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Ab Initio Study of *m*-Benzoquinodimethane

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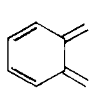
Abstract: The geometries of the $^3B_2$ and $^1A_1$ states of the *m*-benzoquinodimethane diradical (**2**) have been optimized by, respectively, UHF and TCSCF calculations, using the STO-3G basis set. The energies at the optimal geometries have been computed with the Dunning split-valence basis set, using two different schemes for correlation energy recovery. Both schemes lead to the prediction of a $^3B_2$ ground state for **2**, with $^1A_1$ computed to be 10 kcal/mol higher in energy. The geometry of *p*-benzoquinodimethane (**3**) has also been optimized and the energy of its closed-shell ^1A_g ground state computed. The relative energies of the ground states of **2** and **3** are found to depend on the method used for recovering correlation energy. Evidence is presented that variational π configuration interaction (CI) energy differences are likely to be more reliable than estimates made from all-valence-electron CI calculations that use a small number of selected single and double excitations. The energy difference between the two ground states is computed to be 24 kcal/mol by CI calculations involving all π configurations through quadruply excited in an 11-orbital subspace of the full 16-orbital π space. This calculated energy difference is discussed in context of a recent experimental determination.

Quinodimethanes have been the subject of extensive experimental studies in recent years.[2] Benzoquinodimethanes are the simplest members of this class of molecules. Of the three possible benzoquinodimethane isomers (**1**–**3**), the meta (**2**) is perhaps the most interesting, since no classical Kekulé structures can be written for it. Consequently, unlike **1** or **3**, **2** is expected to be a true diradical, possessing two nonbonding molecular orbitals (MO's).[3]



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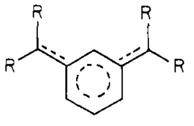

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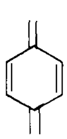

3

Although EPR studies, published in 1970, showed Schlenk's hydrocarbon (**2**, R = Ph) to be a ground-state triplet,[4] it was not until quite recently that the EPR spectrum of the parent *m*-quinodimethane (**2**, R = H) was recorded by Wright and Platz.[5] They found that the EPR signal intensity followed the Curie law, indicating a triplet ground state for the unsubstituted molecule too.

Wright and Platz prepared **2** from dehydro-*m*-quinodimethane by allowing the biscarbene to abstract hydrogen from the host matrix. Migirdicyan and Baudet reported optical spectra that they attributed to triplet **2**, formed by exhaustive photolysis of *m*-xylene.[6] Berson and co-workers prepared *m*-quinomethane, the monooxygen derivative of **2**, in its triplet ground state by photochemical ring opening of 6-methylenebicyclo[3.1.0]hex-3-en-2-one.[7] More recently, Berson's group has obtained evidence for the generation of triplet **2** by an analogous route.[8] Gajewski, Stang, and co-workers suggested the intermediacy of **2**, R = CH_3, in the formation of octamethyl-2,2-*m*-cyclophane from addition of dimethylvinylidene to 6,6-dimethylfulvene.[9]

Two unsuccessful attempts to prepare **2** are significant. Tseng and Michl failed to detect *m*-quinodimethane in the gas-phase dehalogenation of α,α'-dibromo-*m*-xylene by metal atoms under conditions where the corresponding ortho dibromide produced **1**.[10] Hehre and co-workers found that the *m*-methylbenzyl cation cannot be deprotonated to **2** in the gas phase, whereas the *o*- and *p*-methylbenzyl cations undergo deprotonation, respectively, to **1** and to **3**.[11] Combining the measurements of the gas-phase acidities of the latter two benzyl cations with the calculated relative energies of all three cations, Hehre et al. deduced that **2** is at least 23 kcal/mol less stable than **1** and at least 26 kcal/mol less stable than **3**.

