The effects of heteroatom substitution on the singlet–triplet energy differences in diradicals—*ab initio* calculations of ΔE_{ST} in *meta*-benzoquinomethane and in 1,3-naphthoquinomethane

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The large effects on the singlet–triplet energy difference, ΔE_{ST}, of substituting oxygen atoms for one or two methylene groups in trimethylenemethane and in 2,4-dimethylenecyclobutane-1,3-diyl are discussed. In contrast, CASSCF and CASPT2N/6-31G* calculations predict only small changes in ΔE_{ST} on substituting oxygen atoms for one or two methylene groups in *m*-benzoquinodimethane. After corrections for differences in zero-point energies and heat capacities, CASPT2N/6-31G* calculations give $\Delta E_{ST} = 11.0$ kcal mol^{-1} for *m*-benzoquinodimethane, which is very close to the experimental value of $\Delta E_{ST} = 9.6 \pm 0.2$ kcal mol^{-1}. At the same level of theory $\Delta E_{ST} = 9.3$ and 11.8 kcal mol^{-1} are computed for, respectively, *m*-benzoquinomethane and *m*-benzoquinone. The reasons why substitution of oxygen atoms for one or two methylene groups is predicted to have such a small effect on ΔE_{ST} in these three diradicals is discussed. As expected, for 1,3-naphthoquinomethane CASPT2N predicts a value of ΔE_{ST} that is only slightly larger than that in *m*-benzoquinomethane. However, the calculated value of $\Delta E_{ST} = 11.6$ kcal mol^{-1} is 7 kcal mol^{-1} lower than the value measured by photoacoustic calorimetry.

Introduction

The report by Dowd in 1966 of the synthesis and characterization by EPR spectroscopy of triplet trimethylenemethane (TMM)[1] marked the beginning of what has been thirty years of fruitful and exciting research on organic diradicals.[2]

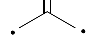
A diradical, by definition, has two orbitals of nearly the same energy that are occupied by a total of two electrons. Three closely related questions of importance about any diradical are: (*a*) is a singlet or the triplet the ground state? (*b*) What are the electronic structures and equilibrium geometries of the lowest energy singlet and triplet states? (*c*) What is the size of the energy difference between these two states at their equilibrium geometries?

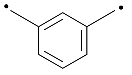
These questions can, of course, be asked about not only hydrocarbon diradicals but also about heteroatom derivatives, in which, for example, one or more methylene groups is replaced by an oxygen atom. Being able to predict, both qualitatively (from simple theories) and quantitatively (*via* calculations), for any hydrocarbon diradical how heteroatom substitution affects (*a*) the spin of the ground state, (*b*) the electronic structures and geometries of the low-lying states, and (*c*) the size of the singlet–triplet energy difference is an important goal of research on diradicals.

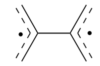
In this paper we report the results of *ab initio* calculations on the singlet–triplet energy separations in the two oxygen-containing diradicals of the title. In order to place the results of these calculations and the conclusions derived from them into context, we first review briefly the findings of theoretical and experimental studies of the singlet–triplet energy differences in several hydrocarbon diradicals and then discuss the effects of substituting oxygen for one or more methylene groups in each of these diradicals. This brief review also allows us to highlight a few of the seminal contributions made by Paul Dowd to the area of diradical chemistry.

Singlet–triplet energy differences in TMM and TME

TMM belongs to a class of molecules known as non-Kekulé hydrocarbons—molecules with fully conjugated π systems for which no classical Kekulé structures can be written.[3] TMM was not the first non-Kekulé hydrocarbon diradical to be prepared. Half a century before Dowd published its synthesis,[1] Schlenk and Brauns had prepared the first non-Kekulé hydrocarbon diradical,[4a] a tetraphenyl derivative of *m*-benzoquinodimethane (MBQDM). The triplet state of the Schlenck–Brauns hydrocarbon was subsequently characterized by EPR spectroscopy and shown to be the ground state.[4b,c] However, the synthesis of TMM was significant because TMM is the simplest non-Kekulé hydrocarbon diradical; and it was also the first molecule of this class to be synthesized, unadorned by stabilizing aryl substituents.


TMM


MBQDM


TME

In 1970 Dowd reported the preparation of a second non-Kekulé hydrocarbon diradical, tetramethyleneethane (TME).[5] Again, Dowd synthesized the parent diradical, devoid of stabilizing aryl substituents; and, again, Dowd identified the triplet state of the diradical by its EPR spectrum.

Although it was the triplet state of both TMM and TME that was characterized by EPR, the detection of a triplet EPR signal does not prove that the triplet is necessarily the ground state of either diradical. However, the subsequent finding that both TMM and TME give linear Curie–Weiss plots[6,7] indicates that in both diradicals the triplet either lies well below or has essentially the same energy as any singlet state with which it is in equilibrium.[8] The former interpretation is certainly the more probable of the two possibilities, but it should be noted that magnetization studies[9] have shown that the latter is the correct interpretation of the linear Curie–Weiss plot found by Dowd for 2,3-dimethylenecyclohexane-1,4-diyl,[10] a cyclic derivative of TME.

A triplet ground state for both TMM and TME is consistent with Hund's rule, which predicts that in a molecule in which a total of two electrons occupy two MOs that have the same or nearly the same energy, the triplet should be the ground state.[11] However, Dowd's syntheses of TMM and TME led theoreticians to consider carefully whether these diradicals really should have triplet ground states or whether one or both of them might actually have a singlet ground state. In fact, qualitative considerations, based on either molecular orbital (MO)[12] or valence bond (VB)[13] theory,[14] predict that, although the triplet state of *planar* TMM lies well below the lowest singlet, the singlet state of *planar* TME is slightly lower in energy than the triplet. Thus, qualitative theory predicts that, unlike TMM, planar TME should violate Hund's rule.[15]

Ab initio calculations that have been performed on both TMM[16] and TME[12,17] provide quantitative support for these qualitative predictions. (10/10)CASPT2N[16i] and (4/4)CAS CISD(Q) calculations[16j] on *planar* TMM both give $\Delta E_{ST} = 17.5$ kcal mol^{-1}. CISD(Q) calculations on *planar* TME give $\Delta E_{ST} = -1.6$ kcal mol^{-1},[17c] where the negative sign means that the singlet is lower than the triplet in energy in planar TME.

