

and the requirement for proper binding of substrates. It should also be realized that the active-site microenvironment, as a whole, determines the catalytic properties of a given enzyme rather than just one or two catalytic groups. Future calculations on the enzymatic reactions discussed above can hopefully reveal some of the rationales behind the particular choices of metal ions, but it seems likely that the general free energy relationships leading

to optimization for  $\text{Ca}^{2+}$  in SNase will be relevant also in other cases.

**Acknowledgment.** J.Å. gratefully acknowledges support from the Swedish Natural Science Research Council. Support from the office of Naval Research (Contact N00014-87-K0507) is also acknowledged.

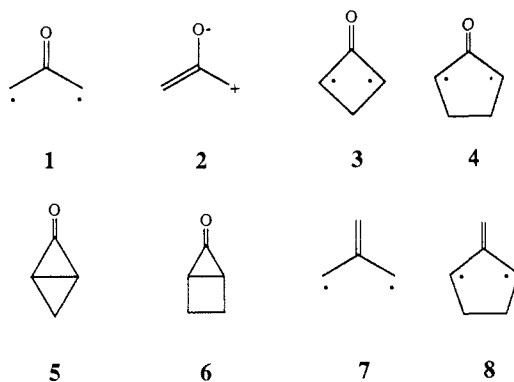
## Ab Initio Computational Study of Methano- and Ethano-Bridged Derivatives of Oxyallyl

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**Abstract:** Ab initio SCF-CI computations on methano-bridged oxyallyl (OA) (3) and ethano-bridged OA (4) indicate that the OA's are ground-state singlet species, with strong C=O bonds and pronounced diradicaloid character in the CI wave functions. The computational excited  $^3B_2$   $\pi$ - $\pi^*$  states of 3 and 4 are  $\sim 4$ -7 kcal/mol higher in energy than the  $^1A_1$  ground-state diradicaloids. The bicyclobutanone analogue of 3S (5) is predicted to be substantially lower in energy than any of the diradicaloid forms, but the bicyclopentanone analogue of 4S (6) is somewhat higher in energy than 4S. Experimental observation of the triplet manifold of these OA derivatives is likely to be rendered quite difficult by their small singlet-triplet gaps and the thermodynamic accessibility of the bicyclic analogues. Qualitative molecular orbital considerations suggest that electron-rich olefins might be trapped by a nonconcerted mechanism, in accord with recent experimental results.

Oxyallyl (OA, 1) and related molecules have been discussed as reactive intermediates or transition states in a number of reactions,<sup>3-8</sup> despite an apparent dearth of clear experimental evidence for their direct observation. In such a situation where experiment has been less than clear-cut, computational chemical methods can be useful to clarify the problem. Semiempirical and ab initio computational studies have been carried out on OA's, with the most sophisticated published study to date predicting a modest preference for a ground-state (GS)  $\pi$ , $\pi^*$   $^3B_2$  state<sup>8</sup> in the parent system 1, despite the possible stabilizing influence on the



$^1A_1$  state of closed-shell zwitterionic resonance structure 2. The computed triplet-singlet (T-S) gap was small enough to leave to question as to whether higher levels of theory might reverse the favoring of a high-spin GS for OA. In addition, consideration of various OA's leads one to query the effects of substitution on the OA state energy ordering, lest by apparently innocuous changes in the OA system one might substantially alter its nature.

Two such likely OA derivatives of interest for experimental study are methano-bridged OA (3) and ethano-bridged OA (4) and their ring-closed bicyclic forms 5 and 6. Similar derivatives have been employed in the study of trimethylenemethane<sup>9,10</sup> (TMM, 7), where general system 8 has been much studied. Since bridging of 7 to 8 is accompanied by strain incorporation, cyclization is less favorable than for the unbridged system, making it is easier to study the diradical. Use of methano and ethano bridging in the OA system could, in principle, lead to a similar favoring of ring-opened forms 3 and 4. The following computational study is aimed at elucidating the GS multiplicity of 3 and 4, the approximate stability of the ring-opened vs the bicyclic forms, and the general electronic nature of the bridged OA's. Given recent theoretical<sup>11,12</sup> and experimental<sup>13,14</sup> interest in un-

(9) For reviews of the chemistry of ethano-bridged TMM's cf. the following: Berson, J. A. *Acc. Chem. Res.* **1978**, *11*, 446. Berson, J. A. In *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1982.

(10) The results of efforts to observe methano-bridged TMM's are summarized in the following: Lahti, P. M.; Berson, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 7011. Lahti, P. M. Ph.D. Thesis, Yale University, New Haven, CT, 1985.

(11) Lahti, P. M.; Ichimura, A. S.; Berson, J. A. *J. Org. Chem.* **1989**, *54*, 958. Cf. also literature references to some earlier computational and theoretical work by various workers on the non-Kekulé molecules discussed in this paper.

(12) Du, P.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1986**, *108*, 8086.

(13) Stone, K. J.; Greenberg, M. M.; Goodman, J. L.; Peters, K. S.; Berson, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 8088.

(14) Zilm, K. W.; Merrill, R. A.; Greenberg, M. M.; Berson, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 1567.

(1) University of Massachusetts.

(2) Oberlin College.

(3) Turro, N. J. *Accs. Chem. Res.* **1969**, *2*, 25.

(4) Liberles, A.; Greenberg, A.; Lesk, A. *J. Am. Chem. Soc.* **1972**, *94*, 8685. Liberles, A.; Kang, S.; Greenberg, A. *J. Org. Chem.* **1973**, *38*, 1922.

(5) Chan, T.; Ong, B. S. *J. Org. Chem.* **1978**, *43*, 2994; *Tetrahedron* **1980**, *36*, 2269.

(6) Schaad, L. J.; Hess, B. A.; Zahradnik, R. *J. Org. Chem.* **1981**, *46*, 1909.

(7) Hoffmann, R. *J. Am. Chem. Soc.* **1968**, *90*, 1475.

(8) Osamura, Y.; Borden, W. T.; Morokuma, K. *J. Am. Chem. Soc.* **1984**, *106*, 5112.

usual bond-deficient species that may be various points of view be described as either non-Kekulé or nonclassical Kekulé molecules, a question of particular interest (also asked by the study of parent OA 1) is whether these OA derivatives are well described as non-Kekulé diradicals, or as zwitterions (e.g., 2).

### Computational Methods

All computations in this work were done on the University of Massachusetts Department of Chemistry Celerity 1260-D UNIX computer. Geometry optimization for all molecules were carried out with the program GAMESS.<sup>15</sup> For the diradicals, only  $\pi-\pi^*$  occupancies were studied for open-shell cases, since  $n-\pi^*$  states have typically been found to be substantially higher in energy for cases such as parent OA 1.<sup>8</sup> Unrestricted Hartree-Fock (UHF) wave functions were used for triplet (T) state optimizations, since it has been noted that they generally give a better account of correlation effects in geometry predictions than do restricted open-shell (ROHF) wave functions.<sup>16</sup> For singlet (S) bicyclic molecules 5 and 6, restricted (RHF) wave functions were used for optimization, while for singlet diradicals 3S and 4S two-configuration SCF (TCSCF) wave functions were used. Computer space considerations prevented our use of the pedagogically preferable multiconfiguration SCF optimization with a reasonable basis set. We also deemed the assumptions necessary in a point by point CI partial optimization to be undesirable. As we shall note below (vide infra), the changes in geometries of the OA's likely to be induced by going from a SCF to a post-Hartree-Fock optimization are unlikely to alter the conclusions we draw in this paper. Therefore, for the diradical  $C_{2v}$  symmetry was imposed on the SCF optimizations, with  $C_s$  symmetry used for the bicyclic molecules. Standard Gaussian split-valence basis sets were used, with modified polarization functions where used. Instead of the usual polarization d-orbital exponent  $\alpha = 0.80$  for all atoms in the first row of the periodic table, for all computations we used  $\alpha_{\text{carbon}} = 0.75$  and  $\alpha_{\text{oxygen}} = 0.85$ .<sup>17</sup> In all cases the root mean square gradients were reduced to 1 mhartree/bohr or less.