Semiempirical, π electron, configuration interaction (CI) calculations have been carried out on **1**–**3**.[12-14] A triplet ground state is predicted only for **2**. The prediction of a triplet ground state for **2** can also be made without recourse to calculations, on the basis of the fact that the number of starred and unstarred atoms differ by two.[15,16] This implies that the nonbonding Hückel MO's, which are shown in Figure 1, cannot be localized to different sets of atoms. Consequently, singlet wave functions constructed from these MO's contain ionic terms that the Pauli principle banishes from the triplet wave function.[17] Because the Hückel MO's lead to ionic terms in singlet wave functions constructed from them, it can additionally be predicted that these MO's are not optimal for either of the two lowest singlet states. Therefore, the bonding in these two states is expected to differ from that in the triplet.[15,17]

The ab initio calculations described in this paper were undertaken in order to (1) obtain equilibrium geometries for the lowest singlet and triplet states of **2**, (2) compute the single–triplet energy splitting in **2**, and (3) determine the relative energies of

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(1) (a) Institute for Molecular Science. (b) University of Washington. (c) Visiting Scientist, Institute for Molecular Science, 1981.

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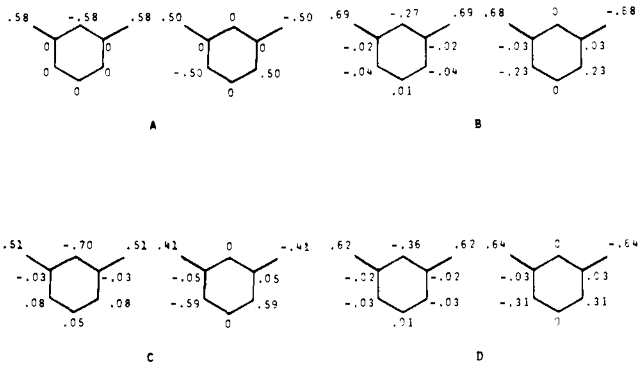

Figure 1. Nonbonding $3b_1$ and $2a_2$ MO's obtained from (A) Hückel theory, (B) $^1A_1$ TCSCF calculation at the $^1A_1$ equilibrium geometry, (C) $^3B_2$ UHF calculation, and (D) $^3B_2$ RHF calculation, both at the $^3B_2$ UHF equilibrium geometry.

2 and its closed-shell para-isomer, **3**. Preforming ab initio calculations on *m*-quinodimethane also provided methodological challenges, since some techniques that can be utilized on smaller diradicals are impractical or inappropriate for a molecule the size of **2**.

Methodology and Results

In our previous work on both radicals[18] and diradicals[17] we have stressed the importance of carrying out geometry optimizations using highly correlated wave functions.[19] However, for a diradical the size of **2**, geometry optimizations with large CI or multiconfigurational self-consistent field (MCSCF) wave functions would be prohibitively expensive, even with a minimal basis set. A possible solution to this problem is our recent suggestion that for low-lying singlet states of neutral alternant hydrocarbon diradicals like **2**, symmetry-constrained geometry optimizations using restricted Hartree–Fock (RHF) or two-configuration SCF (TCSCF) wave functions can often be expected to give reasonable results.[19]

Without symmetry constraints, RHF wave functions for monoradicals, like allyl, spuriously tend to localize the odd electron at one atom, even at symmetrical geometries. This is known as the doublet instability problem.[20] It arises because an RHF wave function provides no correlation between an unpaired electron and electrons of opposite spin in bonding π orbitals.

In singlet diradicals minimization of the mutual Coulombic repulsion energy between nonbonding electrons usually results in their localization to different regions of space.[15,17] In some cases symmetry constraints can be placed on the wave function, in order to prevent spurious additional localization, provided that potential surface explorations are restricted to geometries where the necessary symmetry elements are maintained.

For example, in the $^1B_2$ state of **2**, one nonbonding electron occupies the $3b_1$ MO and the other $2a_2$.

$$^1B_2 = |...3b_1 2a_2(\alpha\beta - \beta\alpha)/\sqrt{2}\rangle \qquad (1)$$

The $3b_1$ and $2a_2$ MO's that emerge from an RHF calculation on $^1B_2$ are expected to be far more localized than the corresponding Hückel nonbonding MO's, in order to prevent the electrons of opposite spin from simultaneously appearing in the same atomic orbital. The localization is thus anticipated to involve a reduction in the coefficients of both the $3b_1$ and $2a_2$ Hückel MO's at the exocyclic methylene carbons, the atoms common to both MO's. This should lead to a wave function in which the bonding may be crudely portrayed as shown in Figure 2. The bond orders for $^1B_2$, obtained from a semiempirical, π electron, CI calculation, are in accord with this depiction.[13]

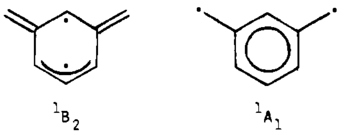

Figure 2. Schematic depiction of the bonding in $^1B_2$ and $^1A_1$. The bonding in the actual wave functions is somewhat more delocalized than is indicated by these structures.