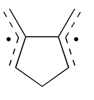
However, in TME neither the singlet nor the triplet has a planar (D_{2h}) equilibrium geometry, and at the twisted (D_2) equilibrium geometry of the triplet, CISD(Q) calculations place the triplet below the singlet by 0.5 kcal mol^{-1}.[17c] Triplet TME is predicted to be metastable at this geometry, in accord with the experimental finding by Dowd and co-workers of a linear Curie–Weiss plot.[7]

For almost three decades after Dowd prepared TMM and TME, the values of ΔE_{ST} in these diradicals could be calculated but not measured. However, quite recently it has become possible to prepare the radical anions of TMM,[18] MBQDM[19] and TME[20] in the gas phase. Photoelectron spectroscopy of these three radical anions has yielded values of ΔE_{ST} for all three diradicals.[19,21,22] The experimental values of $\Delta E_{ST} = 16.1 \pm 0.1$ and -3.0 ± 0.3 kcal mol^{-1} for, respectively, TMM[21] and TME[22] at the geometries of these diradicals that are accessed by electron detachment from the anion radicals are in good agreement with the values calculated at these geometries.[16,17,22]

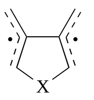
The experimental value of ΔE_{ST} in TME is negative, because Franck–Condon factors for electron photodetachment favor formation of TME at the equilibrium geometry of TME radical anion; and at this geometry singlet TME lies below the triplet.[22] Similarly, Franck–Condon factors favor formation of TMM at the planar equilibrium geometry of TMM radical anion.[21] The equilibrium geometry of the lower energy $^1B_1$ state of TMM, in which one CH_2 group is twisted out of conjugation,[16] is not accessed by the photodetachment of an electron from TMM radical anion. Consequently, the measured value of $\Delta E_{ST} = 16.1$ kcal mol^{-1} for TMM corresponds to the energy difference between the D_{3h} triplet and the planar, Jahn–Teller distorted, C_{2v} singlet, with one short and two long C–C bonds.[21]

Effect of heteroatom substitution on ΔE_{ST} in DMCPD

Qualitative theory predicts that substitution of a heteroatom for carbon can, by lifting the degeneracy of the nonbonding (NB)MOs, selectively stabilize the lowest singlet state of a diradical.[14a] For example, the 2,2-dimethyl derivative [$X = (CH_3)_2C$] of 3,4-dimethylenecyclopentane-1,3-diyl (DMCPD) has been found by Roth and co-workers to have a triplet ground state.[23] However, replacement of the $(CH_3)_2C$ group with heteroatoms (*e.g.* X = O, S and R–N), which are much better π donors than $(CH_3)_2C$, has been found, both computationally[24] and experimentally,[25] to result in the singlet becoming the ground state of these heteroatom derivatives of DMCPD.



DMCPD

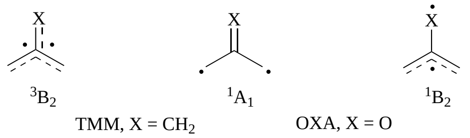


X = O, S, or R-N

In these derivatives of DMCPD the heteroatom is a substituent on the TME moiety, not a part of it. The effects of substituting a heteroatom for one or more of the methylene groups in either TME or in the TME fragment of DMCPD have not yet been investigated. However, the effects of substituting O for CH_2 in TMM have been studied.

Effect on ΔE_{ST} of substitution of O for CH_2 in TMM to form oxyallyl

As discussed above, TMM is calculated to have a much larger value of ΔE_{ST} than TME. However, calculations also predict that substitution of oxygen for one methylene group in TMM should result in the lowest singlet ($^1A_1$) and triplet ($^3B_2$) states of oxyallyl (OXA) being nearly isoenergetic.[26,27] Alkyl substituents on the remaining two methylene groups of OXA are unequivocally predicted to make $^1A_1$ the ground state.[26–28] Experimental results indicate that alkyl derivatives of OXA do, indeed, have singlet ground states.[29]



There are two reasons why substitution of O for CH_2 in planar TMM stabilizes the $^1A_1$ state of OXA, relative to the triplet. The first is related to the difference between the π bonding in the lowest singlet and triplet states of TMM. Minimization of Coulombic repulsion between the electrons of opposite spin in the $^1A_1$ state of TMM causes them to localize at two of the methylene groups, so that there is substantial π bonding only to the third.[16] Thus, if O is substituted for the unique CH_2 group, the bonding in $^1A_1$ allows it to take maximal advantage of the greater strength of C–O, relative to C–C, π bonds.[26,30] In contrast, the $^3B_2$ ($^3A_2'$ in the D_{3h} symmetry of TMM) state has partial π bonds to all three methylene groups. Therefore, substitution of O for CH_2 provides less stabilization for the $^3B_2$ state than for the $^1A_1$ state.

