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Calculations of the Relative Energies of the Low-Lying Electronic States of 2-Methylenedihydrophenalene-1,3-diyl: Effects of a 1,8-Naphtho Bridging Group on Trimethylenemethane and of a Vinylidene Bridging Group on 1,8-Naphthoquinodimethane

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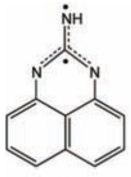
CASSCF and CASPT2/6-31G(d) calculations have been performed on the low-lying electronic states of three, non-Kekulé, hydrocarbon diradicals: 2-methylenedihydrophenalene-1,3-diyl (**2**), trimethylenemethane (**3**), and 1,8-naphthoquinodimethane (**4**). The computational results reveal how addition of ferromagnetic coupling groups (1,8-naphtho to **3** and vinylidene to **4**) modulates the energy differences between the three lowest electronic states of **2**−**4**. The most dramatic effect is the 30.4 kcal/mol change in the relative energies of the $^1A_1$ and $^1B_2$ states on addition of a vinylidene bridging group to **4** to form **2**. The relative energies of the electronic states of **2**−**4** are discussed in terms of the topologies of the pair of nonbonding MOs for each state of each diradical, and a strategy for making $^1A_1$ the ground state of a nitrogen analogue of **4** is proposed.

The generation and EPR spectrum of a trialkyl derivative of triplet diradical **1** has recently been reported.[1] Diradical **1** is a triaza analogue of 2-methylenedihydrophenalene-1,3-diyl (**2**), a previously unknown hydrocarbon diradical. As was pointed out in the paper, describing the synthesis of trialkylated **1**, hydrocarbon **2** can be viewed either as trimethylenemethane (**3**),[2] connected to carbons C1 and C8 of a naphtho substituent, or as 1,8-naphthoquinodimethane (**4**),[3] bridged by vinylidene.

As shown in the drawings, **2**, **3**, and **4** are all alternant hydrocarbons: molecules in which the atoms can be divided into two sets, "starred" and "unstarred", such that two atoms of the same set are not nearest neighbors.[4] In all the Kekulé structures that can be written for **2**−**4**, at least two π electrons are not involved in bonds. Consequently, **2**−**4** are called non-Kekulé, alternant, hydrocarbon diradicals.[5]



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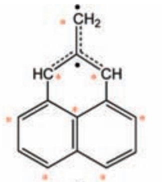

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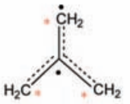

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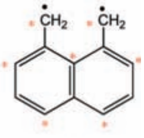

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For any diradical, a vital pair of closely related questions concerns the spin of the ground state—singlet or triplet—and the sizes of the energy differences between the triplet and the two low-lying singlet states.[6] For non-Kekulé hydrocarbon diradicals, the spin of the ground state can easily be predicted,[7] based on either the topology of the nonbonding (NB)MOs[8] or on valence-bond (VB) arguments.[9] When, as in **2**−**4**, the number of starred carbons exceeds the number of unstarred carbons by two, both the MO and VB perspectives unequivocally predict a triplet ground state.

The linear Curie−Weiss plot observed for **3**[10] indicates that, as expected,[8,9] this diradical does, indeed, have a triplet ground state. The size of the singlet−triplet splitting in **3** was the focus of many calculations,[11] until this energy difference was measured by negative ion photoelectron spectroscopy in 1997.[12] The best calculations[11i,j] place the $^3A_2'$ state ($^3B_2$ in C_{2v} symmetry) 17.5 kcal/mol lower in energy than the $^1A_1$ state, in good agreement with the value of 16.1 kcal/mol obtained experimentally.[12,13]

A linear Curie−Weiss plot has also been obtained for trialkylated **1**,[1] a triaza analogue of **2**; and triplet EPR spectra have been observed for both **4**[3a] and a diaza analogue of it.[3b] These findings suggest that triplets are probably also the ground states of **2** and **4**, or at least are very close in energy to the ground states. However, to the best of our knowledge, the singlet−triplet energy separations in **2** and **4** have neither been reliably calculated[14] nor accurately measured.

In this paper, we report the results of ab initio calculations that we performed to predict the energy differences between the triplet and the two lowest lying singlet states of **2** and **4**. These results have enabled us to compare how addition of ferromagnetic coupling groups,[15] 1,8-naphtho to **3** and vinylidene to **4**, modulates the energy differences between the three lowest electronic states of **2**−**4**.

Our two most notable computational findings are the following: (a) in **4**, the $^1A_1$ state is calculated to lie only 3.7 kcal/mol above the $^3B_2$ ground state, and (b) the vinylidene group in **2** increases the energy difference between these two states in **4** by 15.2 kcal/mol but decreases the energy separation between the $^3B_2$ and $^1B_2$ states in **4** by 15.2 kcal/mol. In this paper, we discuss the reasons why (a) the energy difference between the $^1A_1$ and $^3B_2$ states of **4** is comparatively small and (b) addition to **4** of a vinylidene bridging group, to afford **2**, results in a dramatic change of 30.4 kcal/mol in the relative energies of these two singlet states.

Computational Methodology

We have previously found that complete active-space (CAS)SCF calculations, followed by inclusion of the effects of dynamic electron correlation[16] through the use of multireference, second-order perturbation theory (CASPT2),[17] afford singlet−

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TABLE 1: Calculated CASSCF/6-31G(d) and CASPT2/6-31G(d) Energies (kcal/mol) of the Low-Lying Singlet States in 2−4, Relative to the Energies of the $^3B_2$ Ground States

	2				3				4		
	$^3B_2$	$^1A_1$	$^1B_2$	$^1B_1$	$^3B_2$	$^1A_1$	$^1B_2$	$^1B_1$	$^3B_2$	$^1A_1$	$^1B_2$
CASSCF	0	19.8	13.8	14.8	0	19.8	20.2	14.6	0	6.1	27.0
CASPT2	0	18.9	11.8	14.4	0	19.3	19.9	14.9	0	3.7	27.0

triplet splittings that are in good agreement with the experimentally measured values.[7] For these calculations, the 6-31G(d) basis set[18] proved adequate. Therefore, we optimized the geometries of the triplet and two lowest singlet states of **2** and **4** with, respectively, (14/14)- and (12/12)-CASSCF/6-31G(d) calculations.[19] These calculations correlated the electrons in the bonding and nonbonding π MOs in each diradical by using all the possible configurations that can be formed by excitations of electrons into the same number of antibonding π^* MOs as there are bonding π MOs. Single-point (12/12)- and (14/14)-CASPT2 calculations were performed at the CASSCF optimized geometries. All of these calculations were carried out with MOLCAS.[20]

Results and Discussion

Table 1 gives the CASSCF/6-31G(d) and CASPT2/6-31G(d) energies of the $^1A_1$ and $^1B_2$ states, relative to the $^3B_2$ ground states, of **2** and **4**. For comparison, we have also included in Table 1 the results of (4/4)CASSCF/6-31G(d) and CASPT2/6-31G(d) calculations of the relative energies of the low-lying states of trimethylenemethane (**3**).[11k] The energies of the $^1B_1$ states of **2** and **3**, in which a methylene group is twisted out of conjugation with the rest of the π system, are also given in Table 1.

