Calculations of the Relative Energies of the $^2B_{1g}$ and $^2A_{2u}$ States of Cyclobutanetetraone Radical Cation and Radical Anion Provide Further Evidence of a $^3B_{2u}$ Ground State for the Neutral Molecule: A Proposed Experimental Test of the Prediction of a Triplet Ground State for (CO)₄[†]

Xin Zhou, David A. Hrovat, and Weston Thatcher Borden*

Department of Chemistry and the Center for Advanced Scientific Computing and Modeling, University of North Texas, 1155 Union Circle, #305070, Denton, Texas 76203-5070

B3LYP, CCSD(T), and CASPT2 calculations with the 6-311+G(2df) basis set have been performed on the radical anion and radical cation of cyclobutanetetraone (**1**). The very similar energies computed for the $^2B_{1g}$ and $^2A_{2u}$ states of both $\mathbf{1}^{\bullet+}$ and $\mathbf{1}^{\bullet-}$ indicate that the singly occupied b_{1g} and a_{2u} MOs in these two states of the radical cation and anion have nearly the same energies, thus supporting the previously made prediction that neutral **1** has a $^3B_{2u}$ ground state. Reaction of squaric acid with $O^{\bullet-}$, followed by negative ion photoelectron spectroscopy (NIPES) on the $\mathbf{1}^{\bullet-}$ thus formed, is proposed as an experimental test of the startling prediction that tetraketone (**1**), a molecule that would be expected to be a closed-shell singlet, actually has a triplet ground state.

Introduction

Cyclobutanetetraone (**1**), the cyclic tetramer of carbon monoxide, has an aromatic dianion ($\mathbf{1}^{-2}$).[1] However, in all other respects, **1** appears to be an unremarkable, closed-shell molecule. Nevertheless, electronic structure calculations have shown **1** to be unusual and of significant theoretical interest for a number of closely related reasons.[2–4] First, the interaction of the lone pair orbitals on the oxygens of the four carbonyl groups with the C−C σ bonds of the four-membered ring in **1** gives rise to a very high-lying, filled b_{1g} MO, which is shown in Figure 1. Second, the in-phase (a_{2u}) combination of C=O π* orbitals, also shown in Figure 1, provides the very low-lying, unfilled, MO that is doubly occupied in $\mathbf{1}^{-2}$.[1] Third, the simultaneous presence of a highest occupied (HO)MO of unusually high energy and a lowest unoccupied (LU)MO of unusually low energy raises the startling possibility that excitation of one or two electrons from the b_{1g} to the a_{2u} MO might result in a state with 9 or 10 π electrons actually being lower in energy than the expected ground state of **1** with 8 π electrons.

The fourth reason why **1** is such an interesting molecule is that carrying out calculations, reliable enough to establish unequivocally what the ground state of **1** actually is, has proven to be an unexpectedly difficult task. Gleiter and coworkers, who were the first to perform calculations on **1**, found that at the HF/6-31G(d) level of theory, the configuration in Figure 1 with 8 π electrons is lower in energy by 64.6 kcal/mol than the configuration with 10 π electrons.[2] However, upon the inclusion of electron correlation at the MP2 level, the state with 10 π electrons falls below the 8 π state by 25.7 kcal/mol.

This 90.3 kcal/mol change in the relative energies of the two states suggests that the Moeller−Plesset (MPn) perturbation theory[5] is unsuitable for computing their relative energies. In fact, Jiao and coworkers have shown that MPn calculations,
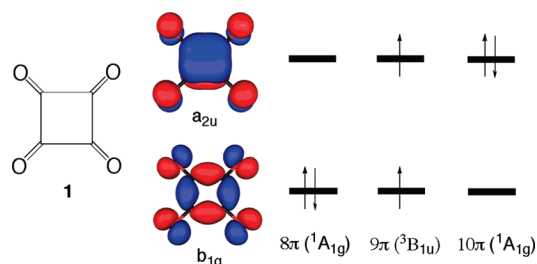

Figure 1. Three electronic configurations that can be formed by distributing two electrons between the b_{1g} σ and the a_{2u} π* MOs of cyclobutanetetraone (**1**).

with $n = 2–4$, on **1** do not converge on an answer as to which singlet state is lower in energy.[3]

Gleiter's (U)HF and (U)MP2 calculations both found the 9 π triplet state to be higher in energy than the 8 π singlet.[2] However, QCISD and CCSD(T) calculations by Jiao and coworkers as well as their DFT calculations with several different functionals found the 9π triplet to be lower in energy than either the 8 π or 10 π singlets.[3] Therefore, Jiao's results indicate that **1**, which would naively be expected to have a singlet ground state, is actually a ground state triplet.