Although the $^3B_2$ state of OXA does have a higher π bond order to oxygen than to the methylene carbons, this requires a change in the π bonding in OXA from that in triplet TMM. Increasing the π bond order to oxygen is achieved only at the cost of reducing the π bond orders to the remaining two methylene groups. Therefore, taking advantage of the greater strength of C–O, relative to C–C π bonds, requires that triplet OXA sacrifice some of the delocalized π bonding that is present in triplet TMM. In contrast, as discussed above, the π bonding in the $^1A_1$ state of TMM is already localized in a way that takes maximal advantage of the greater strength of C–O, relative to C–C π bonds. Thus, the difference in π bonding between the singlet and triplet states of TMM results in a smaller energy separation between $^1A_1$ and $^3B_2$ in OXA than between $^1A_1$ and $^3A_2'$ in TMM.[26,27,30]

However, the greater strength of a C–O than a C–C π bond cannot be the only effect that is responsible for causing $^1A_1$ to be close to or lower in energy than $^3B_2$ in OXA and derivatives. Since the wavefunctions for the $^1A_1$ and the $^3B_2$ states of both TMM and OXA can be viewed as arising from the interaction of a localized C=X (X = CH_2 or O) π bond with the p–π AOs, ϕ and ϕ', on the two additional carbons, and, since $^1A_1$ lies well above $^3B_2$ ($^3A_2'$) in TMM, there must be a second effect that selectively stabilizes $^1A_1$ in OXA. This second effect involves the lowering of the energy of one of the degenerate TMM NBMOs

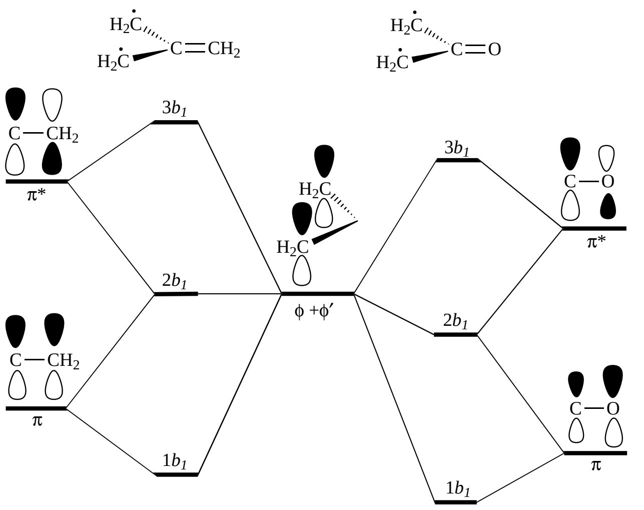


Fig. 1 Schematic depiction of the interaction of the b_1 combination of p–π AOs, φ and φ′, on two carbons with the π and π* orbitals of the C=C bond in TMM and with the π and π* orbitals of the C=O bond in OXA. The a_2 NBMO, φ – φ′, is not shown.

on substitution of O for CH_2 and how this change alters the wavefunction for the $^1A_1$ state of OXA.

As shown in Fig. 1, the π and π* MOs of the C–C double bond in $^1A_1$ TMM and the C–O double bond in $^1A_1$ OXA mix with the in-phase (b_1) combination of the p–π AOs, φ and φ′, on the remaining two carbon atoms. In TMM φ + φ′ lies approximately halfway in energy between π and π*. As a consequence, the stabilization of φ + φ′ by its mixing with π* is almost exactly balanced by the destabilization of φ + φ′ by its mixing with π. Therefore, the $2b_1$ MO that results from the mixing of φ + φ′ with π and π* remains essentially nonbonding and at the same energy as the out-of-phase (a_2) combination of φ and φ′, which does not mix with either π or π*.

The greater electronegativity of oxygen, compared with carbon, causes φ + φ′ in OXA to be closer in energy to π* than to π. Consequently, as shown in Fig. 1, the $2b_1$ MO that results from the mixing of φ + φ′ with π and π* is stabilized, so that it is lower in energy than the a_2 NBMO, φ − φ′.

In both TMM and OXA Ψ_S, the minimally correct wavefunction for the lowest energy planar singlet state ($^1A_1$), consists of two electronic configurations and has the form of eqn. (1).

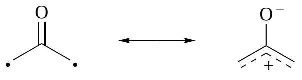
$$\Psi_S = c_1|\cdots 1b_1{}^2 2b_1{}^2\rangle - c_2|\cdots 1b_1{}^2 a_2{}^2\rangle \qquad (1)$$

However, Ψ_T, the wavefunction for the lowest triplet state of each diradical, can be represented by a single electronic configuration in which one electron occupies each non-bonding (NB)MO, eqn. (2).

$$\Psi_T = |\cdots 1b_1{}^2 2b_1{}^{\alpha} a_2{}^{\alpha}\rangle \qquad (2)$$

In singlet TMM, because $2b_1$ and a_2 are both NBMOs with almost exactly the same energy, $c_1 \approx c_2 \approx 1/\sqrt{2}$. Thus, $2b_1$ and a_2 are each occupied by essentially one electron, not only in the triplet state, but also in the lowest planar singlet state. In contrast, in OXA, because the $2b_1$ NBMO is lower in energy than the a_2 NBMO, $c_1 > c_2$ in the wavefunction for the lowest singlet state; so in this state the electron occupancies of the NBMOs are $2b_1 > 1 > a_2$. Since the NBMOs are each occupied by one electron in the triplet, the lowest singlet state of OXA is stabilized, relative to the triplet, by the greater occupancy in the singlet of the lower energy of the two NBMOs.

If $c_1 \gg c_2$ in eqn. (1) for the wavefunction for the lowest singlet state of OXA, the zwitterionic resonance structure for OXA, shown below, would provide a good representation of this state. However, $c_1 < 1.5\ c_2$,[30] and, as a result, the dipole moment of singlet OXA is computed to be only 25% greater than that of cyclopropanone.[31] It is for this reason that the solvent effects on ring opening of cyclopropanone to OXA are both calculated[31] and found[32] to be modest. Consequently, singlet OXA is best regarded as a diradical to which a zwitterionic resonance structure makes only a modest contribution.[26,29,31]



Another indication of the dominance of the diradical, rather than the zwitterionic resonance structure for OXA, is the frequency of 1730 cm^{-1} calculated for the C=O stretch.[28] This frequency indicates a strong C=O π bond in OXA. If the zwitterionic resonance, structure were important, one would expect a lower C=O stretching frequency. Interestingly, in tetramethyl-OXA the C=O stretching frequency is calculated to drop to 1670 cm^{-1},[28] suggesting that the methyl groups act to stabilize the zwitterionic resonance structure and thus lower the C=O stretching frequency.