Table 1 shows that, as expected,[8,9] the ground state of each of the diradicals **2**−**4** is computed to be a triplet. The CASSCF/6-31G(d) bond lengths in the triplets and in each of the low-lying singlet states are given in Figure 1. The π nonbonding (NB)MOs for each of these states of **2**−**4** are drawn in Figure 2.

Different NBMOs for Different Electronic States of a Diradical Lead to Different Geometries. The differences between the geometries of the low-lying electronic states in **3** and in the trimethylenemethane (TMM) moiety of **2** provide important clues as to how the ferromagnetic 1,8-naphtho coupling unit in **2** alters the relative energies of the electronic states of **3**. Similarly, the differences between the geometries of the low-lying electronic states in **4** and in the 1,8-naphthoquinodimethane (NQDM) moiety of **2** furnish information as to how the ferromagnetic vinylidene coupling unit in **2** affects the relative energies of the electronic states of **4**. However, it is essential first to understand why, as shown in Figure 1, the geometries of the low-lying electronic states differ from each other in **2**, in **3**, and in **4**. (Readers who are already familiar with the material in this Section on the wave functions for different, low-lying, electronic states of diradicals may wish to skip it and move on to the next Section.)

For example, unlike the triplet ground state of **3**, which has D_{3h} symmetry, the C−C bond lengths in the $^1A_1$ and $^1B_2$ states of **3** are not all the same. In addition, unlike the triplet state of **3**, which is planar,[2a] the lowest energy singlet state prefers a geometry with one methylene group twisted out of conjugation.[2b,6−8,11]

The reason why the geometries of the singlet states of **2**, **3**, and **4** all differ from those of the triplets is that in the singlet states the nonbonding electrons have opposite spin; so their motions are not correlated by the Pauli exclusion principle. Therefore, minimization of the Coulomb repulsion energy between the nonbonding electrons in the singlet states tends to confine these electrons to different regions of space.[6−8] Consequently, as shown in Figure 2, the $^1A_1$ and $^1B_2$ states of **2**−**4** have very different sets of NBMOs from the $^3B_2$ states, and

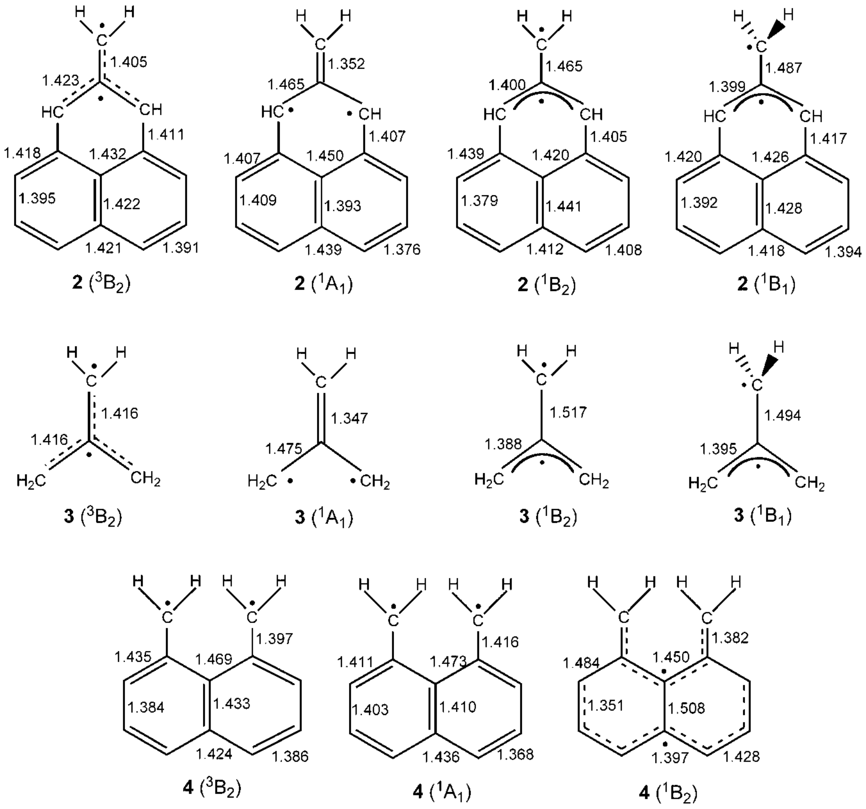


Figure 1. C_{2v} equilibrium C−C bond lengths (Å) in the low-lying electronic states of **2**−**4**, calculated at the CASSCF/6-31G(d) level.