The 8 π and 10 π configurations in Figure 1 both have $^1A_{1g}$ symmetry. Consequently, they both appear in the wave function for the lowest singlet state. If these two configurations are close in energy, then both should be included in the reference wave function for the lowest energy $^1A_{1g}$ state. Therefore, we undertook CASSCF and CASPT2[6] calculations on **1** in which both configurations were included in the active space.[4]

Unfortunately, even with an active space that consisted of 16 electrons, distributed among 16 orbitals, not enough electron correlation could be included to provide an even-handed description of the two lowest $^1A_{1g}$ states at the (16/16)CASSCF level. The occupation numbers of the natural orbitals from a CISD calculation showed that in a CASSCF wave function for the $^1A_{1g}$ state in which the 10 π configuration is dominant, at

* Corresponding author: E-mail: borden@unt.edu.

Prediction of a Triplet Ground State for (CO)$_4$

J. Phys. Chem. A, Vol. 114, No. 3, 2010 **1305**

least four more doubly occupied MOs should be added to the active space beyond the eight doubly occupied σ and π orbitals that we were able to include in our (16/16)CASSCF calculations. Consequently, the weight of the (16/16)CASSCF reference wave function in the (16/16)CASPT2 calculations is considerably smaller for the $^1A_{1g}$ state, in which the 10 π configuration is dominant, than for the $^1A_{1g}$ state, in which the 8 π configuration is dominant.

Second-order perturbation theory, which is used in the CASPT2 calculations, tends to favor spuriously the $^1A_{1g}$ state in which the weight of the CASSCF reference is smaller in the CASPT2 wave function. Therefore, the finding that the 10 π singlet state goes from being 92.6 kcal/mol higher in energy than the 8 π singlet at the (16/16)CASSCF level to being lower by 7.5 kcal/mol at the (16/16)CASPT2 level[4] is understandable but does not necessarily mean that the 10 π singlet is actually the lower of the two states.

However, it is significant that the 9 π $^3B_{2u}$ state is calculated to have nearly the same energy as the 10 π singlet. The smaller weight of the (16/16)CASSCF reference in the CASPT2 wave function for the 10 π singlet should spuriously tend to make its CASPT2 energy lower than that of the triplet. Therefore, the fact that the triplet and 10 π singlet are calculated to have nearly the same CASPT2 energies suggests that the triplet really is lower in energy than the 10 π singlet.

CCSD(T) calculations[7] and several composite methods based on CCSD(T) (e.g., G3B3[8] and ccCA[9]) all predict that the triplet lies 5 to 6 kcal/mol below the 10 π singlet state and 2 to 4 kcal/mol below the 8 π singlet.[4] B3LYP calculations[10] also predict a triplet ground state for **1**[3,4] but a lower energy for the 10 π singlet state than for the 8 π singlet state.

On the basis of the calculations that have been performed to date, perhaps the only unequivocal conclusion one can reach is that the 9 π $^3B_{2u}$ state and the 8 π and 10 π $^1A_{1g}$ states are all very close in energy. Although most of the calculations indicate that the $^3B_{2u}$ state is lowest in energy, experiments, not calculations, will ultimately have to resolve the issue of whether the triplet really is the ground state of **1** and what the energies of the two singlet states of **1** are, relative to the triplet.

Over the years, Carl Lineberger and coworkers have used negative ion photoelectron spectroscopy (NIPES) to determine the relative energies of the lowest singlet and triplet states in a variety of organic molecules,[11] including diradicals such as trimethylenemethane,[12a,b] tetramethyleneethane,[12c] *m*-benzoquinodimethane,[12d] and D_{8h} cyclooctatetraene.[12e] Therefore, if the radical anion of **1** (**1·⁻**) can be successfully generated, then NIPES experiments should, at least in principle, resolve the question of the relative energies of the three lowest-lying states of **1**.