Although substitution of oxygen for CH_2 in TMM lowers substantially the energy of the $^1A_1$ state of OXA, relative to that of $^3B_2$, the energy difference between the $^1B_2$ and $^3B_2$ states increases on going from TMM to OXA.[26,30] This change in relative energies is not due to lifting of the degeneracy of the NBMOs in OXA. Since the $^1B_2$ and $^3B_2$ states of TMM each have one electron in the $2b_1$ and one electron in the a_2 π MO, lifting of the degeneracy of these MOs by replacement of a CH_2 in TMM by O in OXA does not have a significant effect on the relative energies of the $^1B_2$ and $^3B_2$ states of these two diradicals.

What does affect the relative energies of these two states on going from TMM to OXA is the relative amount of π bonding to oxygen in $^1B_2$ and in $^3B_2$ when one CH_2 group in TMM is replaced by O in OXA. In the $^1B_2$ state of TMM, as in the $^1A_1$ state, minimization of the Coulombic repulsion energy between the two electrons of opposite spin in the NBMOs causes the π bonding in this singlet state to be much more localized than the π bonding in the triplet state, where the two electrons in the NBMOs have the same spin.[16] However, unlike the $^1A_1$ state of TMM, which has a strong π bond to the unique methylene group, in $^1B_2$ there is no π bond to this CH_2 group, which, instead, has a non-bonding π electron localized on it. Therefore, substitution of oxygen for this CH_2 group does not lead to any C–O π bonding in $^1B_2$.

In contrast, as already discussed, not only does $^3B_2$ have partial π bonds to all of the CH_2 groups in TMM, but also the bond order of the unique π bond is increased on substitution of O for CH_2. Consequently, the greater strength of a C–O, relative to a C–C π bond stabilizes $^3B_2$, relative to $^1B_2$, on going from TMM to OXA.

Effect of substitution of oxygen for CH_2 on ΔE_{ST} in DMCBD

Qualitative theory[12] and quantitative calculations[33,34] both predict that 2,4-dimethylenecyclobutane-1,3-diyl (DMCBD) has a triplet ground state. This prediction was subsequently verified experimentally by Dougherty[35] and by Dowd and Paik.[36]

Substitution of oxygen atoms for both methylene groups in DMCBD should provide greater selective stabilization for the lowest singlet state of cyclobutane-2,4-dione-1,3-diyl† (CBDOD) than substitution of oxygen for one methylene group in TMM provides for the lowest singlet state of OXA. This expectation has been confirmed computationally.[34] Although ΔE_{ST} is computed to be slightly larger in DMCBD (ΔE_{ST} = 18–20 kcal mol^{-1}) than in planar TMM,[16] the lowest singlet state is calculated to be far below the triplet ($\Delta E_{ST} < -20$ kcal mol^{-1}) in CBDOD, rather than at nearly the same energy, as in OXA.[26]

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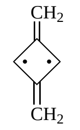
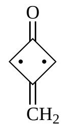
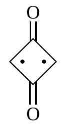
† 2,4-Dioxocyclobutane-1,3-diyl.



DMCBD



MCBOD



CBDOD

Substitution of oxygen for just one methylene group in DMCBD should result in a value of ΔE_{ST} somewhere in between the large positive value in DMCBD and the large negative value in CBDOD. This was, in fact, what was found computationally. ΔE_{ST} in 4-methylenecyclobutan-2-one-1,3-diyl ‡ (MCBOD) was calculated to be 7.7 kcal mol^{-1}, which is much closer to ΔE_{ST} in DMCBD than in CBDOD.[34] The prediction of a triplet ground state for MCBOD provides permissive evidence that the EPR signal, observed by Dowd and Paik and assigned to triplet MCBOD,[36] really does belong to this species.

The reason why substitution of oxygen for one methylene group in DMCBD has considerably less than half the effect on reducing ΔE_{ST} than substitution of oxygen atoms for both methylene groups was traced to the special stability of the triplet state of MCBOD, relative to the triplet states of DMCBD and CBDOD.[34] As shown in Fig. 1, the $\phi + \phi'$ combination of p–π AOs at C_1 and C_3 interacts more strongly with π* of C=O than with π* of C=C. However, $\phi + \phi'$ interacts much more strongly with π of C=C than with π of C=O. In the triplet, the greater stabilization of the *pair* of electrons in the bonding π orbital of C=C than of C=O is more important than the stabilization of the *single* electron in $\phi + \phi'$. Consequently, the lowest triplet state of MCBOD can be described as consisting of a triplet TMM moiety that is only slightly perturbed by the carbonyl group that bridges two of the methylenes.

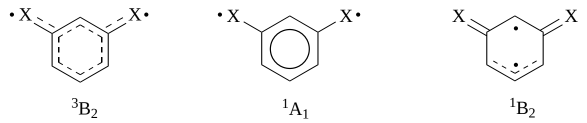
If OXA is viewed as two localized radical centers that are bridged by a carbonyl group, the computational finding that the lowest singlet and triplet states in OXA have nearly the same energy[26,27] indicates that a bridging carbonyl group has a relatively minor effect on altering ΔE_{ST} in hydrocarbon diradicals. Therefore, the computational finding that the bridging carbonyl group in MCBOD lowers ΔE_{ST} in planar TMM by *ca.* 10 kcal mol^{-1}, from 17.5 kcal mol^{-1}[16] to 7.7 kcal mol^{-1},[34] is rather surprising.

It should be noted, however, that the bridging carbonyl group in MCBOD not only interacts electronically with the π orbitals of the TMM moiety, but also constrains a C–C–C bond angle in the TMM moiety to 90°. This angle constraint selectively stabilizes the $^1A_1$ states of MCBOD, DMCBD and CBDOD by increasing the long-range interaction between the p–π AOs on the two methylene groups that are incorporated into the four-membered rings. This interaction is stabilizing in the $2b_1$ NBMO and destabilizing in the a_2 NBMO. The resulting energy difference between the NBMOs selectively stabilizes the $^1A_1$ state, because, as discussed above, its wavefunction [eqn. (1)] allows the lower energy NBMO to have an electron occupation number >1; whereas, in the wavefunction for the triplet [eqn. (2)], one electron occupies each NBMO.