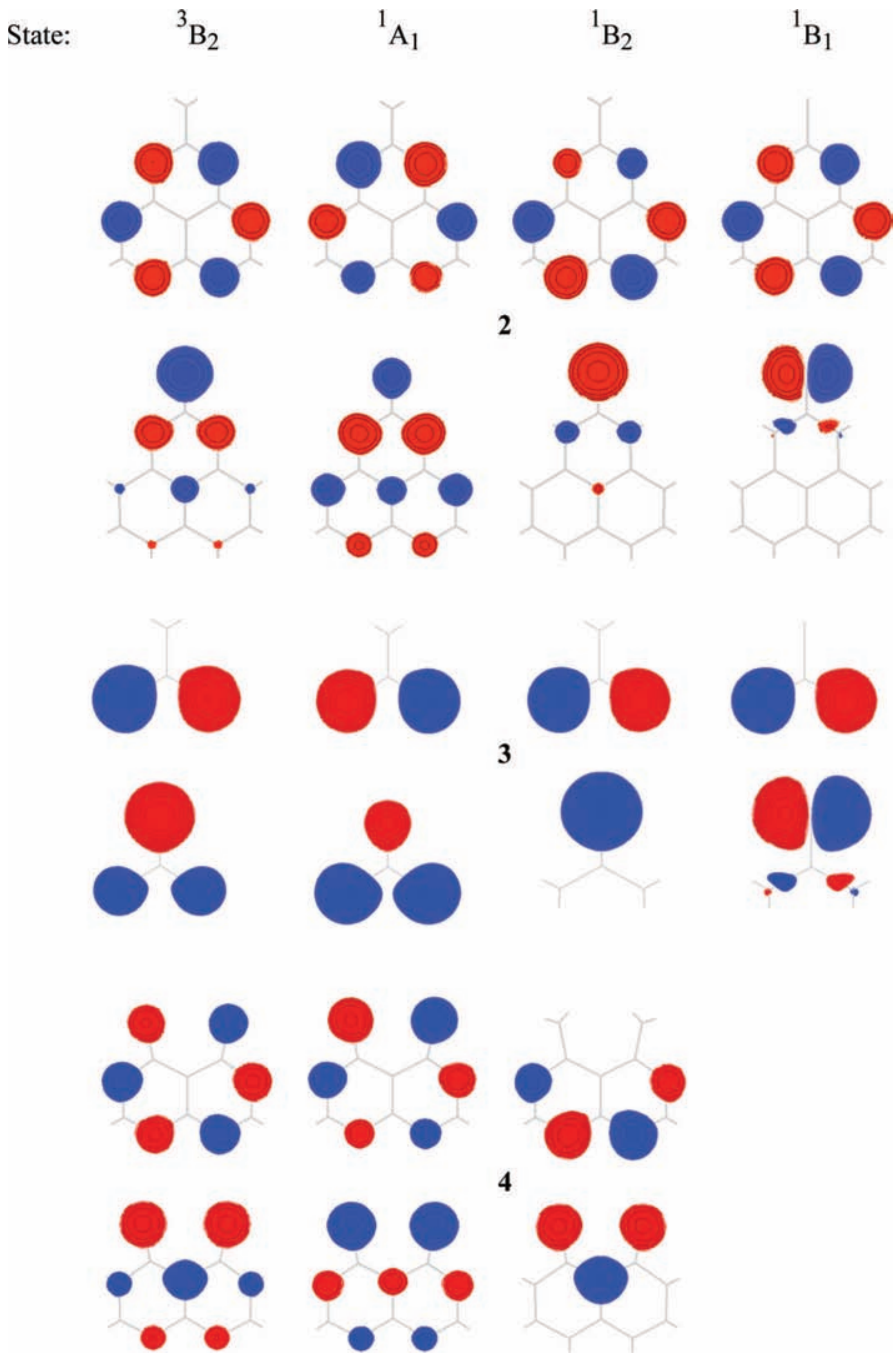


Figure 2. The a_2 (top line) and b_1/b_2 (bottom line) NBMOs for the $^3B_2$, $^1A_1$, $^1B_2$, and $^1B_1$ electronic states of **2**−**4**. Only the upper lobe of each 2p−π AO is shown.

also from each other. Since the π MOs of the singlet states not only differ from those of the triplets but also from each other, the C−C bond lengths in the $^3B_2$, $^1A_1$, and $^1B_2$ states of the same diradical are all different, as shown in Figure 1.

Figure 2 shows that the a_2 and b_1 NBMOs of the $^1B_2$ states of **2**−**4** are, indeed, more localized in different regions of space than the corresponding NBMOs of the $^3B_2$ state. However, the opposite is true for the NBMOs of the $^1A_1$ state. The NBMOs for this singlet state are more localized in the same region of space than the triplet NBMOs. The reason is that in the $^1A_1$ state it is the generalized valence-bond (GVB) orbitals—the sum and difference of the a_2 and b_1 NBMOs—for which localization to different regions of space minimizes the Coulomb repulsion between the nonbonding pair of electrons in a diradical.[6]

The $^1A_1$ states of **2**−**4** consist largely of two configurations of almost equal weight $|\ldots b_1^2\rangle - |\ldots a_2^2\rangle$. This wave function can be factored into $|\ldots(b_1 + a_2)(b_1 - a_2)(\alpha\beta - \beta\alpha)\rangle$.[6] Thus, it is the GVB orbitals, $b_1 + a_2$ and $b_1 - a_2$, that each represent the wave function for one electron in the $^1A_1$ state of diradicals **2**−**4**. The GVB orbitals for the $^1A_1$ state of each of these three diradicals are shown in Figure 3.

From Figure 3, it is easy to see that the GVB orbital, $b_1 + a_2$, results in the localization of one of the two nonbonding electrons in **3** largely at one of the two equivalent methylene groups, whereas the other GVB orbital, $b_1 - a_2$, localizes the second nonbonding electron largely at the other equivalent methylene group. In the $^1A_1$ state of **3**, the probability of simultaneously finding both nonbonding electrons in the $^1A_3$

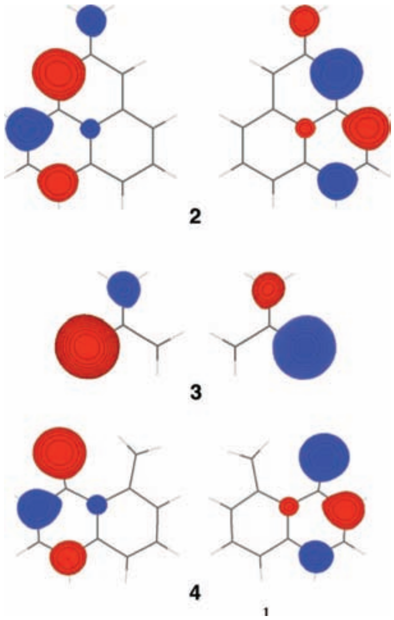


Figure 3. GVB orbitals for the $^1A_1$ state of **2**−**4**.