Unless C_{2v} symmetry is imposed on the $^1B_2$ RHF wave function, further localization of the odd electron in the allylic portion of the molecule is expected, due to the doublet instability problem. Indeed, we have confirmed computationally that this does occur, even at a C_{2v} geometry. It is to be emphasized that this additional localization is spurious. It can be overcome either by using a wave function that provides the interorbital electron correlation that an RHF wave function lacks or by imposing C_{2v} symmetry on the latter type of wave function.

As discussed above, using a highly correlated wave function to optimize the geometry of the $^1B_2$ state of **2** would be prohibitively expensive. In addition, the programs available to us for geometry optimizations, employing analytically evaluated energy gradients, did not allow the imposition of symmetry on the $^1B_2$ RHF wave function. Since the symmetry breaking observed in the RHF wave function at C_{2v} geometries would have led to an incorrect equilibrium geometry for the $^1B_2$ state of **2**, we did not pursue calculations on this state.

Fortunately, semiempirical, π electron, CI calculations on **2** indicate that $^1B_2$ is the second lowest singlet state and that $^1A_1$ lies well below it in energy.[12,13] A TCSCF wave function is required for a minimally correct description of the lowest singlet state of **2**.

$$^1A_1 = c_1^2|...3b_1^2\rangle - c_2^2|...2a_2^2\rangle \qquad (2)$$

This TC wave function can be factored into

$$^1A_1 = |...(c_1 3b_1 + c_2 2a_2)(c_1 3b_1 - c_2 2a_2)(\alpha\beta - \beta\alpha)/\sqrt{2}\rangle \qquad (3)$$

where the singly occupied sum and difference orbitals are often referred to as generalized valence bond (GVB) orbitals.[21]

If, in order to minimize their mutual Coulomb repulsion energy, the electrons in the GVB orbitals for $^1A_1$ are to be localized to different regions of space, eq 3 shows that $3b_1$ and $2a_2$ must span the same set of atoms. In addition, the coefficients at each atom must have nearly the same magnitude, and c_1 and c_2 must be nearly equal. Consequently, the $3b_1$ and $2a_2$ MO's from a TCSCF calculation on the $^1A_1$ state are expected to be much more localized to the exocyclic methylene carbons, the two atoms that the Hückel MO's have in common, than are the Hückel MO's. As shown in Figure 1, comparison of the MO's that actually emerge from a TCSCF calculation on $^1A_1$ with the Hückel MO's bears out this assertion. The coefficients, c_1 and c_2, in eq 3 are also computed to be nearly equal. They are, respectivley, 0.8413 and 0.8405.

Since the nonbonding electrons in the $^1A_1$ state of **2** are largely localized at the exocyclic methylene groups, the bonding in the lowest singlet state of *m*-quinodimethane may be depicted approximately as shown in Figure 2. Because a TCSCF wave function for $^1A_1$ provides no correlation between the nonbonding electrons and those in the bonding π MO's, the degree to which the nonbonding electrons are localized to the exocyclic methylene carbons may be somewhat overestimated by this type of wave function. Nevertheless, a TCSCF wave function does provide at least a qualitatively correct description of the bonding in $^1A_1$; and, consequently, such a wave function can be used to obtain a reasonable equilibrium geometry for this state.[19]

Geometry optimizations on $^1A_1$ were carried out by using a minimal basis set of STO-3G orbitals.[22] Energy gradients were evaluated analytically for the TCSCF wave function.[23] At the

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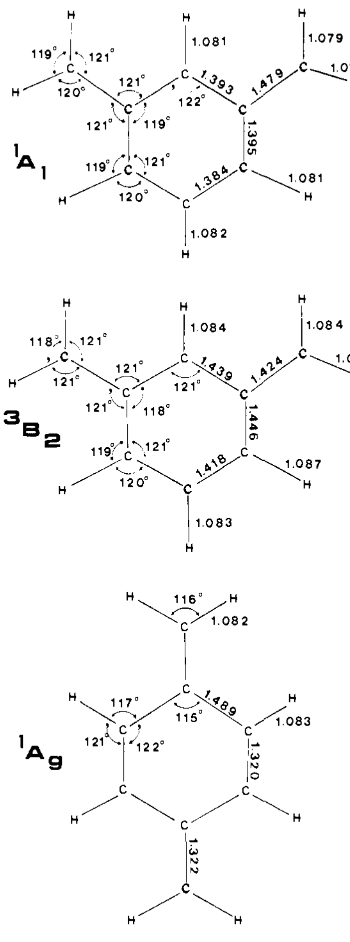