The  $C_{2v}$  geometries for 3T and 4T, as well as the  $C_s$  geometries for 5 and 6, were investigated to ensure that these points were true SCF minima. Analytical second-derivative analysis on these geometries was performed with GAUSSIAN86<sup>18</sup> with the appropriate wave function; in each case, the geometry proved to be a potential minimum with no imaginary vibrations. Analytical frequencies were not available for TCSCF wave functions on our facilities, so we did not do this test for 3S and 4S. However, small distortions of these geometries toward ring closure led to increases in energy at the TCSCF level, so we feel that use of these geometries for the  $^1A_1$  states is not unreasonable. It should be noted that these results do not necessarily preclude different findings for post-Hartree-Fock (e.g., SCF-CI) wave functions. However, all the SCF wave functions used are appropriate for minimal qualitative descriptions of the states involved, so we feel that the tests performed above allow reasonable use of the SCF geometries for post-Hartree-Fock energy computations.

Once appropriate geometries were found at the various levels of theory, single-point configuration interaction (CI) computations were carried out with the MELD series of programs,<sup>19</sup> with basis sets as described above. Excitations up to quadruples (SDTQ-CI) were generated from the ROHF  $^3B_2$  reference for triplets and from a closed-shell  $^1A_1$  reference state that used the TCSCF  $^1A_1$  MO's for singlets. Instead of the can-

Table I. Comparison of Selected Geometric Parameters as a Function of Basis Set for Bridged Oxyallyl Systems 3 and 4

molecule	parameter	3-21G <sup>a</sup>	3-21G(*) <sup>a,b</sup>	6-31G <sup>a</sup>	6-31G** <sup>a</sup>
3 UHF	C <sub>1</sub> -O	128.2	123.4	128.3	123.8
	C <sub>1</sub> -C <sub>2</sub>	144.7	144.8	143.9	144.0
	C <sub>2</sub> -C <sub>3</sub>	154.7	152.6	153.3	151.9
	C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	92.8	92.0	93.0	92.2
	C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub>	85.3	86.0	85.8	86.1
3 TCSCF	C <sub>4</sub> -C <sub>1</sub> -C <sub>2</sub>	90.9	91.0	90.6	90.9
	C <sub>1</sub> -O	120.6	119.5	121.8	118.7
	C <sub>1</sub> -C <sub>2</sub>	148.6	143.7	146.6	146.0
	C <sub>2</sub> -C <sub>3</sub>	154.6	151.4	153.4	152.2
	C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	87.9	85.5	88.4	87.8
4 UHF	C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub>	83.7	80.2	83.5	88.4
	C <sub>4</sub> -C <sub>1</sub> -C <sub>2</sub>	94.2	97.2	94.0	94.4
	C <sub>1</sub> -O	130.9	126.2	130.6	126.2
	C <sub>1</sub> -C <sub>2</sub>	141.8	142.3	141.9	142.1
	C <sub>2</sub> -C <sub>3</sub>	151.4	150.1	150.8	150.0
4 TCSCF	C <sub>3</sub> -C <sub>4</sub>	157.5	156.0	156.5	155.7
	C <sub>5</sub> -C <sub>1</sub> -C <sub>2</sub>	110.4	109.5	110.5	109.7
	C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	110.4	110.5	110.0	110.3
	C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub>	104.4	104.8	104.7	104.8
	C <sub>1</sub> -O	122.1	119.1	123.5	120.0
4 TCSCF	C <sub>1</sub> -C <sub>2</sub>	146.1	145.9	144.9	144.8
	C <sub>2</sub> -C <sub>3</sub>	149.7	148.6	149.4	148.6
	C <sub>3</sub> -C <sub>4</sub>	156.1	154.6	155.0	154.2
	C <sub>5</sub> -C <sub>1</sub> -C <sub>2</sub>	103.9	103.5	104.5	103.8
	C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	94.2	97.2	94.0	94.4
4 TCSCF	C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub>	83.7	80.2	93.5	88.4

<sup>a</sup> Bond lengths in picometers and bond angles in degrees. Optimization performed as described in the paper. <sup>b</sup> 3-21G basis set augmented by polarization functions on carbon and oxygen: cf. Harihan, P. C.; Pople, J. A. *Theor. Chim. Acta* 1973, 38, 213, and ref 17.

Table II. 6-31G\* SDTQ-CI ab Initio Energies of Oxyallyl Species 3 and 4

structure <sup>a</sup>	energy <sup>b</sup>	spin-adapted configs (mult) <sup>c</sup>	S-T gap <sup>d</sup>
3 UHF	-228.584 65	10 830 (T) <sup>d</sup>	3.7
	-228.584 21	5896 (S)	
	-228.581 85	10 830 (T)	0.0
	-228.590 61	5896 (S) <sup>d</sup>	
4 UHF	-267.660 86	33 136 (T) <sup>d</sup>	5.8
	-267.664 15	13 165 (S)	
	-267.659 24	33 136 (T)	0.0
	-267.670 18	13 165 (S) <sup>d</sup>	

<sup>a</sup> See Figure 1 for structural parameters. <sup>b</sup> Energy in hartrees (1 hartree = 27.21 eV = 627 kcal/mol) from 6-31G\* SDTQ-CI computation. <sup>c</sup> Spin-adapted configurations generated by MELD and used in SDTQ-CI computation for the indicated multiplicity at the induced fixed geometry. <sup>d</sup> Lowest energy computed for the indicated multiplicity. <sup>e</sup> Energy (kcal/mol) relative to lowest energy of lowest state.

(15) Original program by: Dupuis, M.; Spangler, D.; Wendoloski, J. J. *National Resource for Computational Chemistry Software Catalog*; 1980; Vol. 1, Program QG01. The Celerity UNIX version of this program was made available to us by Dr. Michael Schmidt of North Dakota State University (Fargo) and was described in: Schmidt, M. W.; Boatz, J. A.; Baldrige, K. K.; Koseki, S.; Gordon, M. S.; Elbert, S. T.; Lam, B. *QCPE Bull.* 1987, 7, 115.

(16) Cf.: Borden, W. T.; Davidson, E. R.; Feller, D. *Tetrahedron* 1982, 38, 737.

(17) The modified set of polarization functions was used, as suggested by: Dunning, T. H., Jr.; Hay, P. J. In *Methods in Electronic Structure Theory*; Schaeffer, H. F., III., Ed.; Plenum Press: New York, 1977; pp 1-27.