The size of the effect of angle constraint on ΔE_{ST} can be estimated computationally. CASSCF calculations find that constraining the C–C–C bond angle in TMM to 90° reduces the energy difference between $^1A_1$ and $^3B_2$ by 14 kcal mol^{-1}.[16i] The similar angle constraint in not only MCBOD but also in DMCBD and CBDOD must certainly act to reduce the size of ΔE_{ST} in these diradicals too.

Effect of substitution of oxygen for CH_2 on ΔE_{ST} in MBQDM

As in DMCBD, in *m*-benzoquinodimethane (MBQDM) both qualitative theory[12] and quantitative *ab initio* calculations[37,38] predict a triplet ground state. Platz and co-workers showed that the triplet is, in fact, the ground state;[39,40] and Wenthold and Lineberger have measured $\Delta E_{ST} = 9.6 \pm 0.2$ kcal mol^{-1}, using photoelectron spectroscopy.[19] This value is in good agreement with those predicted by π CI calculations.[37,38]



MBQDM , X = CH_2 MBQ , X = O

The *ab initio* calculations find that the lowest energy singlet state of MBQDM is $^1A_1$. The $^1B_2$ state is computed to lie above $^1A_1$ by > 10 kcal mol^{-1}, a value which is also in good agreement with that obtained from the photoelectron spectrum.[19] The reason for this energy ordering of the two singlet states is easily understood.

As in TMM, minimization of Coulombic repulsion between electrons of opposite spin in the NBMOs of MBQDM results in the bonding in each of the lowest two singlet states being more localized than in the triplet. As depicted above, the localization of these two electrons on the exocyclic methylene groups in $^1A_1$ leaves the π bonding in the benzene ring largely intact; whereas, the localization of these electrons to carbons in the ring in the $^1B_2$ state destroys the aromaticity of the six-membered ring.

Unlike the case in DMCBD, where substitution of oxygen for both methylene groups is unequivocally predicted to result in a singlet ground state for CBDOD,[34] the same substitution of O for both CH_2 groups in MBQDM is predicted, just as unequivocally, to have little effect on the size of the singlet–triplet splitting in *m*-benzoquinone (MBQ).[38] The reason for this difference between the four- and six-membered rings is that in the lowest singlet state ($^1A_{1g}$) of DMCBD, the methylene groups that are replaced by oxygen atoms in CBDOD have large π bond orders to them; whereas, in the lowest singlet state ($^1A_1$) of MBQDM, the CH_2 groups that are replaced by O in MBQ have little π bonding to them.

In contrast with $^1A_1$, the $^3B_2$ state of MBQDM does have partial π bonds to the exocyclic CH_2 groups, and the strengths of these π bonds are increased upon substitution of O for CH_2 to form MBQ.[38] Consequently, as is the case in forming the $^1B_2$ state of OXA from $^1B_2$ TMM,[30] substitution of O for CH_2 in the $^1A_1$ state of MBQDM actually increases the energy difference between $^1A_1$ and $^3B_2$ in MBQ.

Unlike the $^1A_1$ state of MBQDM, the $^1B_2$ state does have substantial π bonding to the exocyclic methylene groups. Upon substitution of O for CH_2, the strength of the C–O π bonds in the $^1B_2$ state of MBQ reduces the energy difference between $^1B_2$ and $^3B_2$ from *ca.* 25 kcal mol^{-1} in MBQDM to *ca.* 9 kcal mol^{-1} in MBQ. In addition, the strong C–O π bonds in the $^1B_2$ state of MBQ result in this state being calculated to fall well below $^1A_1$ in energy.[38]

In both the $^1B_2$ and $^3B_2$ states of MBQ one electron occupies each NBMO. Thus, any difference between the energies of the NBMOs cannot have a substantial effect on the relative energies of these two states of MBQ. Since $^1B_2$ is the lowest singlet state of this diradical, $^3B_2$ can, therefore, be predicted *unequivocally* to be the ground state.

This situation in MBQ contrasts with those in OXA and CBDOD, where the wavefunction for the lowest singlet state has the form of Ψ_S in eqn. (1). In the latter two diradicals, upon selective stabilization of one of the NBMOs by the substitution of O for CH_2, the NBMO thus stabilized can have an electron occupancy greater than one. As discussed above, the resulting difference between the lowest singlet and triplet in the occupation numbers of the NBMOs can and does allow the singlet to fall below the triplet and to become the ground state of OXA derivatives and of CBDOD.

Although resonance structures can easily explain why the lowest singlet state is $^1A_1$ in MBQDM but $^1B_2$ in MBQ, it is

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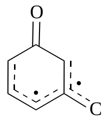
‡ 4-Methylene-2-oxocyclobutane-1,3-diyl.

Table 1 CASSCF/6-31G* and CASPT2N/6-31G* energies (kcal mol^{-1}) of the singlet states of MBQDM, MBQ, MBQM and 1,3-NQM, relative to the triplet ground states, and CASSCF/6-31G* vibrational corrections (kcal mol^{-1}) for differences in zero-point energies and heat capacities

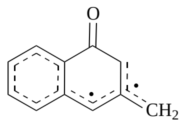
Molecule	State	CASSCF	CASPT2N	ZPE	C_v × 298 K
MBQDM	$^3B_2$	−307.618 32[a]	−308.569 32[a]	85.01	8.20
MBQDM	$^1A_1$	12.9	11.7	−1.23	0.55
MBQDM	$^1B_2$	24.4	24.9	−2.14	0.08
MBQ	$^3B_2$	−379.297 48[a]	−380.308 69[a]	54.77	6.76
MBQ	$^1B_2$	10.8	11.9	−0.37	0.29
MBQ	$^1A_1$	27.2	24.0	−2.07	−0.07
MBQM	$^3A'$	−343.459 60[a]	−344.440 87[a]	69.95	7.47
MBQM	$^1A'$	11.8	9.3	−0.20	0.15
1,3-NQM	$^3A'$	−496.170 26[a]	−497.626 64[a]	—	—
1,3-NQM	$^1A'$	14.2	11.6	—	—