Figure 3. Equilibrium geometries for the $^1A_1$ and $^3B_2$ states of **2** and the ^1A_g state of **3**, obtained from optimizations with, respectively, TCSCF, UHF, and RHF wave functions.

optimized geometry for $^1A_1$, shown in Figure 3, the Cartesian components of the energy gradient at each atom were reduced to less than 10^{-3} hartree/bohr in magnitude. The TCSCF energy was computed to be $E = -303.7806$ hartrees.

Geometry optimizations on the lowest triplet state were carried out by using an unrestricted Hartree–Fock (UHF) wave function for $^3B_2$. Electrons of opposite spins that are forced to occupy identical MO's in a RHF wave function are permitted to occupy different MO's in a UHF wave function. The latter type of wave function thus provides some correlation between the nonbonding electrons and those of opposite spin in the bonding π MO's. Provision of such correlation is essential for obtaining qualitatively correct descriptions of the bonding in triplet states of diradicals. Unlike the case in singlet diradicals, minimization of Coulombic repulsion between the nonbonding electrons does not result in localized triplet wave functions, because the unpaired electrons in a triplet are prevented by the Pauli principle from simultaneously appearing in the same atomic orbital. However, Coulombic repulsion effects, arising from failure to provide correlation between the unpaired electrons and those of opposite spin in bonding MO's, can result in *spurious* localization in RHF wave functions for triplet states. Consequently, UHF, rather than RHF, wave functions should be used for optimizing geometries of triplet states.[19]

Geometry optimizations, employing analytically evaluated energy gradients, were carried out for the $^3B_2$ UHF wave function in a fashion similar to that described above for the $^1A_1$ TCSCF wave function. The UHF energy at the optimized $^3B_2$ geometry, shown in Figure 3, was $E = -303.8586$ hartrees. The UHF and RHF $3b_1$ and $2a_2$ MO's that were obtained at this geometry appear in Figure 1.

Table I. Energies of the $^3B_2$ and $^1A_1$ States of **2** and the ^1A_g State of **3**, Calculated at Different Levels of Theory with the Dunning Split-Valence Basis Set

calculation	$^3B_2$[a]	$^1A_1$[b]	^1A_g[b]
SCF	-307.4407[c]	-1.5[d]	-16.0[c]
SD CI estimate	-308.051	5.6	-4.4
SDQ CI estimate	-308.139	10.0	-6.9
8-π SDTQ CI	-307.5296	10.2	-22.5
11-π SDTQ CI	-307.5375	10.0	-24.2

[a] Energy in hartrees. [b] Energy relative to $^3B_2$ in kcal/mol. [c] RHF. [d] TCSCF.

As shown in this figure, the UHF nonbonding MO's are, as expected, quite delocalized, whereas, in contrast, the RHF triplet MO's are about as localized to the exocyclic methylene carbons as are the nonbonding MO's in the $^1A_1$ state. This result suggests that if the RHF wave function had been used for $^3B_2$ geometry optimization, a spurious equilibrium geometry, close to that for $^1A_1$, would have been obtained. Indeed, the $^3B_2$ RHF energy at the $^1A_1$ equilibrium geometry was 0.0140 hartree (8.8 kcal/mol) lower than the $^3B_2$ RHF energy of -303.7695 hartrees at the optimal $^3B_2$ UHF geometry.

Of the two closed-shell quinodimethane isomers the para was chosen for computational study, since the higher symmetry of **3** (D_{2h}) than **1** (C_{2v}) significantly reduced the expense of geometry optimization and subsequent CI calculations. The STO-3G basis set was again used to optimize the geometry of the ^1A_g ground state of **3**. The optimal geometry is shown in Figure 3. The SCF energy at this geometry was -303.7884 hartrees.