(18) (a) This program was implemented by us on a Celerity 1260-D UNIX computer with a version provided by Dr. Michael Schmidt of North Dakota State University (Fargo), with modification according to the scheme requested by the copyright owners of GAUSSIAN86 (Gaussian, Inc.). The GAUSSIAN set of programs were developed at Carnegie-Mellon University by J. S. Binkley, D. J. DeFrees, K. Raghavachari, R. A. Whiteside, H. B. Schegel, E. M. Fluder, and J. A. Pople. (b) We thank Dr. Angelo Rossi of IBM Corp. and Dr. Mark Murcko of Merck, Sharpe, and Dohme for performing some frequency analyses on the cyclic OA's when our computer was in repair.

(19) This series of programs was developed by the group of Prof. E. R. Davidson at Indiana University and was modified by our group for use on the Celerity 1260-D UNIX computer. We thank Dr. David Feller for making a version of this program available to us.

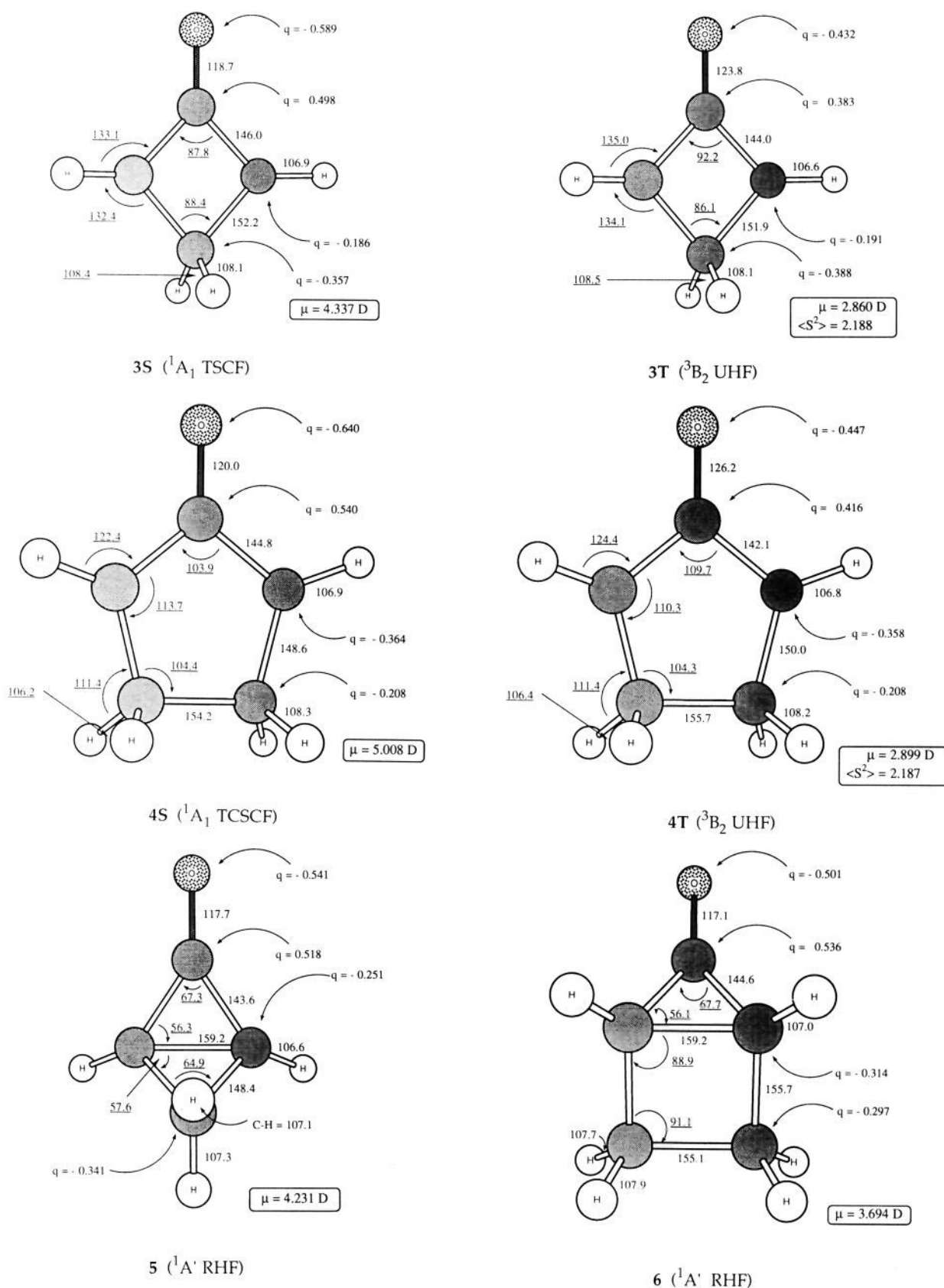
onical virtual orbitals, appropriately transformed K orbitals<sup>20</sup> were used in the CI to recover correlation energy more efficiently. The active orbital space used for configuration generation for the diradicals in most cases consisted only of  $\pi$ -symmetry MO's. As we shall see, this will lead to an important quantitative limitation to our results, although the qualitative findings should not change. For the bicyclic cases, a variety of mixtures of A' and A'' orbitals was used for SDTQ-CI. The orbital space used for CI computations is described in the tables of results where appropriate.

### Results

Figure 1 shows geometric parameters for the  $^3B_2$  and  $^1A_1$  states of 3 and 4, as well as ring-closed bicyclic forms 5 and 6, where a modified 6-31G\* basis set<sup>21</sup> was used for optimization as described earlier. Complete Cartesian coordinate descriptions of these geometries are available in the supplementary material. Table I shows a comparison of a selection of geometric parameters for these species as a function of basis set, to allow some evaluation

(20) Feller, D.; Davidson, E. R. *J. Chem. Phys.* 1981, 74, 3977.

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



**Figure 1.** 6-31G\* ab initio predicted geometries and properties for bridged oxyallyls and kekule isomers. Bond lengths are in picometers and bond angles in degrees (underlined). <sup>3</sup>B<sub>2</sub> geometries obtained with UHF wave functions, <sup>1</sup>A<sub>1</sub> diradical geometries with TCSCF wave functions, and bicyclic geometries with RHF wave functions. Full geometric details are listed in supplementary material. Mulliken total atomic charges are shown as *q* (the charge), where hydrogen atom charges have not been condensed into the heavy atoms. Dipole moment (D) and (for triplets) spin contamination are listed in legend boxes at the bottom of the structures. Mulliken charges, dipole moments, and spin contamination are for UHF-SCF (triplet), TCSCF (diradicaloid singlets), and RHF-SCF (bicyclic) wave functions.

Table III. Selected 6-31G\* SDTQ-CI Energies for Bicyclic Compounds **5** and **6**

structure <sup>a</sup>	energy <sup>b</sup>	spin-adapted configs (MO's) <sup>c</sup>
<b>5</b>	-228.633 59	28 804 ([11a' - 13a'] ⇒ 7xa') (5a'' ⇒ 4xa'')
	-228.638 59	40 405 ([11a' - 13a'] ⇒ 7xa') (5a'' ⇒ 5xa'')
	-228.645 46	21 235 ([11a' - 13a'] ⇒ 5xa') (14a'' - 5a'') ⇒ 3xa''
<b>6</b>	-267.664 70	21 235 ([12a' - 14a'] ⇒ 5xa') (7a'' - 8a'' ⇒ 3xa'')
	-267.665 37	40 405 ([12a' - 14a'] ⇒ 7xa') (8a'') ⇒ 5xa''

<sup>a</sup>See Figure 1 for geometries. <sup>b</sup>Energy in hartrees (1 hartree = 27.21 eV = 627 kcal/mol). <sup>c</sup>Number of spin-adapted configurations generated by MELD with the CI active space noted. [X a' - Y a''] ⇒ Zxa'' means the electrons in orbitals of a' symmetry numbered X - Y are excited up the quadruples level into the lowest lying Z a'' virtual orbitals (as well as other virtuals in the overall active space).

of the differences caused by use of different basis sets in optimization.