[a] Calculated energy for the triplet ground state in hartree.

harder to use resonance structures to predict the electronic structure of the lowest singlet state in the less symmetrical *m*-benzoquinomethane (MBQM). Since no resonance structure can be drawn for MBQM which simultaneously possesses both an aromatic ring and a carbonyl π bond, the question arises as to the electronic structure of the lowest singlet state. The ground state of MBQM is known to be a triplet,[40,41] and one might wonder whether the inability of MBQM to adopt the electronic structure of the lowest singlet state of either MQBDM or MBQ causes ΔE_{ST} in MBQM to be larger than that in either of these other two diradicals.



MBQM



1,3-NQM

Experiments on 1,3-naphthoquinomethane (1,3-NQM), the benzo analog of MBQM, suggest that this might in fact be the case. Like MBQM,[41] 1,3-NQM has been found to have a triplet ground state[42] and, two years before photoelectron spectroscopy was used to measure the singlet–triplet splittings in TMM,[21] cyclooctatetraene (COT),[43] and MBQDM,[19] Goodman and Kahn used photoacoustic calorimetry to obtain the value $\Delta E_{ST} = 18.5$ kcal mol^{-1} in 1,3-NQM.[44] This energy separation between the lowest singlet and triplet states of 1,3-NQM is nearly twice as large as the values measured for MBQDM[19] and calculated for both MBQDM[37] and MBQ.[38]

In this paper we report the results of *ab initio* calculations on the $^1A'$ and $^3A'$ states of MBQM, which we performed in order to elucidate the electronic structure of the lowest singlet state and to predict the value of ΔE_{ST} in this diradical. Exactly the same types of calculation were also performed on MBQDM and MBQ, in order to make the results of the calculations on these three diradicals directly comparable. We also report the results of calculations of ΔE_{ST} in 1,3-NQM, which we computed for comparison with the experimental value measured by Goodman and Kahn.[44]

Computational methods

All geometries were optimized at the complete active space (CAS)SCF level, using the 6-31G* basis set.[45] The active space for MBQDM, MBQ and MBQM consisted of eight π electrons in eight π orbitals. These (8/8)CASSCF/6-31G* optimizations were carried out using the GAUSSIAN 94 suite of programs.[46] The active space for 1,3-NQM consisted of twelve π electrons in twelve π orbitals. The (12/12)CASSCF calculations were too large for GAUSSIAN 94 to handle, so these geometry optimizations were carried out with the gradient package in MOLCAS-3.[47]

(8/8)CASSCF vibrational analyses were performed at the optimized geometries of MBQDM, MBQ and MBQM. The frequencies obtained were used, without scaling, to compute zero-point energy (ZPE) and heat capacity (C_v) corrections. Owing to the size of the active space and the number of degrees of freedom for 1,3-NQM, vibrational analyses on this diradical were not carried out.

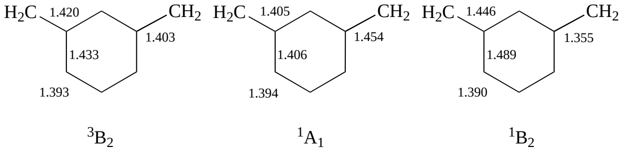


Fig. 2 CASSCF/6-31G* bond lengths (Å) for the $^3B_2$, $^1A_1$ and $^1B_2$ states of MBQDM

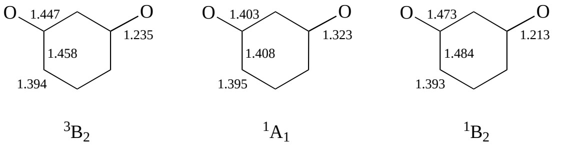


Fig. 3 CASSCF/6-31G* bond lengths (Å) for the $^3B_2$, $^1A_1$ and $^1B_2$ states of MBQ

Dynamic electron correlation was included by performing single point CASPT2N energy calculations at the CASSCF optimized geometries. The CASPT2N method provides electron correlation, beyond that included at the CASSCF level, through the use of multi-reference, second-order perturbation theory.[48] The CASPT2N/6-31G* calculations were carried out using MOLCAS-3.[47]

Results and discussion

The CASSCF/6-31G* optimized C–C bond lengths in the triplet and lowest singlet states of MBQDM, MBQ, MBQM and 1,3-NQM are given in Figs. 2–5. Complete listings of the optimized bond lengths and bond angles have been deposited with the British Library as a supplementary publication [Supp. No. 57334 (5 pp)].§ The CASSCF and CASPT2N energies, computed at the optimized geometries, are summarized in Table 1. At both levels of theory all four diradicals are predicted to have triplet ground states with similar values of ΔE_{ST}.

CASPT2N values for ΔE_{ST} in MBQDM and in MBQ

The reliability of CASSCF and CASPT2N for quantitatively computing ΔE_{ST} for MBQDM can be judged by comparing the calculated values with the experimental value of $\Delta E_{ST} = 9.6 \pm 0.2$ kcal mol^{-1}.[19] As expected, the CASPT2N value, which includes dynamic electron correlation, is in better

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§ For details of the British Library supplementary publications scheme, see 'Instructions for Authors (1998)' on the RSC's Website URL:http// www.rsc.org/authors. The supplementary data can also be accessed directly on the RSC's Website on http://www.rsc.org/suppdata/perkin2/ 1998/1037/.