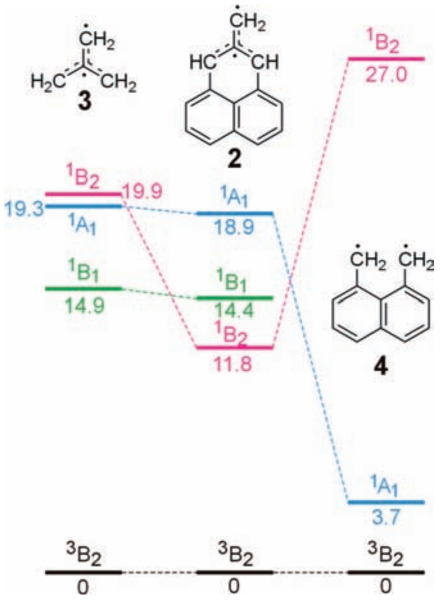


Figure 4. CASPT2 energies (kcal/mol) of the low-lying singlet states of diradicals **2**−**4**, relative to the triplet ground state of each. In D_{3h} symmetry, the proper designation of the triplet ground state of TMM (**3**) is $^3A_2'$.

state of **3** in the 2p$-\pi$ AO on the unique methylene group is obviously much smaller with the GVB orbitals in Figure 3 than if the GVB MOs for this state were formed from the b_1 and a_2 NBMOs in Figure 2 that are optimal for the $^3B_2$ state.

Effects of the 1,8-Naphtho Substituent in 2 on the $^1A_1$ and $^3B_2$ States of TMM. The bond lengths in Figure 1 for TMM (**3**) suggest that the two nonbonding electrons in the $^1A_1$ state are, indeed, largely localized at the two equivalent carbons, to which the 1,8-naphtho bridge is attached in **2**. In contrast, in the $^3B_2$ state of **3** the two, unpaired, nonbonding electrons are distributed equally over all three methylene groups. Therefore, one might expect that adding the 1,8-naphtho bridge to **3**, to form **2**, would provide selective stabilization of the $^1A_1$ state, relative to the $^3B_2$ state.

This is, in fact, calculated to be the case, but Table 1 shows that, on going from **3** to **2**, the selective stabilization of $^1A_1$, relative to $^3B_2$, amounts to only 0.4 kcal/mol. This computational finding is more easily seen in Figure 4, in which the relative CASPT2 energies of the electronic states in **2**−**4** are presented graphically.

The bond lengths for **2** in Figure 1 are consistent with electron delocalization into the 1,8-naphtho bridge being only very slightly larger in $^1A_1$ than in $^3B_2$. The pair of C−C bonds between the TMM moiety and the 1,8-naphtho bridge are shorter in the $^1A_1$ state of **2** than in the $^3B_2$ state, but only by 0.004 Å.

The effects of electron delocalization into the naphthalene bridge of **2** on the bond lengths within the TMM moiety are opposite in the $^3B_2$ and the $^1A_1$ states. In the $^3B_2$ state, the bond to the unique carbon is 0.011 Å shorter and the bonds to the two equivalent carbons are 0.007 Å longer in **2** than in **3**. Delocalization of the unpaired electrons out of the TMM moiety in **2** and into the naphthalene bridge would be expected to result in C−C bond length changes of exactly this type.

Therefore, it is the effects of electron delocalization on the TMM bond lengths in the $^1A_1$ state of **2** that appear to be anomalous. The bond to the unique TMM carbon is 0.005 Å longer in the $^1A_1$ state of **2** than in **3**, and the bonds from the central carbon to the pair of equivalent TMM carbons are 0.010 Å shorter. These bond length changes suggest that the GVB orbitals in the $^1A_1$ state are slightly more localized on the unique TMM carbon and less localized on the equivalent TMM carbons in **2** than in **3**. Comparison of GVB orbitals in Figure 3 for the $^1A_1$ state of **2** and of **3** shows that this is, indeed, the case.

The reason for this difference between the GVB orbitals of **2** and **3** can be readily understood. To the extent that the pair of GVB orbitals for the $^1A_1$ state of **2** are delocalized into the π orbitals of the naphtho bridge, the probability of the electrons in these orbitals *simultaneously* appearing at the exocyclic methylene group in **2** is reduced from that in **3**. The b_1 NBMO contributes to both GVB orbitals, $b_1 + a_2$ and $b_1 - a_2$. Therefore, on going from **3** to **2**, delocalization into the naphtho bridge decreases the Coulomb repulsion between the nonbonding electrons in the $^1A_2$ state. Consequently, both the geometry and the relative energy of this state are a little more like those of $^3B_2$ in **2** than in **3**.

The reason that the 1,8-naphtho bridge in **2** does not provide substantially more stabilization for the $^1A_1$ state of **2** than for the $^3B_2$ state is revealed by inspection of the GVB orbitals for **2** in Figure 3. The GVB orbitals of **2** have not only the 2p$-\pi$ AO on the unique TMM carbon in common but also the 2p$-\pi$ AO on one of the carbons in the naphtho bridging group. Consequently, there is some probability that in the $^1A_1$ state the two nonbonding electrons will simultaneously appear in this AO, thus making a positive contribution to the Coulomb repulsion energy.

In contrast, since electrons with parallel spins have their motions correlated by the Pauli exclusion principle, this energetic cost of delocalization of the nonbonding electrons into the naphtho bridging group is absent from the $^3B_2$ state. Apparently, the cost in Coulomb repulsion of delocalization of the nonbonding electrons in the $^1A_1$ state of **2** almost cancels the advantage that $^1A_1$ has over $^3B_2$, by virtue of the larger coefficients in $^1A_1$ at the two equivalent TMM carbons to which the 1,8-naphtho group is attached. Consequently, adding a 1,8-naphtho substituent to **3** stabilizes the $^1A_1$ state of **2**, relative to the $^3B_2$ state, by only 0.4 kcal/mol, which is much less than one might have guessed just by looking at where the nonbonding electrons are localized in these two electronic states of **3**.

Effects of the 1,8-Naphtho Substituent in 2 on the $^1B_2$ State. As shown in Figure 4, attaching a 1,8-naphtho bridge to the two equivalent carbons of **3**, to form **2**, is more energetically favorable for the $^1B_2$ state than for the $^3B_2$ state by 8.1 kcal/mol. The most dramatic effect on the C−C bond lengths of joining the two equivalent carbons of **3** to C1 and C8 of the naphtho bridging group, to form **2**, is, as shown in Figure 1, the shortening by 0.052 Å of the C−C bond to the unique peripheral carbon in the $^1B_2$ state. This change, coupled with the lengthening by 0.012 Å of each of the C−C bonds to the equivalent carbons in the TMM moiety, indicates that the presence of the 1,8-naphtho group in **2** increases π bonding between the central and the unique peripheral TMM carbons in the $^1B_2$ state and decreases the π bonding between the central and the two equivalent TMM carbons in this state.