Unfortunately, interpretation of the NIPEs spectrum of **1·⁻** could be complicated by the possibility that, like the neutral molecule, the radical anion might have more than one low-lying electronic state. This possibility can be readily appreciated by noting that, as shown in Figure 2, the $^3B_{2u}$ state of **1** could be formed from two different electronic states of **1·⁻**, depending on whether the extra β-spin electron in the radical anion occupies the b_{1g} σ MO or the a_{2u} π MO. If, as suggested by the calculations on the electronic states of the neutral molecule,[2-4] these two MOs are very close in energy, then the radical anion could have two nearly degenerate electronic states, $^2B_{1g}$ and $^2A_{2u}$.

To investigate the low-lying electronic states of **1·⁻**, we have performed ab initio and DFT calculations. Because, as indicated in Figure 2, the $^2A_{2u}$ and $^2B_{1g}$ states of the radical anion differ
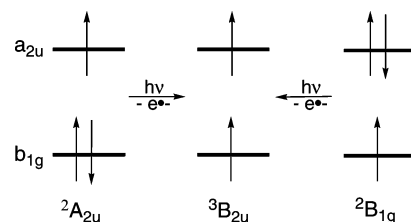
Figure 2. Diagram showing that the $^3B_{2u}$ state of neutral **1** can be formed from two different states, $^2A_{2u}$ and $^2B_{1g}$, of the radical anion **1·⁻** by photodetachment of an electron.

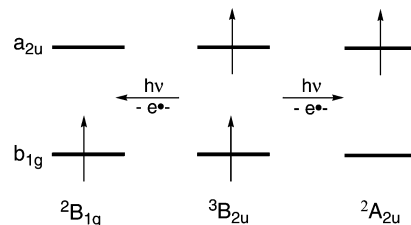**Figure 3.** Diagram showing that two different states, $^2B_{1g}$ and $^2A_{2u}$, of radical cation **1·⁺** can be formed by photodetachment of an electron from the $^3B_{2u}$ state of neutral **1**.

by whether the b_{1g} or a_{2u} MO contains a second electron, the relative energies of these two states provide information about the relative energies of the b_{1g} and a_{2u} MOs. As shown in Figure 3, similar information about the relative energies of these two MOs can be gleaned from the relative energies of the $^2B_{1g}$ and $^2A_{2u}$ states in the radical cation of **1** (**1·⁺**), which differ by whether the b_{1g} or a_{2u} MO is occupied. Therefore, we also carried out ab initio and DFT calculations on **1·⁺**.

In this article, we report the results of our calculations on both radical anion **1·⁻** and radical cation **1·⁺**. Our calculations find that the $^2B_{1g}$ and $^2A_{2u}$ states are, indeed, very close in energy in both **1·⁻** and **1·⁺**. This finding indicates that the energies of the b_{1g} and a_{2u} MOs are nearly the same, thus supporting the previous prediction that **1** is likely to have a triplet ground state.

Computational Methodology

As we did for neutral **1**,[4] for its radical ions, **1·⁻** and **1·⁺**, we performed three different types of calculations: DFT calculations using the B3LYP functional,[10] coupled-cluster calculations at CCSD(T) level,[7] and CASPT2[6] calculations based on CASSCF reference wave functions. The CASSCF active space contained 17 electrons in the anion and 15 electrons in the cation. In both ions, these electrons were distributed among 16 orbitals: four bonding σ, four bonding π, four antibonding σ, and four antibonding π MOs. The 6-311+G(2df) basis set[13] was used for all of these calculations.

Single-point CCSD(T) and CASPT2 calculations were performed at the unrestricted (U)B3LYP/6-311+G(2df) optimized geometry for each of the two low-lying electronic states of **1·⁻** and **1·⁺** as well as at the optimized geometry for ^{3}**1**. Vibrational analyses were carried out to ensure that all five of the optimized geometries were true energy minima. The geometry optimizations, the vibrational analyses, and the single-point CCSD(T) calculations were performed with the Gaussian 03 suite of programs.[14] MOLCAS[15] was used for the CASPT2 calculations.