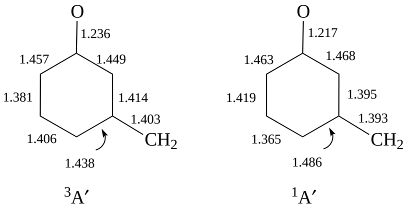

Fig 4. CASSCF/6-31G* bond lengths (Å) for the $^3A'$ and $^1A'$ states of MBQM

agreement with experiment than the CASSCF value, which does not. After correction of the CASPT2N value by −0.7 kcal mol^{-1} for the combined effects of the ZPE and heat capacity corrections, $\Delta E_{ST} = 11.0$ kcal mol^{-1} is obtained. Thus, for MBQDM,[19] as for TMM[16,21] and COT,[15b,43] CASPT2N/6-31G*//CASSCF/6-31G* gives a value of ΔE_{ST} that is within 2 kcal mol^{-1} of that measured by photoelectron spectroscopy.

Although CASPT2N gives a slightly smaller value than CASSCF for the energy difference between the $^1A_1$ and $^3B_2$ states of MBQDM, CASPT2N gives a slightly larger value than CASSCF for the $^1B_2 - {}^3B_2$ energy difference. After correction for vibrational effects, the CASPT2N value of $\Delta E_{ST} = 22.8$ kcal mol^{-1} is again only a little more than 1 kcal mol^{-1} higher than the experimental value of $\Delta E_{ST} \leqslant 21.5$ kcal mol^{-1}.[19]

As discussed previously, the carbonyl groups in MBQ cause the energies of the $^1A_1$ and $^1B_2$ states, relative to each other and to the energy of $^3B_2$, to be very different than in MBQDM.[38] Nevertheless, as in MBQDM, the effect of going from CASSCF to CASPT2N in the calculations on MBQ is to decrease the energy separation between $^1A_1$ and $^3B_2$ and to increase that between $^1B_2$ and $^3B_2$ by about half as much. After vibrational corrections, the CASPT2N energies of $^1A_1$ and $^1B_2$, relative to that of $^3B_2$ are, respectively, $\Delta E_{ST} = 21.9$ and 11.8 kcal mol^{-1}. Based on the comparison between the CASPT2N/6-31G* and the experimental results for MBQDM, these singlet–triplet energy separations in MBQ are both likely to be too high by 1–2 kcal mol^{-1}.

ΔE_{ST} and the bonding in MBQM

In contrast with what might have been expected, the CASPT2N value of $\Delta E_{ST} = 9.3$ kcal mol^{-1} in MBQM is actually smaller than both the $^1A_1 - {}^3B_2$ energy separation in MBQDM and the $^1B_2 - {}^3B_2$ energy separation in MBQ. In MBQM the drop in ΔE_{ST} of 2.5 kcal mol^{-1} on going from CASSCF to CASPT2N is intermediate between the decreases in the $^1A_1 - {}^3B_2$ energy separations in MBQDM (1.2 kcal mol^{-1}) and MBQ (3.2 kcal mol^{-1}), but closer to the latter. The vibrational corrections in MBQM are negligible, so that at the CASPT2N level $\Delta E_{ST} = 9.3$ kcal mol^{-1} is computed for this diradical.

Why is the energy difference between the triplet and the lowest singlet state in MBQM computed to be smaller, not larger, than that in either MBQDM or MBQ? The answer to this question obviously lies in the electronic structure of MBQM, which is reflected in the optimized geometries of the lowest singlet and triplet states. The bond lengths are given in Fig. 4.

As shown in Fig. 4, in both the singlet and triplet states of MBQM the C–C bonds to the carbonyl group are rather long, and the C–O bond in the carbonyl group is relatively short. These C–C and C–O bond lengths in the lowest triplet and singlet states of MBQM are similar to those in the $^3B_2$ and $^1B_2$ states of MBQ, which are given in Fig. 3. As in OXA[26] and in CBDOD,[34] the C–C bonds to the carbonyl group are slightly shorter and the C–O bond in the carbonyl groups slightly longer in the lowest triplet state than in the lowest singlet state of both MBQ and MBQM. These bond length differences indicate greater electron delocalization into the carbonyl group in the triplets than in the singlets.

The remainder of the C–C bond lengths in the lowest triplet state of MBQM are similar to those in the lowest triplet state of MBQDM, which are shown in Fig. 2. However, the C–C bond lengths in the lowest singlet state of MBQM are quite different from those in either of the low-lying states of MBQDM. Instead, the C–C bond lengths in MBQM resemble the (6/6)CASSCF/6-31G* C–C bond lengths in the lowest singlet state of vinyl-TMM, and the C–C bond lengths in the lowest triplet state of MBQM are also similar to those in the lowest triplet state of vinyl-TMM.[49,50] This resemblance is not surprising; for, if one ignores the weakly conjugating carbonyl group in MBQM, the remaining π system is the same as that of planar *cisoid*-vinyl-TMM.

Attachment of a vinyl substituent to one of the methylene carbons of TMM provides allylic delocalization for the nonbonding electron that appears in the p–π AO of that carbon. In the lowest triplet state of vinyl-TMM this additional delocalization causes lengthening of both the C–C bond that joins this carbon to the central carbon of the TMM fragment and of the C=C bond in the vinyl substituent. The allylic delocalization also causes shortening of the C–C bond connecting the vinyl group to the TMM moiety; but, because only two of three TMM resonance structures place an unpaired electron on the carbon to which the vinyl group is attached, this C–C bond to the vinyl group remains longer than the C–C bond within the vinyl group. Additional consideration of the effects of the weak π bonding between the triplet vinyl-TMM fragment and the carbonyl group nicely accounts for the C–C bond lengths, shown in Fig. 4, for the triplet state of MBQM.

In singlet vinyl-TMM maximum stabilization is provided by the vinyl group if it is attached to the carbon at which an electron is completely localized in the $^1B_2$ state of TMM (*vide supra*). The π interaction between this carbon and the central carbon of TMM is slightly antibonding, which is why this carbon prefers to twist out of conjugation.[16] In planar vinyl-TMM this antibonding interaction is minimized if the electron at the unique carbon of TMM is allylically delocalized to the distal carbon of the vinyl group. The same considerations nicely account for the C–C bond lengths, shown in Fig. 4, for the lowest singlet state of MBQM.