Table II shows our modified basis set 6-31G\* SDTQ-CI single-point energies in hartrees for the OA diradicals. For <sup>3</sup>B<sub>2</sub> diradicals **3T** and **4T**, reference configurations (1b<sub>1</sub>)<sup>2</sup>(2b<sub>1</sub>)<sup>2</sup>(3b<sub>1</sub>)<sup>1</sup>(1a<sub>2</sub>)<sup>1</sup> and (1b<sub>1</sub>)<sup>2</sup>(2b<sub>1</sub>)<sup>2</sup>(1a<sub>2</sub>)<sup>2</sup>(3b<sub>1</sub>)<sup>1</sup>(2a<sub>2</sub>)<sup>1</sup> were used; for <sup>1</sup>A<sub>1</sub> diradicals **3S** and **4S**, reference configurations (1b<sub>1</sub>)<sup>2</sup>(2b<sub>1</sub>)<sup>2</sup>(1a<sub>2</sub>)<sup>2</sup> and (1b<sub>1</sub>)<sup>2</sup>(2b<sub>1</sub>)<sup>2</sup>(3b<sub>1</sub>)<sup>2</sup>(1a<sub>2</sub>)<sup>2</sup> were used. For **3T** and **3S**, excitations up to quadruples were carried out into the first four b<sub>1</sub> and four a<sub>2</sub> virtual π-orbitals, for 10 380 and 5896 spin-adapted configurations (SAC's), respectively. For **4T** and **4S**, the excitation scheme was used into the first nine b<sub>1</sub> and six a<sub>2</sub> π-virtuals, giving 33 136 and 13 165 SAC's, respectively. Other SDTQ-CI active spaces were attempted, but this was the largest permitted by the disk space resources available to us. The potential effects of neglecting σ-σ\* excitations will be discussed later in the paper.

Table III shows the SDTQ-CI energies in hartrees of bicyclic ketones **5** and **6**, with different CI active spaces in each case. The best choice of orbital subspace allowed by our space constraints employed the top three a' MO's, plus either one or two a'' MO's with a selection of virtual orbitals (see table). We feel that the choices of Table III that use 21 235 or 40 405 spin-adapted configurations are reasonable estimates of the energies of the bicyclic species relative to their diradical counterparts, since these two computations are energetically comparable for both **5** and **6**. Given the number of generated configurations in these cases, we felt it unlikely that large relative energy decreases would be realized for the ring-closed forms by increases in the CI active space.

## Discussion

The need for polarization functions in describing OA's is evident by the difference in geometric parameters between optimizations with and without polarization. Much of the stabilization of the <sup>1</sup>A<sub>1</sub> state of the OA's comes from a strong C-O bond, which requires polarization to be well described. An earlier study of parent OA by Borden and Morokuma<sup>8</sup> clearly showed selective stabilization by use of polarization functions of the <sup>1</sup>A<sub>1</sub> state with its short C-O bond. In our ensuing discussions we shall only discuss results where optimization and energy SCF-CI computations were both carried out with the 6-31G\* split-valence-polarized basis set.

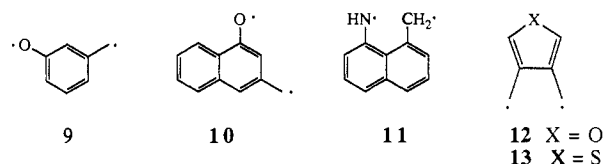
Comparison of the 6-31G\* geometries for the <sup>3</sup>B<sub>2</sub> and <sup>1</sup>A<sub>1</sub> states of both ethano- and methano-bridged OA shows the greater delocalization of the <sup>3</sup>B<sub>2</sub> state, as expected by analogy to 3-21G<sup>8</sup> and more recent<sup>22</sup> double-ζ with polarization (DZP) MCSCF computations by Borden and Morokuma. The <sup>3</sup>B<sub>2</sub> C-O bond lengths for **3T** and **4T** (123.8 and 126.2 pm, respectively) are quite comparable to a recently computed length of 124.3 pm found by Borden and Morokuma for <sup>3</sup>B<sub>2</sub> OA **1** at a DZP-CI level of the-

ory.<sup>22</sup> The C-C π bonds for the <sup>3</sup>B<sub>2</sub> state are in relatively good correspondence with the 145.3 pm found by the latter workers.<sup>22</sup>

The <sup>1</sup>A<sub>1</sub> diradicals have very short C-O bond lengths, 118.7 and 120.0 pm for **3S** and **4S**, respectively. These compare fairly well to the 122.7 pm found by Borden and Morokuma for **1** at the DZP-CI level.<sup>22</sup> Our C-C bond lengths also compare well to the 146.3 pm found for OA by these workers. The short C-O and reasonably long C-C π bonds found by ourselves and the other workers seem to argue against representing OA's with a major component of zwitterionic resonance structure **2**, if one is implying a long C-O<sup>-</sup> bond by structure **2**. The similarity of the C-O bond lengths for both triplet and singlet OA's, as well as the bicyclic ketones **5** and **6**, implies structural similarity of *all* these carbonyl moieties. This view is reinforced by a great similarity in the SCF charge distributions of the "carbonyl" moieties for both singlet OA's **3S** and **4S** as well as ketones **5** and **6** (see Figure 1). All of these C-O bonds are short and highly polar, with total SCF dipole moments for **3S**, **4S**, **5**, and **6** of 4.337, 5.077, 4.231, and 3.694 D, respectively. It seems reasonable to formulate *all* these carbonyl groups as C<sup>+</sup>-O<sup>-</sup> bonds naturally shortened by strong coulombic attractive forces, rather than insisting that a zwitterionic structure (e.g., **2**) must have a long C-O<sup>-</sup> bond. In this way we may consider the OA singlet structures as being diradicaloid with carbonyl bonds similar in nature to the carbonyls in the corresponding bicyclic ketones. The remaining OA free-valence π-electron density, furthermore, is fairly localized on the peripheral carbons in both triplet and singlet OA's (structure **1**). Similarly, a diradicaloid view of OA **1** has been advanced in a previous study.<sup>8</sup> However, these ketone-like OA's still have substantial zwitterionic charge separation, consistent with experimental results described later in this paper.

Comparison of the four- and five-ring cases shows an appreciably shorter C-O bond length for the smaller ring in both <sup>3</sup>B<sub>2</sub> and <sup>1</sup>A<sub>1</sub> states. If one accepts that the geometric results of Borden and Morokuma<sup>22</sup> may be directly compared to ours, in the <sup>1</sup>A<sub>1</sub> manifold particularly it seems that r<sub>C-O</sub> decreases as the allyl C-C-C angle decreases. This is logical in terms of hybridization arguments, whereby a decrease in the C-C-C angle will lead to increased s character in the C-O bond with commensurate C-O shortening.