These changes in bond lengths suggest that the b_1 NBMO is less localized to the unique TMM carbon in the $^1B_2$ state of **2** than of **3**. Comparing these two b_1 NBMOs in Figure 2 confirms that the b_1 NBMO for the $^1B_2$ state is, indeed, much more delocalized in **2** than in **3**.

In **3**, the a_2 NBMO is localized to the two equivalent TMM carbons; but, in **2**, the a_2 MO is strongly delocalized into the naphtho bridging group. Therefore, the probability of an electron in the a_2 NBMO appearing in the 2p–π AOs on the two equivalent TMM carbons is considerably lower in **2** than in **3.** Consequently, in the $^1B_2$ state, delocalization of the electron in the b_1 NBMO from the 2p−π AO on the unique carbon to the 2p−π AOs on the equivalent pair of TMM carbons creates less Coulomb repulsion in **2** than in **3**. It is for this reason that, in the $^1B_2$ state, the bond to the unique carbon is much shorter in **2** than in **3** and that the energy of this state, relative to the energies of $^3B_2$, and $^1A_1$, is lower by ca. 8 kcal/mol in **2** than in **3**.

This explanation of the changes in bond lengths and energies, relative to $^3B_2$, that occur in the $^1B_2$ state on going from **3** to **2** can be tested computationally. As already noted, the lowest singlet state of **3** is actually $^1B_1$, a state in which the unique methylene group is twisted out of conjugation with the central carbon.[2b,6−8,11] Since the nonbonding electron that is localized on the unique methylene group in the $^1B_1$ state of **3** cannot be delocalized upon attachment of a 1,8-naphtho bridging group, the energy difference between the $^1B_1$ and $^1B_2$ states should decrease and possibly even change sign on going from **3** to **2**.

Inspection of Figure 4 confirms that this is, in fact, the case. $^1B_1$ goes from being 5.0 kcal/mol lower in energy than $^1B_2$ in **3** to being 2.6 kcal/mol higher than $^1B_2$ in **2**. Thus the energy of $^1B_1$, relative to $^1B_2$, increases by a total of 7.6 kcal/mol on going from **3** to **2**.[21]

Both the a_2 NBMO for the $^1B_1$ state of **2** and the bond lengths in this state lead to its best being described as a perinaphthyl radical, very weakly perturbed by the orthogonal methylene group. Comparison of the bond lengths in Figure 1 for the $^1B_2$ and $^1B_1$ states of **2** shows how the π bonding to the exocyclic methylene group in the $^1B_2$ state affects the bond lengths in other parts of **2**.

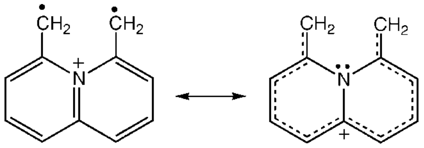
The Low-Lying Electronic States of 4. A different perspective on the bonding in **2** is obtained by comparing the changes that occur in the relative energies of the $^3B_2$, $^1A_1$, and $^1B_2$ states of 1,8-naphthoquinodimethane (**4**) on attaching both methylene groups to a vinylidene bridging group. Figure 4 shows that the effect is to destabilize the $^1A_1$ state relative to the $^3B_2$ state by 15.2 kcal/mol and to stabilize $^1B_2$, relative to $^3B_2$, by the same amount. The 30.4 kcal/mol change in the relative energies of these two singlet states that occurs on going from **4** to **2** certainly is large enough to warrant an explanation.

We begin with the relative energies of the low-lying electronic states of **4**. As shown in Table 1, in **4** the $^1A_1$ state is calculated to be only 3.7 kcal/mol above the $^3B_2$ ground state. Figure 2 reveals that the NBMOs for the $^1A_1$ state are very similar to those for the $^3B_2$ state. The biggest difference between the nonbonding MOs for these two states is the contribution of the 2p−π AO at one carbon of the naphthalene ring system to the b_1 MO. As can be seen in Figure 3, this is the only AO that the GVB MOs for the $^1A_1$ state have in common.

Figure 2 shows that the contribution of this AO to the b_1 NBMO of **4** is smaller in the $^1A_1$ state than in the $^3B_2$ state. The size of the coefficient of this AO in the $^1A_1$ state is a compromise between minimizing the Coulomb repulsion between the nonbonding electrons of opposite spin in the GVB orbitals for this singlet state, while maintaining the same amount of delocalization that these π electrons have in the triplet state.

Nevertheless, the $^1A_1$ state of **4** does have one advantage over the $^3B_2$ state. In the triplet state, the a_2 and b_1 NBMOs are each occupied by one electron, but the wave function for the $^1A_1$ state, $c_1|...b_1^2\rangle - c_2|...a_2^2\rangle$, allows the occupancies of these two NBMOs to be different, if their energies are different. In fact, non-nearest-neighbor interactions between the 2p–π AOs on the exocyclic carbons make the b_1 NBMO lower in energy than the a_2 NBMO. Consequently, the occupation number of b_1 is 1.17, which is 40% greater than the occupation number of 0.83 for a_2. The presence of more than one electron in the lower of the two NBMOs contributes to making the energy difference between $^1A_1$ and $^3B_2$ only 3.7 kcal/mol.[22]

With the energy of $^1A_1$ calculated to be only 3.7 kcal/mol higher than that of $^3B_2$ in **4**, it is hard to resist the temptation to devise a strategy to make the singlet the ground state by further stabilizing the b_1, relative to the a_2 NBMO. Figure 2 provides such a strategy, because it shows that the b_1 NBMO has density on one carbon at which a_2 has a node. Therefore, substitution of N^+ for C at this position, to afford diradical **5**, should stabilize the b_1, relative to the a_2 NBMO, and thus possibly change the ground state from $^3B_2$ in **4** to $^1A_1$ in **5**.[23]



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In fact, (12/12)CASSCF/6-31G(d) calculations on **5** predict that the $^1A_1$ state of **5** is lower in energy than the $^3B_2$ state by 3.3 kcal/mol, which increases to 9.7 kcal/mol at the CASPT2/6-31G(d) level of theory. The expected stabilization of the b_1 NBMO, relative to the a_2 NBMO, is reflected in the increase in the occupation number of the former from 1.17 in **4** to 1.55 in **5**, whereas the occupation number of the latter NBMO drops by nearly 50%, from 0.83 in **4** to 0.45 in **5**.