Results and Discussion

Table 1 summarizes the results of our calculations on the two lowest electronic states of **1·⁻** and **1·⁺**. Table 1 also shows

TABLE 1: Results of B3LYP, CCSD(T), and CASPT2 Calculations on the $^3B_{2u}$ State of 1 and on the $^2A_{2u}$ and $^2B_{1g}$ States of $1 \cdot^-$ and $1 \cdot^+$ at B3LYP/6-311+G(2df) Optimized Geometries

	$1 - ^3B_{2u}$	$1 \cdot - ^2A_{2u}$	$1 \cdot - ^2B_{1g}$	$1 \cdot + ^2B_{1g}$	$1 \cdot + ^2A_{2u}$
$R(C-C)^a$	1.554	1.515	1.509	1.641	1.619
$R(C=O)^a$	1.184	1.221	1.215	1.155	1.151
$E[B3LYP]^b$	0^c	-78.6^d	-81.3^d	223.7^e	224.2^e
$E[CCSD(T)]^b$	0^f	-79.0^d	-78.0^d	212.1^e	215.9^e
$E[CASPT2]^b$	0^g	-71.9^d	-76.2^d	222.4^e	214.0^e

[a] Bond lengths in angstroms. [b] Relative energies in kilocalories/mole. [c] $E = -453.382073$ hartree. [d] EA of the $^3B_{2u}$ state of **1**. [e] IE of the $^3B_{2u}$ state of **1**. [f] $E = -452.525302$ hartree. [g] $E = -452.492347$ hartree.

how the geometries and energies of these states compare with the energy of the triplet state of neutral **1** (^{3}**1**).

What changes in bond lengths would one, in fact, expect upon oxidation or reduction of ^{3}**1**? Both the a_{2u} and b_{1g} MOs are C−C bonding and C−O antibonding.[16] Therefore, the addition of an electron to either singly occupied (SO)MO of the triplet should lead to a shorter C−C bond length and a longer C−O bond length. Depopulation of either SOMO of the triplet should have the opposite effect.

These are exactly the types of changes observed in the computed bond lengths in Table 1. Upon adding an electron to either the b_{1g} σ or the a_{2u} π^* MO of ^{3}**1**, to form the $^2A_{2u}$ and $^2B_{1g}$ states of $1 \cdot^-$, the C−C bond length decreases, and the C=O bond length increases. The opposite changes in these two bond lengths occur upon removing either the σ or π^* electron from one of the singly occupied (SO)MOs in ^{3}**1**.

A notable feature of the calculated bond lengths for $1 \cdot^-$ in Table 1 is that they are very similar, no matter to which SOMO, σ or π, of ^{3}**1** an electron is added. Likewise, the bond lengths calculated for $1 \cdot^+$ are very similar, no matter from which SOMO an electron is removed. Upon adding an electron to ^{3}**1**, the calculated C−C bond length decreases are 0.039 and 0.045 Å for forming, respectively, the $^2A_{2u}$ and $^2B_{1g}$ states of radical anion $1 \cdot^-$, and the corresponding C=O bond length increases are, respectively, 0.037 and 0.031 Å. Upon removing an electron from ^{3}**1**, the C−C bond length increases are 0.087 and 0.065 Å for forming, respectively, the $^2B_{1g}$ and $^2A_{2u}$ states of radical cation $1 \cdot^+$, and the corresponding C=O bond length decreases are, respectively, 0.029 and 0.033 Å.

The similar changes in bond lengths that occur upon adding an electron to either of the SOMOs of ^{3}**1** or upon removing an electron from either of the SOMOs of ^{3}**1** are indicative of not only similar nodal patterns but also very similar amounts of C−C bonding and C=O antibonding in both SOMOs.[16] The similar sizes of these bond length changes suggest that the SOMOs of $^3B_{2u}$ have very similar energies, and this is, indeed, found to be the case. The UB3LYP/6-311+G(2df) Kohn−Sham energies of the b_{1g} and a_{2u} SOMOs of $^3B_{2u}$ are, respectively, −0.28096 and −0.28336 hartree, so that their Kohn−Sham orbital energies differ by only 1.5 kcal/mol.

The near degeneracy of the two SOMOs of ^{3}**1** is also reflected in the nearly equal energies that are computed for the $^2A_{2u}$ and $^2B_{1g}$ electronic states of both $1 \cdot^-$ and $1 \cdot^+$. B3LYP and CASPT2

calculations predict that the addition of an extra electron to the π^* MO of the triplet is more exothermic than the addition of an extra electron to the σ MO, whereas CCSD(T) makes the opposite prediction. The differences between the absolute energies of the two states of the radical anion range from a low of 1.0 kcal/mol for CCSD(T) to a high of 4.3 kcal/mol for (17/16)CASPT2.