At the (6/6)CASSCF/6-31G* level of theory the energy difference between the lowest singlet and triplet states of planar vinyl-TMM is computed to be 12 kcal mol^{-1}.[49] This is essentially the same as the value of $\Delta E_{ST} = 11.8$ kcal mol^{-1} that we compute for MBQM at the (8/8)CASSCF level of theory. Since, as discussed above, joining two localized radical centers to a carbonyl group to form OXA is calculated to leave the lowest singlet and triplet states nearly degenerate in energy, it is not surprising that bridging two termini of vinyl-TMM with a carbonyl group to form MBQM causes little change in the calculated value of ΔE_{ST}.

ΔE_{ST} and the bonding in 1,3-NQM

As shown in Table 1, at both the CASSCF and CASPT2N levels of theory our calculations find that ΔE_{ST} in 1,3-NQM is 2.3 kcal mol^{-1} greater than that in MBQM. If, as in MBQM, vibrational effects in 1,3-NQM have little effect on the value of ΔE_{ST}, our CASPT2N calculations predict $\Delta E_{ST} = 11$–12 kcal mol^{-1} in 1,3-NQM. Based on the comparison between calculations and experiment in MBQDM, the CASPT2N value of ΔE_{ST} for 1,3-NQM is likely to be too high by 1–2 kcal mol^{-1}. Nevertheless, even the CASPT2N value for ΔE_{ST} is *ca.* 7 kcal mol^{-1} lower than that measured by Goodman and Kahn, using photoacoustic calorimetry.[44]

The slightly larger calculated value of ΔE_{ST} in 1,3-NQM than in MBQM makes good physical sense. If MBQM can be viewed as a slightly perturbed, planar, vinyl-TMM, 1,3-NQM can be viewed as a slightly perturbed, planar, phenyl-TMM. The differences between the geometries of the lowest singlet states in these two molecules and also between the lowest triplet states (compare Figs. 4 and 5) are consistent with those expected on replacing the vinyl group in vinyl-TMM with the slightly less

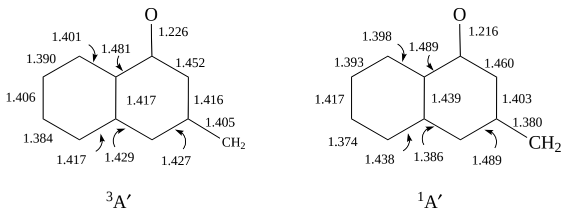

Fig. 5 CASSCF/6-31G* bond lengths (Å) for the $^3A'$ and $^1A'$ states of 1,3-NQM

radical-stabilizing phenyl group. Since the vinyl group in planar vinyl-TMM lowers the CASSCF value[49] of ΔE_{ST} by *ca.* 7 kcal mol^{-1} from that between the $^1B_2$ and $^3A_2'$ states of TMM,[16h] the lesser radical stabilizing ability of the phenyl substituent in phenyl-TMM would be expected to have a smaller effect on lowering the energy difference between these two states of TMM.

The lowering of ΔE_{ST} in TMM by vinyl is about 50% of the lowering of the BDE of a primary C–H bond by vinyl,[51] and the lowering of the BDE of a primary C–H bond by phenyl is 1–2 kcal mol^{-1} less than that by vinyl.[52] Thus, the difference in radical stabilizing abilities between phenyl and vinyl is expected to result in a value of ΔE_{ST} that is *ca.* 1 kcal mol^{-1} greater in phenyl-TMM than in vinyl-TMM. Therefore, the difference between the radical stabilizing abilities of phenyl and vinyl can account for at least some of the calculated 2.3 kcal mol^{-1} difference between ΔE_{ST} in 1,3-NQM and in MBQM.

Conclusions

Our CASPT2N/6-31G* calculations on MBQDM give $\Delta E_{ST} = 11.0$ kcal mol^{-1}, which is larger than the experimental value by a little more than 1 kcal mol^{-1}. The lowest singlet state changes from $^1A_1$ in MBQDM to $^1B_2$ in MBQ, but the CASPT2N values of ΔE_{ST} in these two diradicals are almost identical. Vibrational corrections are, however, predicted to make ΔE_{ST} in the latter diradical about 1 kcal mol^{-1} larger than in the former.

ΔE_{ST} is predicted to be *ca.* 2 kcal mol^{-1} smaller in MBQM than in MBQDM. The value of ΔE_{ST} in MBQM is computed to be very similar to that in vinyl-TMM.[49] The former diradical may be viewed as a derivative of the latter, perturbed only by bridging of two of the terminal carbons of vinyl-TMM by a carbonyl group. As in OXA, the bridging carbonyl group in MBQM is expected to have little effect on the value of ΔE_{ST}; so the reason why very similar values of ΔE_{ST} are calculated for vinyl-TMM and MBQM can be easily understood.

1,3-NQM may be viewed as a derivative of phenyl-TMM that is perturbed by a carbonyl group in a similar way to that in which the carbonyl group perturbs the vinyl-TMM moiety in MBQM. This structural relationship between 1,3-NQM and MBQM makes the 2 kcal mol^{-1} difference between the calculated values of ΔE_{ST} in these two diradicals seem very reasonable. Consequently, confirmation that the experimental value in MBQM is close to or slightly larger than our predicted value of $\Delta E_{ST} = 9$ kcal mol^{-1} would suggest our prediction, that the current experimental value of $\Delta E_{ST} = 18.5$ kcal mol^{-1} for 1,3-NQM[44] is too high by at least 7 kcal mol^{-1}, is also correct.

The measurement of ΔE_{ST} in MBQM will thus provide both a test of the accuracy of our calculated value of ΔE_{ST} in this diradical and also a good indication of whether our value of ΔE_{ST} in 1,3-NQM is correct. Therefore, we look forward to the measurement of ΔE_{ST} in MBQM by photoelectron spectroscopy in the near future.[53]

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