CASSCF and CASPT2N Calculations Predict Singlet Cyclopentan-2-one-1,3-diyl is Stable toward Closure to Bicyclo[2.1.0]pentan-5-one

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Ab initio SCF-CI calculations find that substituted oxyallyl diradicals have singlet ground states.[1–3] For example, CI calculations by Lahti and co-workers on the ethano-bridged oxyallyl, cyclopentan-2-one-1,3-diyl (1) predict that the ground-state is a singlet.[2] The study of Miyashi, Akiyama, and co-workers on a derivative of 1 provide confirmatory experimental data.[4]

The CI calculations of Lahti and co-workers also found that diradical 1 is slightly lower in energy than the ring-closed isomer bicyclo[2.1.0]pentan-5-one (2). Unfortunately, these CI calculations included excitations among only a small number of orbitals; so this result must be viewed as suggestive rather than conclusive. However, the recent low-temperature experiments of Sorensen and co-workers do indicate that 1 cannot be substantially higher in energy than 2.[5]

In order to predict unequivocally which of these two isomers is, in fact, lower in energy, we have performed calculations at much higher levels of theory than that used by Lahti and co-workers.[2] Our (4/4)-CASSCF and CASPT2N calculations predict that singlet diradical 1 is, indeed, lower in energy than 2.[6] In addition, we find that the CASSCF carbonyl stretching frequencies of the singlet and triplet states of 1 and the singlet state of 2 are all sufficiently different that it should be possible to use IR spectroscopy to confirm our prediction that generation of 1 will produce a singlet diradical which is stable toward ring closure.

The geometries of 1 and 2 were optimized with the 6-31G* basis set[7] at the complete active space (CAS) SCF level of theory. The active space consisted of four electrons in four orbitals. For 1 the four orbitals were the oxyallyl π orbitals; for 2 they were the π and π^* orbitals of the carbonyl group and the σ and σ^* orbitals of the scissile bond. Vibrational analyses at the (4/4)-

Table 1. Relative Energies (kcal/mol) of Singlet (S) and Triplet (T) 1, Singlet 2, and the Transition State Connecting Singlet 1 and Singlet 2

molecule	basis set	CASSCF	CASPT2N	ZPE	Cv (cal/mol K)
1S	6-31G*	0[a]	0[b]	63.9	18.9
1T	6-31G*	1.6	6.0	62.9	19.5
2	6-31G*	4.0	1.3	65.3	17.6
TS	6-31G*	6.3	4.5	64.3	16.6
1S	6-311G(2d,p)	0[c]	0[d]	–	–
1T	6-311G(2d,p)	2.8	7.0	–	–
2	6-311G(2d,p)	5.1	4.3	–	–

[a] Relative to $E = -267.6547$ hartrees. [b] Relative to $E = -268.4374$ hartrees. [c] Relative to $E = -267.7285$ hartrees. [d] Relative to $E = -268.7444$ hartrees.

CASSCF/6-31G* level of theory were used to identify optimized geometries as minima or transition states. The CASSCF calculations were carried out with the Gaussian 92 package of *ab initio* programs.[8] Optimized geometries are available as supplementary material.[9]

Dynamic electron correlation was included by performing CASPT2N calculations[10] at all the CASSCF stationary points. The CASPT2N calculations were carried out using MOLCAS.[11] CASPT2N single-point calculations on 1 and 2 were performed with both the 6-31G* and the 6–311G(2d,p)[12] basis sets.

The (4/4)-CASSCF/6-31G* geometries[9] of singlet and triplet 1 and singlet 2 are similar to, respectively, the GVB, UHF, and RHF geometries reported by Lahti and co-workers.[2] Vibrational analyses showed that all three species are energy minima. The transition state connecting singlet 1 and 2 was located, and its geometry is also available as supplementary material.[9,13] The CASSCF and CASPT2N/6-31G* energies of all four stationary points are given in Table 1.

With inclusion of dynamic electron correlation at the CASPT2N/6-31G* level, the CASSCF/6-31G* singlet–triplet energy difference in 1 increases from 1.6 to 6.0 kcal/mol. The latter value is in good agreement with Lahti's CI value of 5.8 kcal/mol with the same basis set. Correction for zero-point energy differences between the two states reduces the amount by which the singlet is calculated to be the ground state to 5.0 kcal/mol at the CASPT2N/6-31G* level of theory.

At the CASSCF/6-31G* level, singlet and triplet 1 both lie below the closed form by 4.0 and 2.4 kcal/mol, respectively. Because CASPT2N correlates the electrons in the two strained bonds of 2 that are not correlated at the (4/4)-CASSCF level, CASPT2N selectively stabilizes 2, dropping it 4.7 kcal/mol below triplet 1 but leaving 2 still 1.3 kcal/mol above singlet 1. The zero-point energy of 2 is calculated to be 1.4 kcal/mol greater than that of singlet 1; so, with inclusion of this correction, singlet 1

(1) Coolidge, M. B.; Yamashita, K.; Morokuma, K.; Borden, W. T. *J. Am. Chem. Soc.* **1990**, *112*, 1751.

(2) Ichimura, A. S.; Lahti, P. M.; Matlin, A. R. *J. Am Chem. Soc.* **1990**, *112*, 2868.

(3) Calculations of solvent effects on the opening of cyclopropanones to oxyallyls have also been reported: Lim, D.; Hrovat, D. A.; Borden, W. T.; Jorgensen, W. L. *J. Am Chem. Soc.* **1994**, *116*, 3494.