Energetically, the most notable qualitative result of our results is that both species **3** and **4** possess singlet ground states (GS's) by modest energetic margins. If one were to accept that OA's are diradicals, Hund's rule predicts a triplet ground state. More sophisticated parity-based qualitative models<sup>23,24</sup> also predict a triplet GS for OA. Recent experimental experience for substituted diradicals seems to indicate that the simple splitting of an orbital near degeneracy by substitution effects need not make a high-spin GS unachievable. Triplet ground states have been found for *m*-benzoquinomethane (**9**),<sup>25</sup> *m*-naphthoquinomethane<sup>25,26</sup> (**10**), and **11**,<sup>27</sup> all of which possess substantial SOMO splitting even



at the simple Hückel level of theory. At times, recent results might seem to tempt one to suspect that any heteroatom-for-methylene substitution in a diradical will leave the GS spin multiplicity qualitatively unchanged, as has been proposed by at least one theoretical model of polyradicals.<sup>24</sup>

A weakness of this simple assumption may be shown by the following analysis. The larger the energetic splitting between the

(23) Longuet-Higgins, H. C. *Theor. Org. Chem., Pap. Kekule Sympos.* **1958**, 9-19.

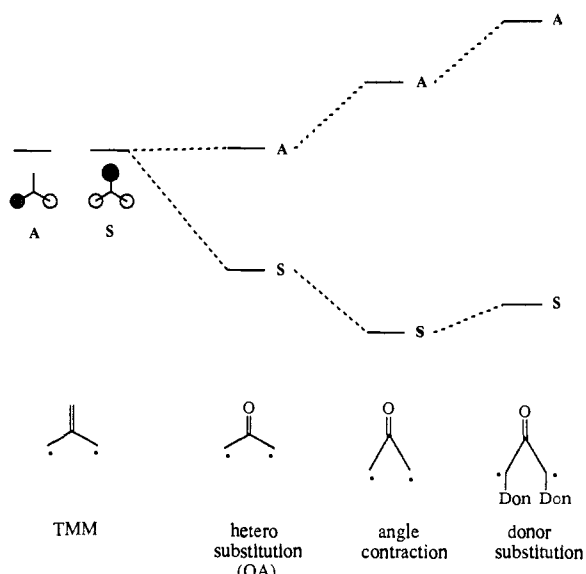
(24) Ovchinnikov, A. A. *Theor. Chim. Acta* **1978**, *47*, 297.

(25) Rule, M.; Matlin, A. R.; Seeger, D. E.; Hilinski, E. F.; Dougherty, D. A.; Berson, J. A. *Tetrahedron* **1982**, *38*, 787.

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(27) Platz, M. S.; Burns, J. R. *J. Am. Chem. Soc.* **1979**, *101*, 4425.

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**Figure 2.** Perturbation effects upon frontier molecular orbitals in bridged oxyallyls relative to trimethylenemethane. All effects shown are qualitative and not to scale. The smaller effects of through-bond coupling by ethano vs methano bridging of oxyallyl are not included. Cf. ref 28 for a discussion of this effect.

SOMO's of a diradical system, the larger the energy incurred to keep the electrons spin-parallel in different orbitals and the more favorable the singlet becomes relative to the triplet. At some point, a critical value must, in principle, be surpassed where a large HOMO-LUMO gap requires a singlet GS. The questions are as follows: What is a large HOMO-LUMO gap and how may one relate this variable to experiment? In the area where the critical value is surpassed, a small difference in the HOMO-LUMO gap changes a molecule qualitatively from triplet to singlet GS. Experimentally, at present we, in almost all cases, can find with some confidence only the qualitative GS multiplicity, not the quantitative T-S or S-T energy gap. A decreased T-S gap in a heterosubstituted diradical such as *m*-benzoquinonemethane is expected by qualitative theory, but cannot experimentally be probed at present. It is thus likely that a number of such species that would qualitatively be expected to have reduced T-S gaps have still been observed to have high-spin GS's. Sooner or later heterosubstituted species with low-spin GS's were bound to be elucidated, on the basis of the above argument. 3,4-Dimethylenefuran (**12**) and 3,4-dimethylenethiophene (**13**) are species that computationally<sup>11,12</sup> we feel are best defined as diradicals, which experimentally<sup>13,14</sup> have been found to have singlet ground states. We propose that, like these species, the bridged OA's **3** and **4** also have crossed the subtle energetic borderland that separates a heterosubstituted diradical with a Hund's rule high-spin GS from a system with sufficient HOMO-LUMO splitting to have a singlet GS.

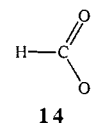
Qualitative MO considerations show why the bridged OA's are particularly suited to possess HOMO-LUMO splitting sufficient to favor a singlet GS. Figure 2 shows the effect of conceptually activating various orbital effects in OA relative to its hydrocarbon analogue, TMM. Oxygen for methylene substitution will qualitatively depress the energy of the symmetric  $b_1$  orbital, leaving the  $a_2$  orbital unaffected to a crude approximation. Decrease of the allyl C-C-C angle due to the constraints of ring formation will reinforce this trend by through-space interactions that will raise the  $a_2$  orbital energy and decrease the  $b_1$  orbital energy. Finally, there will be a through-bond effect of the bridging group in the OA's, which is in opposite directions for the methano vs ethano bridge. This effect has been predicted by Schoeller to be of potential importance in the bridged TMM cases—the reader is referred to the literature<sup>28</sup> for a more complete description of the direction and nature of qualitative through-bond interactions

in the TMM system. Overall, the through-bond effect should be too small to overwhelm the combined effects of substitution and angle contraction in the bridged OA's and so will be of secondary importance.

The previous analysis may be confirmed in a crude qualitative manner. We carried out RHF singlet computations upon the singlet GVB geometries of **3S** and **4S** as a measure of HOMO-LUMO splitting in the four- vs five-membered ring systems. We found at the 6-31G\* level that the  $\pi$  HOMO-LUMO gap for **3S** was  $-(-0.302 - -0.015) = 0.287$  hartree or 7.8 eV. For **4S** the analogous gap is  $-(-0.251 - -0.120) = 0.131$  hartree or 3.6 eV. Since the actual CI computations are based upon TCSCF MO's, it would be wrong to overinterpret these RHF numbers, but in terms of the crude HOMO-LUMO gap analysis the trend of increased gap with decreased C-C-C angle is obvious.

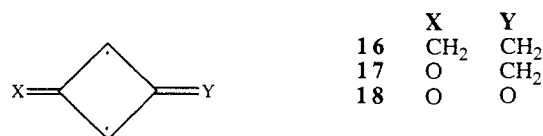
Borden and Morokuma's results to date<sup>22</sup> indicate that parent OA **1** retains a small preference ( $\sim 1$  kcal/mol) for a  $^3B_2$  GS, in agreement with the qualitative connectivity models.<sup>23,24</sup> Given the influence of angle contraction in the bridged OA systems, our computed S-T gaps of  $\sim 4$ – $6$  kcal/mol seem quite in line with the qualitative MO arguments above. Thus, it seems less surprising that, despite substantial efforts, there is to our knowledge no direct experimental evidence for observation of a triplet OA species. On the basis of our SCF +  $\pi$  SDTQ-CI results, OA simply appears to be a system where HOMO-LUMO splitting reduces the T-S gap until small effects such as bridging and the C-C-C angle may reverse the "expected" triplet GS preference. This effect is reinforced in the bridged OA's by the previously mentioned (vide supra) hybridization effects that shorten and strengthen the C-O bond, favoring the  $^1A_1$  state more than in unbridged **1**.