The stabilization of $^1A_1$ relative to $^3B_2$, on going from **4** to **5**, can be explained by resonance theory as well as by MO theory. The second resonance structure shows that **5** may be regarded as an undecyl carbocation with a nitrogen attached to C2, C6, and C10, at which the LUMO of the undecyl carbocations has nodes. Similarly, attachment of an amino substituent to C2 of the allyl carbocation yields what may be regarded as an immonium derivative of **3**, for which $^1A_1$ has been calculated to be lower in energy than $^3B_2$.[24]

In both the $^1B_2$ and $^3B_2$ states of **5**, one electron occupies each of the NBMOs. Therefore, the stabilization of the b_1 NBMO, relative to the a_2 NBMO, is calculated to leave the energy difference between these two states of 28.4 kcal/mol at the (12/12)CASSCF level and 27.9 kcal/mol at CASPT2 nearly unchanged from the value of 27.0 kcal/mol for **4** at both levels of theory, as given in Table 1.

The NBMOs for **4** in Figure 2 reveal the reason for the very high energy of the $^1B_2$ state, relative to $^3B_2$. Like the $^3B_2$ state, the $^1B_2$ state has one electron in the a_2 NBMO and one in the b_1 NBMO. In the $^3B_2$ state, these two NBMOs span nearly the same set of atoms. Consequently, if the electrons in these two NBMOs did not have parallel spins, to prevent the electrons from simultaneously appearing in the same 2p−π MO, they would experience a very large, mutual Coulomb repulsion energy.

The very large Coulomb repulsion energy, which would result from electrons of *opposite spin* occupying the b_1 and a_2 NBMOs that are optimal for the triplet, can be reduced by confining the NBMOs for the $^1B_2$ state of **4** to different regions of space. Figure 2 shows that this is exactly what happens to these MOs in the $^1B_2$ state. The optimal b_1 and a_2 NBMOs for the $^1B_2$ state of **4** are, in fact, disjoint.

Although localization of the NBMOs for $^1B_2$ to different regions of space minimizes the Coulomb repulsion between the electrons of opposite spin in these NBMOs, this decrease in Coulomb repulsion comes at the price of making the bonding in $^1B_2$ much more localized than that in $^3B_2$ or in $^1A_1$. Indeed the b_1 and a_2 NBMOs in the $^1B_2$ state of **4** are essentially those for, respectively, a pentadienyl radical, localized at the two exocyclic carbons and three of the naphthalene carbons, and a heptatrienyl radical, localized at the remaining seven naphthalene carbons. The optimized C−C bond lengths for the $^1B_2$ state of **4** in Figure 1 confirm that the description of this state of **4**, as consisting of largely noninteracting pentadienyl and heptatrienyl radicals, is really quite accurate.

Effects of the Vinylidene Bridging Group in 2 on the Energies of the Low-Lying Electronic States of 4. Having understood the bonding in the low-lying electronic states of **4**, it is possible to understand how bridging the exocyclic carbons of **4** with a vinylidene group results in the electronic states of **2**. In the triplet state, the b_1 NBMO of **4** can mix with both the π and π^* MOs of the vinylidene group. This mixing lowers the energy of the π MO of the vinylidene group, leaves the energy of the NBMO unchanged, and raises the energy of π^*. Since π^* is unoccupied, the only energetic change of any consequence, caused by this mixing, is the lowering of π.

As can be seen in Figure 2, the mixing of the π and π^* MOs of the vinylidene group with the b_1 NBMO for the $^3B_2$ state of **4** results in a large coefficient for the AO on the exocyclic carbon in the b_1 NBMO for the $^3B_2$ state of **2**. In principle, the same type of mixing could also result in a large coefficient for the AO on the exocyclic carbon in the b_1 NBMO for the $^1A_1$ state of **2**. However, the GVB NBMOs, $b_1 + a_2$ and $b_1 - a_2$, for this state of **2** would then have this AO in common, thus resulting in a large Coulomb repulsion energy between the electrons of opposite spin in this state of **2**. Consequently, as can be seen in Figure 2, the AO on the exocyclic carbon makes a much larger contribution to the b_1 NBMO for the $^3B_2$ state of **2** than to the b_1 NBMO for the $^1A_1$ state.

As a result of the much larger effect of the mixing of the π and π^* MOs of the exocyclic double bond into the b_1 NBMO for the $^3B_2$ state than for the $^1A_1$ state of **2**, bridging the methylene groups of **4** with a vinylidene group should stabilize the $^3B_2$ state, relative to the $^1A_1$ state. In fact, Figure 4 shows that, on going from **4** to **2**, $^3B_2$ is stabilized, relative to $^1A_1$, by 15.2 kcal/mol.

In contrast, Figure 4 shows that, on going from **4** to **2**, the $^1B_2$ state is stabilized, relative to $^3B_2$, by about the same amount that $^1A_1$ is destabilized. Figure 2 reveals the reason for the large stabilization of $^1B_2$, relative to $^3B_2$. The b_1 and a_2 NBMOs of the $^1B_2$ state of **4** are both altered by the vinylidene group in **2**. The contributions of the 2p−π AOs on the pair of exocyclic carbons of **4** are greatly reduced in the b_1 NBMO for this state of **2**, as this NBMO becomes largely localized on the exocyclic carbon of the vinylidene bridging group. The localization of the b_1 NBMO largely to the exocyclic carbon of **2**, where a_2 has a node, allows the a_2 NBMO for the $^1B_2$ state of **2** to delocalize to what were the exocyclic carbons of **4**, without engendering a substantial increase in Coulomb repulsion energy.

As a result of the substantial changes in both the b_1 and a_2 NBMOs for the $^1B_2$ state on going from **4** to **2**, it may not be particularly useful to describe this state of **2** in terms of the $^1B_2$ state of **4**, perturbed by a vinylidene bridge. As already noted, a better decription of the $^1B_2$ state of **2** is as a perinaphthyl radical, weakly perturbed by the exocyclic $^\bullet CH_2$ group. Table 1 shows that twisting the exocyclic methylene group in **2** out of conjugation raises the energy of the $^1B_2$ state of **2** by only 2.6 kcal/mol.