In order to evaluate the relative energies of the $^1A_1$ and $^3B_2$ states of **2** and of the ^1A_g state of **3**, CI calculations were carried out at the equilibrium geometries shown in Figure 3. For the CI calculations the Dunning [3s,2p/2s] split-valence (SV) basis set was used,[24] with a scale factor of 1.2 for hydrogen.

In order to recover variationally the greatest amount of correlation energy with the smallest possible number of configurations, the virtual orbitals from the TCSCF calculation on $^1A_1$ and the RHF calculations on $^3B_2$ and ^1A_g were transformed to K orbitals.[25] These improved virtual orbitals are usually able to recover 20–25% more correlation energy than are the untransformed MO's, when CI's involving the same number of configurations are carried out with each set.

All single and double excitations that left the eight carbon 1s orbitals doubly occupied were generated from the TCSCF and RHF wave functions. This amounted to 864 157 spin-adapted configurations for $^3B_2$, 407 342 for $^1A_1$, and 102 633 for ^1A_g. Second-order perturbation theory was used to select the energetically most important configurations. This selection process resulted in CI's involving on the order of 19 700 configurations for $^3B_2$, 9600 for $^1A_1$, and 5700 for ^1A_g.

From the correlation energy recovered variationally by these CI's ($\Delta E_{\mathrm{var}}^{\mathrm{CI}}$), the total singles and doubles (SD) CI energy lowering ($\Delta E_{\mathrm{SD}}^{\mathrm{CI}}$) was estimated by multiplying $\Delta E_{\mathrm{var}}^{\mathrm{CI}}$ by the ratio of the perturbation theory estimate of the total SD energy lowering ($\Delta E_{\mathrm{SD}}^{\mathrm{pert}}$) to the perturbation theory estimate of the energy lowering from the configurations kept in the variational calculation ($\Delta E_{\mathrm{kept}}^{\mathrm{pert}}$).

$$\Delta E_{\mathrm{SD}}^{\mathrm{CI}} = \Delta E_{\mathrm{var}}^{\mathrm{CI}} \times \Delta E_{\mathrm{SD}}^{\mathrm{pert}} / \Delta E_{\mathrm{kept}}^{\mathrm{pert}} \qquad (4)$$

Adding $\Delta E_{\mathrm{SD}}^{\mathrm{CI}}$ to the SCF energy gives $E_{\mathrm{SD}}^{\mathrm{CI}}$, the estimated total energy with the inclusion of SD CI. The SD energies are shown in Table I. Also shown in Table I are the estimated energies ($E_{\mathrm{SDQ}}^{\mathrm{CI}}$) that are obtained when the effects of quadruple excitations (ΔE_{Q}) are added via the Davidson correction,[26]

$$\Delta E_{\mathrm{Q}} = (1 - c_0^2)\Delta E_{\mathrm{SD}}^{\mathrm{CI}} \qquad (5)$$

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Table II. Second-Order Perturbation Theory Analysis of the SD Correlation Energy for $^3B_2$ and ^1A_g

	$^3B_2$		^1A_g	
type of excitation	no. of configurations	ΔE^a	no. of configurations	ΔE^a
$\sigma \to \sigma$; $\sigma,\sigma \to \sigma,\sigma$	646 356	−0.3751	74 326	−0.3632
$\sigma,\sigma \to \pi,\pi$	37 279	−0.0123	4 724	−0.0139
$\pi,\pi \to \sigma,\sigma$	31 455	−0.0091	4 724	−0.0103
$\pi \to \pi$; $\pi,\pi \to \pi,\pi$	1 844	−0.0859	346	−0.1114
$\sigma,\pi \to \sigma,\pi$	147 222	−0.2717	18 512	−0.2862
	864156	−0.7541	102632	−0.7850

^{a} Energy lowering in hartrees.

where c_0^2 is the coefficient of the reference configuration(s) in the CI expansion.

A troubling feature of these CI calculations was that the large size of **2** and **3** resulted in variational recovery of only about 57% of the total estimated SD correlation energy for $^3B_2$ and $^1A_1$ and 73% for ^1A_g. This leads to large uncertainties in ΔE_{SD}^{CI} and even larger uncertainties in ΔE_Q. Not only does ΔE_{SD}^{CI} appear in eq 5 for ΔE_Q, but in a CI calculation with selected configurations, in which only 57–73% of the SD correlation energy is recovered variationally, the size of c_0^2 could be rather different from that in the full SD CI wave function.