One may conceptually divide the orbitals of OA into  $\pi$  and  $\sigma$  space, but  $\sigma$ - $\sigma^*$  excitations were not used in our CI computations due to the space requirements of such computations at the SDTQ-CI level. For these systems the cumulative effect of such excitations would be large. In computational studies of hydrocarbon  $\pi$  diradicals,  $\sigma$ - $\pi$  orbital energy separability could be assumed without major errors in relative state energies.<sup>29</sup> However, a study of formyloxy (**14**) by Borden, Davidson, and



Feller<sup>30</sup> clearly showed that  $\sigma$  excitations can be important for even a qualitative description of state ordering in an open-shell system where a heteroatom may bear unpaired spin. Such considerations could confound our study with only  $\pi$  excitations, due to the energetically high lying lone-pair orbital of the OA system (Figure 2).

Results for other systems suggest that, while one may question the quantitative S-T gaps in our study, still the qualitative GS spin multiplicity—the only property presently verifiable by experiment—will be as we predict. SDTQ-CI 6-31G\* computations by us on **1** with selected  $\pi$ - and  $\sigma$ -orbital subspaces clearly show a selective stabilization of the  $^1A_1$  state relative to the  $^3B_2$  state for the  $\sigma + \pi$  schemes. Recent higher level computations on **1** and analogues confirm this trend.<sup>22,31</sup> Calculations by Borden and co-workers<sup>31</sup> on the set of molecules **16**–**18** examines the GS



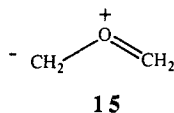
(29) Cf. discussion in Kato, S.; Morokuma, K.; Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1983**, *105*, 1791.

(30) Feller, D.; Huyser, E. S.; Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1983**, *105*, 1459.

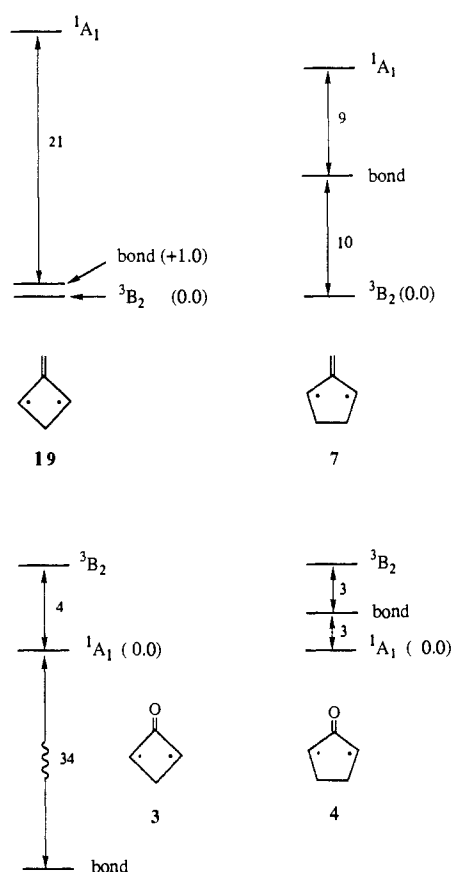
(31) Du, P.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1989**, *111*, 2773.

spin multiplicities of these diradical species. In this work, hydrocarbon diradical **16** was found to have a triplet GS in agreement with experimental work.<sup>32</sup> A similar computational result is found for **17**, also in apparent accord with experiment.<sup>33</sup> However, the carbonyl group in **17** appears to play little part in the  $\pi$  system of the diradical, which computationally appears<sup>31</sup> to be a perturbed trimethylenemethane. Most germane to our work, compound **18** with two carbonyl groups is found to be a singlet GS by 13–21 kcal/mol at various SCF-CI levels. The CI analysis of **18** clearly shows that, even at low levels of treatment, the molecule does not show much diradical character in the ratio-squared value for the largest two coefficients in the  $^1A_1$  CI wave function. The effect of the  $\sigma$  single excitations (S- $\sigma$ -CI) is selectively to lower the more ionic  $^1A_1$  states in **16–18**,<sup>31</sup> most strongly so where bond polarization is most likely (in **18**). The increase in the S-T gap from 12.9 to 20.7 kcal/mol going from multireference  $\pi$ -space double excitations (MR-SD- $\pi$ -CI) to MR- $\sigma$ -S-CI plus MR- $\pi$ -SD-CI demonstrates this effect.<sup>31</sup> Likewise, for the acyclic OA systems studied in the accompanying paper,<sup>22</sup> the effect of including  $\sigma$ -S-CI is selectively to lower in energy the more ionic  $^1A_1$  state. These results for **18** and in the accompanying work for the OA's have an important bearing on our  $\pi$ -SDTQ-CI results for **3–6**. Since our  $\pi$ -only CI results already predict a  $^1A_1$  GS for both **3** and **4**, we felt that the necessarily incomplete inclusion of  $\sigma$  excitations with their commensurate demands in CPU time and disk space were not required to answer what one might expect for the GS spin multiplicity of the bridged OA's.

One may argue that the bridged OA's at least should not be classified as diradical, non-Kekulé species but as some sort of zwitterionic, Kekulé species such as the resonance structure **2** shown earlier. Aside from the evidence of our optimized geometries, we note that the CI wave functions describing the  $^1A_1$  ring-opened structures **3S** and **4S** indicate intermediate diradical character. Borden has used the square of the ratio of the two largest coefficients  $C_1$  and  $C_2$  in the CI wave function of a singlet species as a relative measure of diradical nature.<sup>12</sup> Where  $C_1$  and  $C_2$  are comparable ( $[C_1/C_2]^2 \sim 1.00$ ), a two-configuration wave function is required for a good electronic description of the molecule, which is a hallmark of a diradical. For a Kekulé species that is well described by a single electronic configuration,  $C_1 \gg C_2$  and  $[C_1/C_2]^2 \gg 1.00$ . For the  $^1A_1$  bridged OA's **3S** and **4S**,  $[C_1/C_2]^2$  values are 4.16 and 4.05, respectively. This is greater than the 1.00–2.50 range that one might expect for a nearly "pure" diradical but still indicates substantial diradical character. Borden found that  $[C_1/C_2]^2 = 1.73$  for the putative diradical **12** but a value of 5.06 for carbonyl ylide **15**.<sup>12</sup> By this comparison our OA's are more diradicaloid than carbonyl ylide but less so than 3,4-dimethylenefuran and related compounds.



Alternatively, one can consider the occupation numbers of the CI natural orbitals (NO's), which can reflect the diradical nature of the two SOMO's<sup>34</sup> without the extreme sensitivity to small changes in  $C_1$  and  $C_2$  that affect the ratio  $[C_1/C_2]^2$ . We find the  $^1A_1$  ring-opened OA's **3S** and **4S** to have 6-31\* SDTQ-CI  $3b_1/1a_2$  NO occupancies of 1.608/0.390 and 1.549/0.401. These results agree with the ratio-squared results in showing an intermediate range of diradical behavior for the bridged OA's. A pure diradical would have SOMO<sub>1</sub>/SOMO<sub>2</sub> NO occupation numbers of 1.00/1.00, while a Kekulé molecule would have a SOMO<sub>1</sub> occupancy of  $\sim 2.00$  and a SOMO<sub>2</sub> occupancy of  $\sim 0.00$ . We find that parent OA at a similar level of theory has NO occupancy numbers in the  $^1A_1$  state of 1.37/0.64, showing substantially more



**Figure 3.** Comparison of relative energies for methano- vs ethano-bridged trimethylenemethane, oxyallyl, and kekule isomers. The reference zero of energy in each comparative scheme is chosen arbitrarily to allow relative comparisons between different species—no comparison of absolute energies between different species is implied in the scheme. Energies are relative to the zero energy in each species, (kcal/mol) Bond = Kekulé isomer. Energies for the trimethylenemethanes are from refs 36–37.

diradical nature than the bridged species. By our results, OA's might best be described as diradicaloid, but less so than a classical diradical such as TMM.