Summary and Conclusions

As expected from qualitative theory,[8,9] non-Kekulé hydrocarbon diradicals **2** and **4** are, like the very well-studied TMM diradical (**3**),[2,11] calculated to have triplet ground states. Bridging two of the methylene groups of **3** with a 1,8-naphtho group, to give **2**, selectively stabilizes the $^1B_2$ state, relative to both the $^3B_2$ and $^1A_1$ states. Unlike the case in **3**, where the $^1B_1$ state, with one methylene group twisted out of conjugation, is 5.0 lower in energy than the planar geometry of the $^1B_2$ state, in **2** the twisted $^1B_1$ state is 2.6 kcal/mol higher in energy than the planar geometry of the $^1B_2$ state.

Diradical **4** has a much smaller singlet−triplet energy difference than either **2** or **3**. Except for one atom in the naphthalene ring, the b_1 and a_2 NBMOs for the $^3B_2$ state span the same set of atoms. Consequently, the GVB MOs for the $^1A_1$ state, $b_1 + a_2$ and $b_1 - a_2$, have in common only the 2p−π AO on that atom, and the energy difference between the $^3B_2$ and $^1A_1$ states is computed to amount to only 3.7 kcal/mol.

Substituting a positively charged nitrogen for this carbon in **4** gives **5**. Since the additional proton in the nitrogen atom stabilizes only the b_1 NBMO of **5**, the occupation number of this NBMO in the $^1A_1$ state increases from 1.17 in **4** to 1.55 in **5**. In contrast, the occupation number of the b_1 NBMO in both the $^3B_2$ and $^1B_2$ states of **4** and **5** is 1.00. Consequently, the energy difference between these two states remains relatively unchanged on going from **4** to **5**, but the $^1A_1$ state is stabilized relative to both B_2 states. In fact, $^1A_1$ is calculated to be the ground state of **5**.

The b_1 and a_2 NBMOs for the $^3B_2$ state of **4** have six atoms in common. Therefore, to minimize the repulsion between the electrons of opposite spin in these NBMOs, the optimal NBMOs for the $^1B_2$ state are forced to be much more localized than those for the $^3B_2$ state. Consequently, the energy difference between the $^3B_2$ and $^1B_2$ states in **4** is computed to be 27.0 kcal/mol.

Attaching a vinylidene group to the two exocyclic carbons of **4**, to form **2**, is calculated to change the relative energies of the $^1A_1$ and $^1B_2$ states of **4** by 30.4 kcal/mol. The vinylidene group in **2** provides additional delocalization, beyond that in **4**, for the $^3B_2$ state, but not for the $^1A_1$ state. Therefore, the energy separation between $^3B_2$ and $^1A_1$ is calculated to increase by 15.2 kcal/mol on going from **4** to **2**.

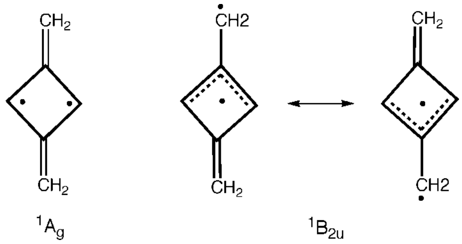

Figure 5. Schematic depiction of the $^1A_1$ (^1A_g in D_{2h} symmetry) and $^1B_2$ ($^1B_{2u}$ in D_{2h} symmetry) states of 2,4-dimethylenecyclobutane-1,3-diyl (**6**).

In contrast, adding a vinylidene group to **4** allows the b_1 NBMO to become largely localized at the exocyclic methylene group in the $^1B_2$ state of **2**. Consequently, the a_2 NBMO of **4** can become much more delocalized in this singlet state of **2**, without increasing the Coulomb repulsion between the electrons of opposite spin in the two NBMOs. The resulting increase in electron delocalization decreases the energy difference between the $^3B_2$ and $^1B_2$ states by 15.2 kcal/mol on going from **4** to **2**.

The results of our calculations on the effects of the ferromagnetic vinylidene coupling group in **2** on perturbing the relative energies of the electronic states of **4** are particularly interesting, because they are very different from the calculated effects of the vinylidene bridging group in 2,4-dimethylenecyclobutane-1,3-diyl (**6**, Figure 5) on perturbing the energies of the electronic states of **3**. Rather than stabilizing the $^1B_2$ state, relative to the $^1A_1$ state, by 30.4 kcal/mol, as in going from **4** to **2**, adding a vinylidene bridging group to **3**, to form **6**, actually stabilizes $^1A_1$ (^1A_g in D_{2h} symmetry) relative to $^1B_2$ ($^1B_{2u}$ in D_{2h} symmetry) at the CASSCF level of theory[25] and has little effect on the relative energies of these two states at the CASPT2 level.[25c]

Therefore, it would appear that even the most qualitative effects of the attachment of a ferromagnetic coupling unit to two carbons of a diradical depend not only on the ferromagnetic coupling unit but also on the diradical to which it is being attached. Trying to develop some general rules for how different ferromagnetic coupling units affect the energies of the low-lying electronic states of different diradicals presents an interesting challenge for future research.

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Supporting Information Available: CASSCF/6-31G(d) geometries and CASPT2/6-31G(d) energies for the low-lying electronic states of **2**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Quast, H.; Nüdling, W.; Klemm, G.; Kirschfeld, A.; Neuhaus, P.; Sander, W.; Hrovat, D. A.; Borden, W. T. *J. Org. Chem.* **2008**, *73*, 4956.

(2) (a) Dowd, P. *J. Am. Chem. Soc.* **1966**, *88*, 2587. (b) Experimental work on TMM has been reviewed by: Berson, J. A. In *Diradicals*; Borden, W. T., Ed.; Wiley-Interscience: New York, 1982; pp 151−194.

(3) (a) Pagni, R. M.; Burnett, M. N.; Dodd, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 1972. (b) A diaza derivative of **4** has also been generated: Platz, M. S.; Carrol, G.; Pierrat, F.; Zayas, J.; Auster, S. *Tetrahedron* **1982**, *38*, 777.

(4) Coulson, C. A.; Longuet-Higgins, H. C. *Proc. R. Soc. A* **1947**, *192*, 16.

(5) Longuet-Higgins, H. C. *J. Chem. Phys.* **1950**, *18*, 265.