The CASPT2 value for this energy difference is probably too high because the weights of the (17/16)CASSCF reference wave functions in the (17/16)CASPT2 wave functions are 0.726 and 0.718, respectively, for the $^2A_{2u}$ and $^2B_{1g}$ electronic states of $1 \cdot^-$. As already noted, a lower weight of a CASSCF reference wave function means that less of the CASPT2 energy is recovered variationally and more is recovered via second-order perturbation theory. Because second-order perturbation theory tends to overestimate the amount of dynamic electron correlation energy that is recovered nonvariationally, CASPT2 should tend to overestimate the amount by which $^2B_{1g}$ is lower in energy than $^2A_{2u}$.

In forming the radical cation from ^{3}**1**, B3LYP and CCSD(T) both predict that it should be easier to remove the electron from the a_{2u} π SOMO of the triplet than from the b_{1g} σ SOMO, but CASPT2 makes the opposite prediction. CASPT2 almost certainly overestimates the amount by which $^2A_{2u}$ is lower in energy than $^2B_{1g}$ in $1 \cdot^+$ because the weight of the (15/16)CASSCF reference wave function in the (15/16)CASPT2 wave function is 0.746 for $^2B_{1g}$ but only 0.722 for $^2A_{2u}$. Indeed, the reason that CASPT2, unlike B3LYP and CCSD(T), predicts that it is easier to remove an electron from the σ SOMO than from the π SOMO of ^{3}**1** may very well be that CASPT2 overestimates the effect of dynamic correlation in the $^2A_{2u}$ state of the radical cation.

The results of our B3LYP calculations predict that 2.7 kcal/mol more energy is liberated by the addition of an electron to the π SOMO of ^{3}**1**, but 0.5 kcal/mol more energy is required to remove an electron from the σ SOMO. Therefore, in forming the radical anion and cation from the triplet, B3LYP finds that the average difference between selectively occupying the σ and π SOMOs is only $(2.7 - 0.5)/2 = 1.1$ kcal/mol, with occupancy of the a_{2u} π MO being calculated to give a lower energy than the occupancy of the b_{1g} σ MO. This computational result is consistent with the relative energies of the B3LYP Kohn−Sham orbitals, given above.

In contrast, the results of our CCSD(T) calculations predict that 1.0 kcal/mol more energy is liberated by the addition of an electron to, and 3.8 kcal/mol more energy is required for removing an electron from, the σ than the π SOMO of $^3\mathbf{1}$. In forming the radical anion and radical cation from the triplet, CCSD(T) finds that the average difference between selectively occupying the σ and π SOMOs is $(1.0 + 3.8)/2 = 2.4$ kcal/mol, with the b_{1g} σ MO being calculated to give a lower energy than the a_{2u} π MO.

The difference between B3LYP and CCSD(T) in the relative energies of the b_{1g} and a_{2u} MOs in $\mathbf{1}\cdot^-$ and $\mathbf{1}\cdot^+$ is consistent with the ordering of the 8 π and 10 π singlet states in $\mathbf{1}$ by these two methods. B3LYP finds the 10 π singlet, in which the a_{2u} π MO is doubly occupied and the b_{1g} σ MO is left empty, to be lower in energy by 2.0 kcal/mol than the 8 π singlet, in which the b_{1g} σ MO is doubly occupied and the a_{2u} π MO is left empty. In contrast, CCSD(T) places the 8 π singlet below the 10 π singlet by 3.5 kcal/mol.

It would be interesting to know from experiment whether B3LYP or CCSD(T) correctly orders the energies of the b_{1g} and a_{2u} orbitals by determining the relative energies of the $^2B_{1g}$ and $^2A_{2u}$ states of $\mathbf{1}\cdot^-$ and $\mathbf{1}\cdot^+$ and the relative energies of the 8 π and 10 π singlet states of $\mathbf{1}$. However, the fact that both B3LYP and CCSD(T) predict the b_{1g} and a_{2u} orbitals to have nearly the same energies means that $\mathbf{1}$ should really be regarded as a diradical. Because diradicals frequently (although not always) have triplet ground states,[18] the very similar energies of the $^2B_{1g}$ and $^2A_{2u}$ states of $\mathbf{1}\cdot^-$ and $\mathbf{1}\cdot^+$ are wholly consistent with the computational prediction that $\mathbf{1}$ has as its ground state a triplet, rather than either an 8π or 10π, closed-shell, singlet state.[3,4]

