ state of **OA** is 2.5 times larger than that for $\psi_A$.[34] Thus, it is the greater flexibility of the wavefunction for $^1A_1$, relative to that for $^3B_2$ ,that allows the singlet to fall below the triplet in derivatives of **OA**.[34-36]

In cyclobutane-2,4-dione-1,3-diyl (**CBDOD**), the dioxa derivative of **DMCBD** that is shown in Figure 9, the in-phase combination of the two p-$\pi$ AOs at $C_1$ and $C_3$ interacts with the $\pi^*$ orbitals of both carbonyl groups in $\psi_S$ .[37] Consequently, one might expect a larger energy difference between $\psi_S$ ($2b_{1u}$) and $\psi_A$ ($1b_{3g}$) in **CBDOD** than in **OA**. This should result in a larger occupancy of $\psi_S$ and a lower energy for $^1A_{1(g)}$, relative to $^3B_{2(u)}$, in **CBDOD** than in **OA**. Both of these predictions have been confirmed by the results of calculations.[9b,37]

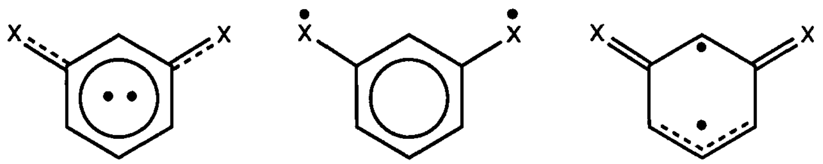
$^3B_{2g}$ $^1A_{1g}$

Figure 9 Bonding in the lowest electronic states of **DMCBD** ($X = CH_2$) and in **CBDOD** ($X = O$).

In **DMCBD** itself transannular interaction between the p-π AOs at $C_1$ and $C_3$, which stabilizes $\psi_S$ and destabilizes $\psi_A$, results in the square of the coefficient of $|\ldots\psi_S^2>$ being about 2.7 times larger than the square of the coefficient of $|\ldots\psi_A^2>$ in the $^1A_{1g}$ wavefunction.[9b] Nevertheless, despite the energy difference between $\psi_S$ and $\psi_A$ in **DMCBD**, the fact that the NBMOs in this AH diradical are non-disjoint results $^1A_{1g}$ being calculated to lie on the order of 20 kcal/mol above $^3B_{2u}$. However, in **CBDOD** the ratio of the squares of the coefficients increases to 12.6 in the most highly correlated wavefunction for $A_{1g}$, and this state is calculated to lie about 20 kcal/mol *below* $^3B_{2u}$.[9b]

From the results for **OA** and **CBDOD** one might imagine that the substitution of oxygen for methylene in a non-disjoint AH diradical would always result in a dramatic reduction of the energy difference between the lowest singlet and triplet states, with the former quite possibly becoming the ground state. That this is not the case is shown by the results of *ab initio* calculations on the effect of replacing the two exocyclic methylene groups in **MBQDM** with the two oxygens in *m*-benzoquinone (**MBQ**).[10b]

The calculations find that $^3B_2$ is the ground state of both non-Kekulé diradicals. In **MBQDM** the next lowest state is $^1A_1$, which is calculated to lie about 14 kcal/mol above the triplet ground state of this non-disjoint AH. The singlet state, $^1B_2$, that has the same orbital occupancy as the triplet lies about 12 kcal/mol higher still in energy. The bonding in each of these states is depicted schematically in Figure 10, which also gives their relative energies in kcal/mol.



| | $^3B_2$ | $^1A_1$ | $^1B_2$ |
|---|---|---|---|
| X = $CH_2$ | 0 | 14 | 26 |
| X = O | 0 | 27 | 9 |

Figure 10 Relative energies (kcal/mol) of the low-lying states of **MBQDM** (X = $CH_2$) and **MBQ** (X = O).

The relative energies of the corresponding states of **MBQ** are also given in Figure 10. The substitution of the two oxygens in **MBQ** for two methylene groups in **MBQDM** actually increases the energy of $^1A_1$, relative to that of $^3B_2$, by about 13 kcal/mol. However, the relative energy of $^1B_2$ decreases by 17 kcal/mol, so that in **MBQ** it lies 18 kcal/mol below $^1A_1$. Because in **MBQDM** $^1B_2$ lies about 26 kcal/mol above $^3B_2$, despite the 17 kcal/mol selective stabilization of $^1B_2$ in **MBQ**, $^1B_2$ still lies 9 kcal/mol above the $^3B_2$ ground state.

The changes in the relative energies of the low-lying states on replacing the two methylene groups in **MBQDM** by the two oxygens in **MBQ** can be easily understood. As discussed in connection with the effect of substituting an oxygen for one methylene group in **TMM** to form **OA**, of major importance is the greater strength of a C-O, compared to a C-C, π bond. This effect undoubtedly also plays a role in the stabilization of $^1A_{1g}$, relative to $^3B_{2u}$, on going from **DMCBD** to **CBDOD**;[9b] since, in **DMCBD** $^1A_{1g}$ has more π bonding than $^3B_{2u}$ to the exocyclic methylene groups, which become oxygen atoms in **CBDOD**.

In contrast, as shown in Figure 10, there is little or no π bonding to the exocyclic methylene groups in the lowest singlet state ($^1A_1$) of **MBQDM**. Consequently, substitution of oxygen for these two methylene groups to give **MBQ** does not result in the formation of strong C-O π bonds in $^1A_1$. However, in both $^1B_2$ and $^3B_2$ of **MBQDM** there is π bonding to the exocyclic methylene groups, so that substitution of oxygen for them does result in the formation of C-O π bonds in both these states of **MBQ**. Consequently, both $^1B_2$ and $^3B_2$ are stabilized, relative to $^1A_1$, on going from **MBQDM** to **MBQ**.

Since $^1B_2$ of **MBQDM** has stronger π bonds to the exocyclic methylene groups than does the more highly delocalized $^3B_2$,the singlet state is stabilized more than the triplet on going from **MBQDM** to **MBQ**. However, there is no concern that $^1B_2$ might fall below $^3B_2$ in **MBQ**; since, unlike $^1A_1$, $^1B_2$ has the same orbital occupancy -- one electron in each NBMO -- as the triplet. Consequently, because the NBMOs in **MBQDM** (and, by inference, those in **MBQ**) are non-disjoint, $^3B_2$ can confidentally be predicted to be lower in energy than $^1B_2$ in **MBQ**. The prediction of a triplet ground state for **MBQ** awaits experimental verification.[38]

## CONCLUSIONS

Classification of the NBMOs of a non-Kekulé hydrocarbon as being disjoint or non-disjoint can be used to predict the spin of the ground state and whether the size of the energy difference between it and the lowest excited state is likely to be small or large. In addition, if the NBMOs are non-disjoint, the bonding in the low-spin excited states can be predicted to be more localized than that in the high spin ground state. The nature of the localized π bonding in the lowest excited states allows the prediction of which will be most stabilized by heteroatom substitution and whether it is possible that the substituted molecule will have a ground state of different spin multiplicity than that of the parent hydrocarbon.

The same predictions can be made using VB, rather than MO, theory. Eq. 1, which is derived from VB theory, allows the prediction of the spin of the ground state of an AH. Application of this equation only requires counting the number of starred and unstarred atoms, which makes its use very attractive. However, additional considerations are necessary in order to predict the relative size of the energy difference between the ground state and the lowest excited states, the nature of the bonding in these states, and how heteroatom substitution is likely to affect their relative energies.

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