(4) Hirano, T.; Kumagai, T.; Miyashi, T.; Akiyama, K.; Ikegami, Y. *J. Org. Chem.* **1991**, *56*, 1907.

(5) Masters, A. P.; Parvez, M.; Sorensen, T. S.; Sun, F. *J. Am Chem. Soc.* **1994**, *116*, 2804.

(6) Similar calculations have found that 2,2-difluorocyclopentane-1,3-diyl also has a singlet ground state, but in contrast to 1, the fluorinated diradical is thermodynamically unstable with respect to ring closure. Xu, J. D.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1994**, *116*, 5425–5427.

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

(8) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, W. P. M.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, D.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Steward, J. J. P.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1992.

(9) Ordering information is given on any current masthead page.

(10) Andersson, K.; Malmqvist, P.-Å.; Roos, B. O. *J. Chem. Phys.* **1992**, *96*, 1218.

(11) Andersson, K.; Blomberg, M. R. A.; Fülscher, M. P.; Kellö, V.; Lindh, R.; Malmqvist, P.-Å.; Noga, J.; Olsen, J.; Roos, B. O.; Sadlej, A. J.; Seigbahn, P. E. M.; Urban, M.; Widmark, P.-O. MOLCAS, Version 2, University of Lund, Sweden 1991.

(12) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265.

(13) Calculations also predict that ring opening of cyclopropanone requires passage over a transition state, in order to reach oxyallyl.[3]

Table 2. Calculated Carbonyl Stretching Frequencies (cm⁻¹) for Singlet (S) and Triplet (T) 1 and Singlet 2

molecule	CASSCF/6-31G*	scaled^a
1S	1936	1736
1T	1549	1387
2	2044	1830

^{a} CASSCF/6-31G* frequencies scaled by 0.8955 (see text).

is calculated to be 2.7 kcal/mol lower in energy than **2** at the CASPT2N/6-31G* level of theory.

Having confirmed that the previous ordering of the energies of singlet **1** and **2**[2] survives a more rigorous treatment of electron correlation, we also investigated the effect of expanding the basis set from 6-31G* to 6-311G-(2d,p). The latter basis set contains a third valence basis function and a second set of polarization functions on carbon and oxygen plus a set of polarization functions on hydrogen.

As shown in Table 1, CASPT2N calculations with this expanded basis set find that singlet **1** lies 4.3 kcal/mol lower in energy than **2** and 7.0 kcal/mol below triplet **1**. This finding provides very strong computational evidence that the singlet diradical really is the lowest energy of these three species, since the (4/4)-CASSCF/6-31G* result survives both inclusion of dynamic electron correlation and expansion of the basis set.

The differences between the carbonyl stretching frequencies of singlet and triplet **1** and of **2** make a major contribution to the differences between their zero-point energies. The differences between the CASSCF/6-31G* carbonyl stretching frequencies are large enough that IR spectroscopy should be useful in detecting and in distinguishing between **1** and **2** in matrix isolation.

The C=O stretching frequency of singlet **1** is computed to be 1936 cm⁻¹ (Table 2). Since it has been shown that the carbonyl group in oxyallyl is only slightly perturbed by delocalization of the nonbonding electrons,[2,3] it is understandable that the CASSCF/6-31G* C=O stretch-

ing frequency in **1** is very similar to the TCSCF/6-31G* value of 1943 cm⁻¹ for cyclopentanone. Dividing the experimental value of 1740 cm⁻¹ for the C=O stretch in cyclopentanone[14] by the calculated value, a scaling factor of 0.8955 is obtained. A scaling factor of about 0.89 is often used to correct calculated frequencies for anharmonicity and other effects.[15]

After scaling by 0.8955, the predicted C=O stretch of singlet **1** is 1736 cm⁻¹, and the C=O stretch of triplet **1** is predicted to appear at 1387 cm⁻¹. The lower frequency that is calculated for the triplet is consistent with the reduced double bond character in the triplet C–O bond.[1] Before scaling, the calculated C=O stretching frequency for **2** is 2044 cm⁻¹, which is close to the C=O stretch of 2063 cm⁻¹ that is computed for cyclopropanone at an equivalent level of theory. Scaling the CASSCF/6-31G* C=O frequency for **2** gives a predicted experimental value of 1830 cm⁻¹.

The calculated carbonyl frequencies of 1736 cm⁻¹ for singlet **1**, 1387 cm⁻¹ for triplet **1**, and 1830 cm⁻¹ for **2** are so different that it should be easy to identify which species are present when **1** is generated under conditions where an IR spectrum can be obtained. Our calculations predict that the major absorption observed in the C=O stretching region should be that characteristic of singlet **1**.

Supplementary Material Available: (4/4)-CASSCF/6-31G* geometries for singlet **1**, **2**, the transition state connecting them, and triplet **1** (4 pages).

JO9503280

(14) Bellamy, L. J. *The Infrared Spectra of Complex Molecules*; John Wiley & Sons: New York, 1975; p 168.

(15) See, for example: Pople, J. A.; Head-Gordon, M.; Fox, D. J.; Raghavachari, K.; Curtiss, L. A. *J. Chem. Phys.* **1989**, *90*, 5622. Pople, J. A.; Scott, A. P.; Wong, M. W.; Radom, L. *Isr. J. Chem.* **1993**, *33*, 345.