As noted in the Introduction, the best way to confirm this prediction and to ascertain whether the energy difference between the triplet and lowest singlet is more accurately predicted by B3LYP ($\Delta E_{ST} = 11.2$ kcal/mol) or by CCSD(T) ($\Delta E_{ST} = 2.4$ kcal/mol) would be to generate $\mathbf{1}\cdot^-$ and to obtain its NIPE spectrum. Although our calculations indicate that two electronic states of $\mathbf{1}\cdot^-$, $^2B_{1g}$ and $^2A_{2u}$, will be populated around room temperature,[19] this is unlikely to prove to be a serious problem. If thermal equilibrium between the two low-lying states of $\mathbf{1}\cdot^-$ is established, even the 1.0 kcal/mol difference, predicted by CCSD(T), between the energies of the $^2B_{1g}$ and $^2A_{2u}$ states should give a factor of five difference in the intensities of the sets of peaks in the NIPE spectrum that are due to photodetachment of electrons from each of the states of $\mathbf{1}\cdot^-$. Cooling the radical anions should further increase the differences in peak intensities that are due to the different populations of the $^2B_{1g}$ and $^2A_{2u}$ states.

Studies of the angular distribution of the photoelectrons that are associated with the more intense (and higher energy) triplet peak in the NIPE spectrum of $\mathbf{1}\cdot^-$ could lead to the identification of whether the $^2B_{1g}$ or $^2A_{2u}$ state of $\mathbf{1}\cdot^-$ gives rise to this peak.[20] Therefore, NIPES on $\mathbf{1}\cdot^-$ could, at least in principle, establish whether $^2B_{1g}$ or $^2A_{2u}$ is the lowest-energy doublet state of $\mathbf{1}\cdot^-$. With the energetic ordering of these two doublet states of $\mathbf{1}\cdot^-$ established, studies of the angular distributions of the photoelectrons that are associated with the singlet peaks in the NIPE spectrum of $\mathbf{1}\cdot^-$ could lead to the establishment of whether the 8 π or 10 π $^1A_{1g}$ state is the lowest-energy singlet state of $\mathbf{1}$.

Radical anions for NIPES of diradicals can frequently be generated in the gas phase by reaction of a suitable precursor with O•⁻, which abstracts a hydrogen atom and a proton.[11,12a–d] Therefore, as shown in Scheme 1, commercially available "squaric acid" (**2**) might prove to be a suitable precursor of $\mathbf{1}\cdot^-$.

SCHEME 1
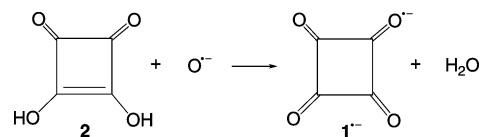
B3LYP/6-311+G(2df) calculations predict the reaction in Scheme 1 to be energetically favorable by 128 kcal/mol. Therefore, reaction of **2** with O•⁻ and NIPES on the $\mathbf{1}\cdot^-$ thus formed could, at least in principle, provide an experimental test of the extraordinary prediction that $\mathbf{1}$ should have a triplet ground state[3,4] and also lead to the energetic ordering of the $^2B_{1g}$ and $^2A_{2u}$ states of $\mathbf{1}\cdot^-$ and of the 8 π and 10 π $^1A_{1g}$ states of $\mathbf{1}$.

References and Notes

(1) See, inter alia: (a) West, R.; Niu, H.-Y.; Powell, D. L.; Evans, M. V. *J. Am. Chem. Soc.* **1960**, *82*, 6240. (b) Ito, M.; West, R. *J. Am. Chem. Soc.* **1963**, *85*, 2580. (c) *Oxocarbons*; West, R., Ed.; Academic Press: New York, 1980. (d) von Ragué Schleyer, P.; Najafian, K.; Kiran, B.; Jiao, H. *J. Org. Chem.* **2000**, *65*, 426. and the references cited therein.

(2) Gleiter, R.; Hyla-Kryspin, I.; Pfeifer, K.-H. *J. Org. Chem.* **1995**, *60*, 5878.