One way to increase the precision of CI calculations is to reduce the number of configurations generated by truncating the orbital space in which the CI is carried out. This can be accomplished for planar conjugated hydrocarbons by restricting the CI to the π space. We have found that this approach yields reasonable results for the state orderings in neutral alternant hydrocarbons, though not in conjugated ions.[17-19]

There is, however, no a priori reason to believe that CI in just the π space would provide a reasonable estimate of the energy difference between a diradical like **2** and a closed-shell molecule like **3**. In **2** the unpaired π electrons should polarize the spins of the σ electrons, statically in $^3B_2$ and dynamically in $^1A_1$.[17,27] Spin polarization does not occur in the ^1A_g ground state of **3**; so omitting this effect in **2**, by not allowing single σ excitations, should spuriously favor **3** over **2**.

On the other hand, because the nonbonding electrons in **2** are well correlated, in $^3B_2$ by the Pauli principle and in $^1A_1$ by localization to different regions of space, the ^1A_g state of **3** has more ionic terms in its π wave function. The energetic impact of such ionic terms can be reduced by σ–π correlation, involving the simultaneous excitation of one σ and one π electron from the SCF configuration.[28] Thus, omitting excitations in the σ space would fail to include this type of correlation and so tend to favor **2** over **3**.

The two types of σ–π correlation effects that are neglected by deleting all configurations involving σ excitations work in opposite directions; one tends to favor **2** and the other **3**. In ignoring both these effects by carrying out CI in just the π space, some cancellation would be expected. Therefore, it is possible that π CI might prove a viable means of comparing the energies of **2** and **3**.

In order to investigate the extent to which such a cancellation occurs, the perturbation theory estimates of the SD correlation energy in $^3B_2$ of **2** and in ^1A_g of **3** were partitioned by the class of excitation involved. The results are shown in Table II. The two largest contributors, both in terms of numbers of configurations and predicted energy lowering, are excitations within the σ space and coupled σ and π excitations. The former provides 0.0119 hartrees more correlation energy for $^3B_2$ than for ^1A_g, as expected from the foregoing discussion. Also as anticipated, the latter type of excitation provides 0.0145 hartrees more correlation energy for ^1A_g. The cancellation between the two effects is predicted by perturbation theory to be rather good, the residual energy difference amounting to less than 2 kcal/mol.

Table II also shows that SD excitations generate a rather small number of π configurations, which account for less than 15% of the total SD correlation energy that is predicted by second-order perturbation theory. Nevertheless, the difference in the correlation energy between $^3B_2$ and ^1A_g that is due to these excited π configurations (0.0255 hartree) amounts to 82.5% of the total $^3B_2$–^1A_g SD correlation energy difference that is predicted by perturbation theory. Thus, perturbation theory leads one to expect that π CI should be quite successful in predicting the energy difference between **2** and **3**.[29]

π CI calculations were carried out that treated variationally all excitations through quadruples (SDTQ) in a portion of the full π orbital space. The full 16-orbital π space could not be used, since the number of SDTQ excitations grows very rapidly with the number of orbitals. Half the total number of π orbitals, which corresponds to the eight π MO's in the conceptual minimal basis set for **2** and **3**, was initially chosen for the π CI calculations. K orbitals were again used to minimize the effect of the orbitals neglected in the CI. The energies calculated by this eight-orbital π SDTQ CI are listed in Table I.

In order to test the convergence in the energy differences obtained from these π CI calculations, a second set of calculations was performed in which the number of π MO's was expanded to 11. The addition of three more virtual K orbitals to the π subspace in which SDTQ CI was carried out increased the number of configurations for $^3B_2$ and $^1A_1$ by about a factor of 10 and for ^1A_g by roughly a factor of 6. The numbers of spin-adapted configurations for the three states were, respectively, 9972, 8308, and 3983. As shown in Table I, the additional three virtual orbitals lowered the SDTQ π CI energy by about 0.008 hartree for both $^3B_2$ and $^1A_1$ and by a bit less than 0.011 hartree for ^1A_g. Thus, there is little reason to believe that addition of further virtual K orbitals would have a significant effect on the calculated energy differences.