In experiments generating diradicals, it has often been of importance to evaluate the role of potential ring-closed products that could deplete the ring-opened form population. For instance, the role of bicyclopentane **8** in the chemistry of the ethano-bridged TMM system **7** is experimentally quite important.<sup>9</sup> Our results suggest that the ring-closed systems **5** and **6** are thermodynamically quite competitive with the ring-opened states. For the five-membered ring case, bicyclopentanone **6** lies between (+3.0 kcal/mol) the GS diradicaloid  $^1A_1$  and  $^3B_2$  states. For the four-membered ring case, bicyclobutanone **5** lies a surprising 34 kcal/mol below the  $^1A_1$  diradicaloid.<sup>35</sup>

A study analogous to ours for OA was carried out by Dixon and co-workers for ethano-<sup>36</sup> and methano-bridged<sup>37</sup> TMM. In this study, ring-closed **8** was found to lie 10 kcal/mol higher than  $^3B_2$  diradical TMM **7**, with the  $^1A_1$  state 19 kcal/mol above the  $^3B_2$  (Figure 3). By comparison, methylenebicyclobutane **20** was found to be essentially degenerate with the analogous  $^3B_2$  TMM **19** and most likely lies even lower in energy due to the basis set level used in this computation: the  $^1A_1$  state of **19** lies approximately unchanged relative to the  $^3B_2$  at +22.0 kcal/mol.

(35) These qualitative results are reflected even in the RHF-SCF energies of the various species, before correlation effects are included. At this level, **5** lies well below the SCF energies of **3S** and **3T**, while **6** has an energy similar to those of **4S** and **4T**. It is possible that the lack of inclusion of  $\sigma$ -CI in our computations could somewhat affect this gaps between the bicyclic and diradicaloid forms of the molecules.

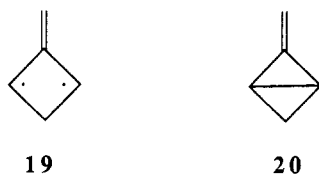
(36) Dixon, D. A.; Dunning, T. H., Jr.; Eades, R. A.; Kleier, D. A. *J. Am. Chem. Soc.* **1981**, *103*, 2878.

(37) Dixon, D. A. Private communication. We thank Dr. Dixon for permission to refer to this work.

(32) Snyder, G. J.; Dougherty, D. A. *J. Am. Chem. Soc.* **1985**, *107*, 1775; **1989**, *111*, 3927, 3942.

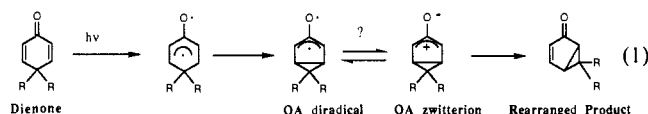
(33) Dowd, P.; Paik, Y. H. *J. Am. Chem. Soc.* **1986**, *108*, 2788.

(34) See discussion and references in: Michl, J.; Bonacic-Koutecky, V. *Tetrahedron* **1988**, *44*, 7559.



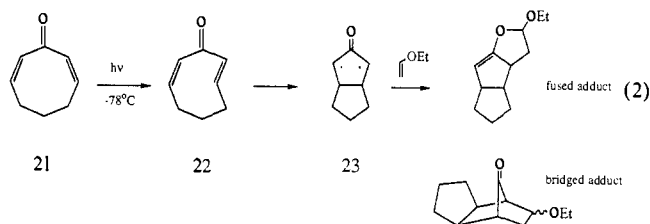
The stabilization of the ring-closed form relative to the diradicals by methano vs ethano bridging for the TMM's and OA's is analogous, for reasons that are probably based upon the ring strain in **3** relative to **4**. In the methano-bridged system, both the OA and the ring-closed form retain a substantial amount of small-ring strain that will tend to cancel in considering the gap between the opened and closed forms. In this case, the extremely short C–O bond and extra C–C bond in **5** will cause it to be favored thermodynamically over open form **3**. In the ethano-bridged system, presence of the short C–O bond and extra C–C bond in **6** will be offset in open form **4** by a lack of major ring strain in the five-membered ring. As a result, one might expect the closed and opened five-membered ring forms to be energetically more comparable by this analysis than is the case for the four-membered ring case, as is predicted by our computations. The high degree of strain in OA **3** and the relative stability of closed form **5** would seem to render the four-membered ring OA system to be a less attractive experimental target than the five-membered ring. In a similar attempt to study methano-bridged TMM system **19**,<sup>10</sup> no evidence for a TMM was obtained, but only unrelated products apparently derived from a thermally allowed bicyclobutane to butadiene rearrangement of **20**.

Zwitterionic OA systems have been widely invoked as key reactive intermediates in the photoisomerization of cross-conjugated dienones (eq 1).<sup>38</sup> The evidence supporting the intermediacy



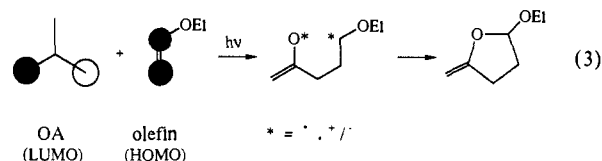
of a zwitterionic species rests largely on the results of trapping studies with nucleophiles such as alcohols and halides.<sup>39</sup> The photoreaction can give a variety of deep-seated rearrangements and fragmentation products that are highly dependent on both the structure of the dienone and the reaction medium. An OA zwitterion has been suggested as an observable intermediate that is stable at reduced temperature in some related photochemical solution-phase work.<sup>40</sup> Observation of the dienone photorearrangement in the gas phase has in some cases been interpreted as meaning that the isomerization may proceed through a diradical and not a zwitterionic intermediate.<sup>41</sup> The zwitterionic interpretation of the photoreaction may also be consistent with our description of the ground state of **4** as being diradicaloid, rather than a true diradical. It is possible that a polar reaction medium may cause an altering of reactivity such that trapping chemistry is observed that is consistent with that usually interpreted as being from a zwitterionic molecule.