(3) Jiao, H.; Frapper, G.; Halet, J.-F.; Saillard, J.-Y. *J. Phys. Chem. A* **2001**, *105*, 5945.

(4) Zhou, X.; Hrovat, D. A.; Gleiter, R.; Borden, W. T. *Mol. Phys.* **2009**, *107*, 863.

(5) (a) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Hehre, W. J.; Radom, L.; von Ragué Schleyer Schleyer, P.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley Interscience: New York, 1986; pp 38–40.

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

(7) (a) Purvis, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910. (b) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. H. *Chem. Phys. Lett.* **1989**, *157*, 479.

(8) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764.

(9) DeYonker, N. J.; Cundari, T. R.; Wilson, A. K. *J. Chem. Phys.* **2006**, *124*, 114104.

(10) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(11) Review: Wenthold, P. G.; Lineberger, W. C. *Acc. Chem. Res.* **1999**, *32*, 597.

(12) (a) Wenthold, P. G.; Hu, J.; Squires, R. R.; Lineberger, W. C. *J. Am. Chem. Soc.* **1996**, *118*, 475. (b) Wenthold, P. G.; Hu, J.; Lineberger, W. C. *J. Am. Soc. Mass Spectrom.* **1998**, *10*, 800. (c) Clifford, E. P.; Wenthold, P. G.; Lineberger, W. C.; Ellison, G. B.; Wang, C. X.; Grabowski, J. J.; Vila, F.; Jordan, K. D. *J. Chem. Soc. Perkin Trans.* **1998**, *2*, 1015. (d) Wenthold, P. G.; Kim, J. B.; Lineberger, W. C. *J. Am. Chem. Soc.* **1997**, *119*, 1354. (e) Wenthold, P. G.; Hrovat, D. A.; Borden, W. T.; Lineberger, W. C. *Science* **1996**, *272*, 1456.

(13) Krishnan, R.; Binkely, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

(14) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.;

Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision D.02; Gaussian, Inc.: Wallingford, CT, 2004.

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

(16) There is a good reason for the similarities between the a_{2u} and b_{1g} MOs of **1**. They can each be viewed as the in-phase combination of one of the sets of the degenerate π^* MOs of four molecules of CO: the π^* MOs that lie in the molecular plane in the case of b_{1g} and the π^* MOs that are perpendicular to the molecular plane in the case of a_{2u}. Because these π^* MOs are vacant in CO, there is obviously a difference between the MOs that are occupied in all three of the low-lying states of **1** and in four molecules of CO, thus making concerted decomposition of the former to the latter a reaction that is forbidden by orbital symmetry.[17]

(17) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781.

(18) Review: Borden, W. T. In *Diradicals*; Borden, W. T., Ed.; Wiley-Interscience: New York, 1982; pp 1−72.

(19) The radical anion, **1**·⁻, differs from the radical anions of trimethylenemethane (TMM)[12a,b] and *m*-benzoquinodimethane (MBQDM),[12d] in that the two nearly degenerate states of **1**·⁻ are both predicted to be energy minima. In contrast, our UB3LYP/6-31+G* calculations find that the $^2B_1$ state of TMM·⁻ is a transition structure for pseudorotation between $^2A_2$ minima, which are computed to be 0.4 kcal/mol lower in energy. Similarly, our UB3LYP/6-31+G* calculations find that the $^2A_2$ state of MBQDM·⁻ has one imaginary frequency for a symmetry-breaking vibration that takes it to the $^2B_1$ energy minimum, which is computed to be 2.1 kcal/mol lower in energy.

(20) Although b_{1g} and a_{2u} are both C−C bonding and C−O antibonding, they differ in the fact that the former MO has the nodal pattern and symmetry of a $4d_{xy}$ AO, whereas the latter MO has the nodal pattern and symmetry of a $3p_z$ AO. The difference between these two MOs in angular momentum about the four-fold (z) axis of symmetry in **1** should result in different angular distributions of the photoelectrons that are ejected from the b_{1g} and a_{2u} MOs. See, for example, the discussion in section IIIB of: Schwartz, R. L.; Davico, G. E.; Ramond, T. M.; Lineberger, W. C. *J. Phys. Chem. A* **1999**, *103*, 8213.