Discussion

As shown in Table I, the $^3B_2$ RHF energy is higher than the $^1A_1$ TCSCF energy. This is also the case with the STO-3G basis set. This result simply reflects the fact, discussed in the preceding section, that the $^3B_2$ UHF geometry is not optimal for a $^3B_2$ RHF wave function. Indeed, as with the STO-3G basis set, the Dunning SV RHF energy of −307.4467 hartrees for $^3B_2$ at the optimized $^1A_1$ geometry is 3.8 kcal/mol lower than the RHF energy for $^3B_2$ at the UHF optimized $^3B_2$ geometry. As discussed above, this apparent anomaly arises because the $^1A_1$ geometry is closer to the optimal $^3B_2$ RHF geometry than is the $^3B_2$ UHF geometry.

With correlated $^3B_2$ wave functions, the situation is reversed, and the $^1A_1$ geometry gives a higher triplet energy than does the $^3B_2$ UHF geometry. For instance, $E_{SDQ} = -308.130$ for $^3B_2$ at the $^1A_1$ geometry, which is 5.6 kcal/mol above the SDQ energy for $^3B_2$ at the optimized $^3B_2$ geometry. These results supply additional evidence for our previous assertion that UHF, rather than RHF, wave functions should be used for optimizing triplet geometries when geometry optimization at the MCSCF or CI levels is impractical.[19]

The energy difference between the $^3B_2$ and $^1A_1$ states of **2** seems to be relatively insensitive to the method of correlation energy recovery. Whether the correlation energy is estimated from SD CI calculations that involve both σ and π electrons, with the addition of the Davidson correction for quadruples, or whether

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(27) Kollmar, H.; Staemmler, V. *Theor. Chim. Acta* **1978**, *48*, 223.

(28) See, for instance: Borden, W. T.; Davidson, E. R.; Hart, P. *J. Am. Chem. Soc.* **1978**, *100*, 338.

(29) We have found that π CI is quite successful in calculating the energy difference between trimethylenemethane, the simplest non-Kekulē hydrocarbon diradical, and butadiene, its closed-shell isomer. These molecules are small enough that a large amount, roughly 87%, of the SD CI correlation energy can be recovered variationally. Therefore, the estimated SDQ CI energies for these molecules should be reliable. The difference between the estimated SDQ CI energies for their ground states ($^3A'_2$ and ^1A_g, respectively) is 37.0 kcal/mol. The full π space CI's give a variational energy difference of 38.3 kcal/mol. The close agreement between these two values provides additional evidence that correlation involving σ orbitals makes, at most, a small contribution to the energy differences between non-Kekulē hydrocarbon diradicals and their closed-shell isomers. Feller, D.; Davidson, E. R.; Borden, W. T. *Isr. J. Chem.*, in press.

just the π correlation energy is obtained by SDTQ CI calculations in a portion of the full π space, a single–triplet energy difference of 10 kcal/mol is obtained. This is roughly two-thirds of the singlet–triplet energy separation calculated for trimethylenemethane,[17,30] the best studied non-Kekulé hydrocarbon.

The computed energy difference between the $^3B_2$ ground state of **2** and the ^1A_g ground state of **3** does depend on the method of correlation energy recovery. This is not really surprising since the open-shell $^3B_2$ RHF (and $^1A_1$ TCSCF) wave function should have less correlation energy than the closed-shell ^1A_g wave function. Consequently, the calculated $^3B_2$–^1A_g energy difference will depend critically on the relative amount of the ^1A_g correlation energy that is recovered.

The estimated SDQ energies place ^1A_g below $^3B_2$ by about 7 kcal/mol. However, as discussed in the previous section, this number is probably not reliable, due to the relatively small amount of the SD correlation energy recovered variationally and the resulting uncertainties in both ΔE_{SD} and in ΔE_Q. As shown in Table I, the quadruples corrections estimated by eq 5 are substantial (>50 kcal/mol), because of the large number of σ and π valence electrons being correlated in **2** and **3**. As a result, the particularly large uncertaintes in ΔE_Q could result in a substantial error in the energy difference computed between ^1A_g and $^3B_2$.

We believe that the variational SDTQ π CI energies provide a better estimate of the energy difference between the ground states of **2** and **3**.[29] In fact, the 11-orbital π CI energy difference of 24 kcal/mol probably represents a lower bound to the actual energy difference between ^1A_g and $^3B_2$. As shown in Table II, perturbation theory suggests that CI calculations that included the σ orbitals would provide a small amount of additional differential stabilization for ^1A_g.