Recently one of us conducted an olefin-trapping study supporting the intermediacy of a bridged OA system (eq 2).<sup>42</sup> Photochemical irradiation of **21** at reduced temperature leads to a storable new reactive molecule, believed to be isomer **22**. The likely presence of OA **23** is deduced by the lack of olefin-trapping products attributable to trapping by **22**, but only of products logically derivable from **23**, possibly by a zwitterionic or diradical mechanism. To our knowledge, this is the first example of the



capture of a putative OA system by a simple monoolefin, although conjugated dienes have been observed to give [3+4] adducts with OA intermediates.<sup>43</sup>

The experimental results of the olefin and diene-trapping studies are reasonable in terms of simple molecular orbital (MO) models of OA. As shown earlier in Figure 2, the OA HOMO will be of  $b_1$  symmetry and the LUMO of  $a_2$  symmetry. Since the HOMO is substantially lowered relative to the HOMO of TMM, one might expect OA's to act more as electron acceptors than TMM's, as observed experimentally (eq 2). Equation 3 shows the interaction



of the HOMO of an electron-rich olefin with the LUMO of an OA. A concerted cycloaddition cannot occur with these MO's; hence, a stepwise zwitterionic or diradical path is likely, as postulated in experimental studies. The finding of fused and bridged adduct-type products in the reaction of eq 2 is consistent with such a stepwise mechanism. As a result, one might expect stereochemical scrambling in trapping studies where such effects might be monitored. Experimental studies are underway by one of us to test the stereochemical outcome of olefin trapping by OA's and will be reported in due course.

## Summary and Conclusions

This computational study of model bridged oxyallyl derivatives highlights several characteristics of these species that are worthy of experimental verification as part of the present interest in elucidating factors determining ground-state multiplicity and electronic nature in diradicals and related bond deficient species.

(1) Both methano- and ethano-bridged OA's favor a  $^1A_1$  ground state with a strong C–O bond. Structurally, they do appear to be well-described by a fairly charge-separated diradicaloid structure **1** with free valence  $\pi$  electrons not involved in the C–O bonding being localized on the periphery carbons of the  $\pi$  system, rather than being strongly interacting as in the trimethylene-methane diradicals. Efforts to observe the low-lying  $^3B_2$  state are likely to be impeded by energetically favorable intersystem crossing to the singlet manifold, aided by spin-orbit coupling due to the presence of the oxygen atom.

(2) The bridged OA's, although they possess a fair degree of diradical nature in their CI wave functions, at our level of theory seem to be better described as diradicaloid singlet molecules, rather than true diradicals. This conclusion is based on a comparison of our ab initio CI wave functions to those computed by others for heteroatom-containing bond-deficient species.

(3) The bicyclic species **5** and **6** are of potential experimental importance for methano- and ethano-bridged systems. The stability of bicyclobutanone **5** relative to the ring-opened species **3S** and **3T** is such that efforts to observe the latter diradicaloids are likely to be extremely difficult unless a high barrier to ring closure of **3S** to **5** exists. Given the allowed nature of this cyclization, such a barrier seems fairly unlikely. The relative stability of bicyclopentanone **6** is similar to that of the ring-opened forms of OA **4**; hence, the potential role of **6** in the chemistry of the

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(43) (a) Turro, N. J. *Pure Appl. Chem.* **1971**, *27*, 679. (b) Wasserman, H. H. *Top. Curr. Chem.* **1974**, *47*, 73. (c) Crandall, J. K.; Haseltine, R. P. *J. Am. Chem. Soc.* **1968**, *90*, 6251. (d) For cycloaddition reactions of OA-iron carbonyl complexes see: Noyori, R. *Accs. Chem. Res.* **1979**, *12*, 61.



five-membered ring OA's is not clear.

**Acknowledgment.** This research was supported in part by the Office of Naval Research. Support for the University of Massachusetts department of chemistry computational facility was provided by the National Science Foundation (Grant CHE-8712319) and the University of Massachusetts. P.M.L. acknowledges helpful and interesting discussions with Prof. Weston T. Borden, who made available to us a version of the accompanying

paper in advance of publication. Finally, P.M.L. acknowledges a stimulating discussion with members of the Connecticut Quantum Theory Group (especially Prof. Kenneth B. Wiberg) concerning the nature of the C–O bond in OA's by comparison to the carbonyl bond in ketones.

**Supplementary Material Available:** Tables of 6-31G\* optimized structures (6 pages). Ordering information is given on any current masthead page.

## The Metal–Nitroxyl Interaction in MNO Metallacycles (M = Cu, Pd). An ab Initio SCF/CI Study

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**Abstract:** Ab initio SCF and CI calculations have been carried out on the isoelectronic and isostructural complexes (CH<sub>3</sub>)<sub>2</sub>NOCuBr<sub>2</sub> and (CH<sub>3</sub>)<sub>2</sub>NOPdCIPH<sub>3</sub>, where dimethyl nitroxide is a model for 2,2,6,6-tetramethylpiperidinyl-1-oxy (TMPO). Calculations show that the CuBr<sub>2</sub> and PdCIPH<sub>3</sub> radicals have quite a different electronic structure, the magnetic orbital being delocalized with major weight on the ligands for CuBr<sub>2</sub> and mainly localized on the metal for PdCIPH<sub>3</sub>. The different nature of the metal fragments influences the  $\eta^2$  coordination of the nitroxyl radical. In the copper complex, the bonding interaction is largely delocalized over the five atoms of the molecular plane. Through-space interactions between the bromine atoms and the nitroxide group contribute to stabilize the molecule. The net charge of the nitroxide is not significantly modified with respect to the free (CH<sub>3</sub>)<sub>2</sub>NO radical. In the palladium complex, a significant charge transfer occurs from the metal to the NO  $\pi^*$  orbital, resulting in a strong, covalent interaction between these orbitals. The other ligands have little contribution in the bonding. Both the Cu and the Pd complexes are computed to be strongly diamagnetic, with respective singlet–triplet energy separations of 5000 and 17 000 cm<sup>-1</sup>.

### 1. Introduction

The complexes of transition metals with nitroxyl ligands are the subject of a thorough physical and chemical investigation in relation with the design of new magnetic materials.<sup>1–4</sup> Concerning more specifically copper(II)–nitroxyl species, the magnetic properties have been shown to strongly depend upon the coordination geometry: an equatorial coordination of the nitroxyl ligand induces either strong antiferromagnetism or diamagnetism,<sup>3</sup> whereas an axial coordination generally yields complexes with a ferromagnetic behavior.<sup>4</sup> The importance of the metal–ligand distances and of the electronic structures of the metal and ligand have also been recognized.<sup>2c</sup> All copper(II)–nitroxyl complexes studied up to recent times were characterized by an  $\eta^1$ -O coordination mode. The only exception concerns the adduct of copper(II) bromide with 2,2,6,6-tetramethylpiperidinyl-1-oxy (TMPO) in which both the oxygen and the nitrogen atoms are at bonding distance from the metal ( $d_{\text{Cu-O}} = 1.860 \text{ \AA}$ ,  $d_{\text{Cu-N}} = 1.998 \text{ \AA}$ ).<sup>5</sup> The X-ray characterization of the geometrical structure has revealed some other remarkable features of the molecule: (i) planarity of the CuBr<sub>2</sub>(NO) moiety, corresponding to a distorted square-planar coordination for Cu, and (ii) a slight increase of the NO bond length and more pronounced pyramidalization of the nitrogen atom with respect to the geometry of the isolated TMPO.

Although these structural features are unprecedented with copper, they are reminiscent of the M–NO metallacycles characterized with various metals (M = V(III,V), Mo(II,IV,VI),

U(VI), and Pd(II)).<sup>6–8</sup> Among these molecules the two complexes of palladium(II), PdCl(PPh<sub>3</sub>)TMPO<sup>7</sup> and Pd(C<sub>3</sub>HF<sub>6</sub>O<sub>2</sub>)(C<sub>9</sub>-

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