(6) Reviews: (a) Borden, W. T. In *Diradicals*; Borden, W. T., Ed.; Wiley-Interscience: New York, 1982; pp 1−72. (b) Borden, W. T. In *Encyclopedia of Computational Chemistry*; Schleyer, P. v. R., Allinger, N. L., Clark, T., Gasteiger, J., Kollman, P. A., Schaefer, H. F., III, Schreiner, P. R., Eds.; Wiley: Chichester, UK, 1998; pp 708−722.

(7) Review: Borden, W. T. In *Magnetic Properties of Organic Materials*; Lahti, P. M., Ed.; Marcel Dekker: New York, 1999; pp 61−102.

(8) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4587.

(9) Ovchinnikov, A. A. *Theor. Chim. Acta* **1978**, *47*, 297.

(10) Baseman, R. J.; Pratt, D. W.; Chow, M.; Dowd, P. *J. Am. Chem. Soc.* **1976**, *98*, 5726.

(11) (a) Yarkony, D. R.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1974**, *96*, 3754. (b) Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1977**, *99*, 2053. (c) Davis, J. H.; Goddard, W. A., III *J. Am. Chem. Soc.* **1977**, *99*, 4242. (d) Hood, D. M.; Schaefer, H. F., III; Pitzer, R. M. *J. Am. Chem. Soc.* **1978**, *100*, 8009. (e) Dixon, D. A.; Dunning, T. H., Jr.; Eades, R. A.; Kleier, D. A. *J. Am. Chem. Soc.* **1981**, *103*, 2878. (f) Auster, S. B.; Pitzer, R. M.; Platz, M. S. *J. Am. Chem. Soc.* **1982**, *104*, 3812. (g) Feller, D.; Tanaka, K.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1982**, *104*, 967. (h) Ma, B; Schaefer, H. F., III *Chem. Phys.* **1996**, *207*, 31. (i) Cramer, C. J.; Smith, B. A. *J. Phys. Chem.* **1996**, *100*, 9664. (j) Hrovat, D. A.; Borden, W. T., results tabulated by: Bally, T.; Borden, W. T. In *Reviews in Computational Chemistry*; Lipkowitz, K. B., Boyd, D. B., Eds.; VCH: New York, 1998; 1−99. (k) The CASPT2 results for **3** in Table 3 of the Review in ref 11j differ slightly from those in Table 1 of this paper, because the former were obtained with IPEA shift = 0.0 in MOLCAS, whereas the latter were obtained with IPEA shift = 0.25. (l) Brabec, J.; Pittner, J. *J. Phys. Chem. A* **2006**, *110*, 11765.

(12) Wenthold, P. G.; Hu, J.; Squires, R. R.; Lineberger, W. C. *J. Am. Chem. Soc.* **1996**, *118*, 475.

(13) The lowest energy singlet state of **3** is calculated to be $^1B_1$, in which one methylene group is twisted out of conjugation with the central carbon atom.[11] However, this state is not directly accessible by vertical electron loss from the radical anion of 3.[12]

(14) The results of single-configuration calculations of the energies of the $^3B_2$ and $^1B_2$ states of **4** have been published: Datta, S. N.; Jha, P. P.; Ali, Md. E. *J. Phys. Chem. A* **2004**, *108*, 4087. However, a singlet diradical cannot be properly represented by a wave function consisting of a single configuration.

(15) Dougherty, D. A. *Acc. Chem. Res.* **1991**, *24*, 88.

(16) Borden, W. T.; Davidson, E. R. *Acc. Chem. Res.* **1996**, *29*, 67.

(17) (a) Andersson, K.; Malmqvist, P. A.; Roos, B. O. *J. Phys. Chem.* **1992**, *96*, 1218. (b) Andersson, K.; Malmqvist, P. A.; Roos, B. O.; Sadlej, A. J.; Wolinski, K. *J. Phys. Chem.* **1990**, *94*, 5483.

(18) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(19) The CASSCF optimized geometries and the CASSCF and CASPT2 energies are available in the Supporting Information for this paper.

(20) *MOLCAS*, Version 6.4: Karlstrøm, G.; Lindh, R.; Malmqvist, P.-Å.; Roos, B. O.; Ryde, U.; Veryazov, V.; Widmark, P.-O.; Cossi, M.; Schimmelpfennig, B.; Neogrady, P.; Seijo, L. *Comput. Mater. Sci.* **2003**, *28*, 222.

(21) Since the NBMOs of the $^1B_1$ states of **2** and **3** are disjoint, $^3B_1$ is calculated to lie below $^1B_1$ by only a few tenths of a kcal/mol in both diradicals. Consequently, like the energies of the twisted $^1B_1$ states, the energies of the twisted $^3B_1$ states, relative to the planar $^3B_2$ states, are calculated to be nearly the same in **2** and **3**. Therefore, the energies required to twist a methylene group out of conjugation are nearly the same in the $^3B_2$ states of both diradicals. Given the very similar bond lengths between the central carbons and the methylene groups in the planar, $^3B_2$, ground states of **2** and **3**, this finding is not at all surprising.

(22) For the same reason, the occupancy of the b_1 NBMO (1.07) in the $^1A_1$ state of **2** is greater than the occupancy of the a_2 NBMO (0.94). However, in **3**, the NBMOs are nearly degenerate (and exactly so at D_{3h} geometries). Therefore, their occupation numbers are both nearly 1.00−1.02 for b_1 NBMO and 0.99 for a_2 NBMO.

(23) A similar strategy for making $^1A_1$ the ground state of 1,3-benzoquinodimethane was proposed by: West, A. P., Jr.; Silverman, S. K.; Dougherty, D. A. *J. Am. Chem. Soc.* **1996**, *118*, 1452.

(24) Li, J.; Worthington, S. E.; Cramer, C. J. *J. Chem. Soc., Perkin Trans. 2* **1998**, 1045.

(25) (a) Davidson, E. R.; Borden, W. T.; Smith, J. *J. Am. Chem. Soc.* **1978**, *100*, 3299. (b) Our (6/6)CASSCF/6-31G(d) calculations place the ^1A_g and $^1B_{2u}$ states of **6** respectively 19.8 and 27.1 kcal/mol above the $^3B_{2u}$ ground state. (c) Inclusion of dynamic electron correlation by CASPT2 reduces the CASSCF energy differences to 18.0 and 18.6 kcal/mol.

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