Even a $^3B_2$–^1A_g energy difference substantially less than 24 kcal/mol would probably be consistent with Hehre's lower limit of 26 kcal/mol for the energy difference between **2** and **3**.[11] It seems likely that the rate constant for deprotonation of the singlet *m*-methylbenzyl cation to the $^3B_2$ ground state of **2** would be very small, due to the unfavorable entropy of activation term expected for intersystem crossing. Therefore, even if deprotonation of the cation to $^3B_2$ were thermodynamically favorable, the ground state of the cation might be kinetically inaccessible under Hehre's ICR conditions.

Deprotonation of *m*-methylbenzyl cation to the $^1A_1$ state of **2** should not have an unfavorable entropy of activation, since no spin multiplicity change is required during this reaction.[31] Therefore, it seems plausible that it is the difference in energy between this excited state of **2** and the ground state of **3** upon which a lower limit of 26 kcal/mol can be placed from the data of Hehre et al. We calculate that $^1A_1$ lies 10 kcal/mol above $^3B_2$. Therefore, the difference between the $^3B_2$ ground state of **2** and the ^1A_g ground state of **3** could be as low as 16 kcal/mol and still be consistent with the experimental data of Hehre et al. Nevertheless, our theoretical results indicate that the energy difference between the ground states is at least 50% higher than this lower bound.

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Registry No. 2, 32714-83-3; **3**, 502-86-3.

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[30] Hood, D. M.; Pitzer, R. M.; Schaefer, H. F. *J. Am. Chem. Soc.* **1978**, *100*, 8009.

[31] It remains to be investigated whether deprotonation of the *m*-methylbenzyl cation to form the $^1A_1$ state of **2** might require a higher activation enthalphy than deprotonation of the ortho or para cation, beyond that expected solely on the basis of the difference in thermodynamic stabilities of the products. More generally, it may be asked whether there are unusual features that are present transition state connecting a closed-shell carbocation or carbanion with a diradical and that destabilize the transition state.

Luminescent Iridium(I), Rhodium(I), and Platinum(II) Dithiolate Complexes

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Abstract: A new series of Ir(I) complexes $[Ir(L)(L')(mnt)]^-$ (L = L′ = CO, $P(OPh)_3$; L + L′ = 1,2-bis(diphenylphosphino)ethane; L = CO, L′ = PPh_3, CN^-; mnt = maleonitriledithiolate) have been prepared which luminesce in the solid state at room temperature and in frozen glass media. Emission is also observed from the corresponding Rh(I) and Pt(II) complexes including the new compounds $[PtL_2(mnt)]$ (L = $P(OEt)_3$, $P(OPh)_3$; L_2 = 1,5-cyclooctadiene, bis(diphenylphosphino)methane). At 77 K the solid-state emissions are highly structured and the highest energy emission maxima fall between 13.7 and 18.1 kcm^{-1}. Excitation spectra are also highly structured, mirroring the emission spectra. The Stokes shifts for these complexes are relatively small (typically ~400 cm^{-1}), indicating an excited-state geometry similar to that of the ground state. Structure in the emission and excitation spectra is attributed to vibrations within the metal–mnt moiety, with the dominant progression (~1400 cm^{-1} in emission spectra and ~1250 cm^{-1} in excitation spectra) corresponding to the mnt C=C vibration. Emission lifetimes range from 8 to 400 μs. From the evidence presented, the emission–absorption system for all of the complexes studied is assigned as a common singlet–triplet d–π^*(mnt) metal-to-ligand charge transfer.

The discovery of metal complexes having long-lived excited states is important to the development of new metal complex photochemistry.[1] Excited states in these systems may be of ligand field, charge transfer, or intraligand origin, and the nature of them is often probed through detailed spectroscopic and lifetime measurements. The observation of high-resolution vibrational structure in electronic emission and absorption spectra is particularly useful and provides information about changes in metal–ligand bonding between ground and excited states. This in-

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[1] See, for example: (a) Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979. (b) Wrighton, M. S., Ed. *Adv. Chem. Ser.* **1978**, *No. 168*. (c) Adamson, A. W.; Fleischauer, P. D., Eds. "Concepts of Inorganic Photochemistry"; Wiley: New York, 1975.

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