at moderate cost, AM1 should prove useful as an aid in interpreting proton transfer in chemistry and biochemistry.

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Ab Initio Calculations of the Singlet–Triplet Energy Separation in 3,4-Dimethylenefuran and Related Diradicals

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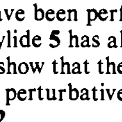
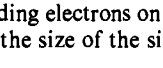
Abstract: Ab initio π CI calculations predict a singlet ground state for the title diradical (**2**). In order to determine the effect of the oxygen in **2** on the singlet–triplet splitting, additional calculations on the diradicals in which this heteroatom was replaced by a methylene (**1**) or by an amino group (**3**) have been performed, and the singlet–triplet splitting in carbonyl ylide (**5**) has also been computed. The results of these calculations show that the π nonbonding electrons on oxygen have but a mildly perturbative effect on the size of the singlet–triplet splitting in **2**.

Violations of Hund's rule[1] have been predicted to be possible for diradicals in which the two nonbonding MOs are confined to disjoint sets of atoms.[2,3] Berson and co-workers have obtained experimental evidence that indicates a singlet ground state for 3,4-dimethylenefuran (**2**)[4]—a diradical which, if viewed as a derivative of planar tetramethyleneethane,[2,3,5] is disjoint. In this paper we report the results of ab initio calculations on **2**. In agreement with Berson's experimental results and with a previous semiempirical study,[6] our calculations indicate a singlet ground state for **2**.



1: X = CH_2
2: X = O
3: X = NH



4: X = CH_2
5: X = O
6: X = NH

In order to determine the effect of the oxygen in **2** on the singlet–triplet splitting, calculations on the diradicals in which this heteroatom was replaced by a methylene (**1**) or by an amino group (**3**) have been performed, and the singlet–triplet splitting in carbonyl ylide **5** has also been computed. The results of these calculations show that the π nonbonding electrons on oxygen have but a mildly perturbative effect on the size of the singlet–triplet splitting in **2**.

The geometries of **1**–**3** were optimized by unrestricted Hartree–Fock (UHF) calculations[7] on the lowest triplet state of each diradical, using the STO-3G basis set.[8] Previous work has shown that triplet UHF optimizations should give reasonable geometries for these diradicals.[9,10] The optimized geometries are available as supplementary material.

In order to calculate the singlet–triplet energy splittings in **1**–**3**, CI calculations[11] were performed at the optimized geometries, using the Dunning [9s,5p] → [3s,2p] split-valence (SV) basis set.[12] Two types of CI calculations were performed for the lowest singlet and triplet state of each diradical. The first included all excitations through quadruples (SDTQ CI) within a conceptual minimal basis set of 7 π MOs for **2** and **3** and 8 π MOs for **1**.[13] The second involved multi-reference SD CI, using the entire π orbital basis set. Included in the reference space were all those configurations with SDTQ CI coefficients larger than 0.12 and most of the configurations with coefficients greater than 0.10. Comparable configurations were included in the reference space for the singlet and triplet states to ensure that the configuration selection did not bias the computed energy differences. The results of our CI calculations are contained in Table I.

In **1** the in-phase combination of the allylic nonbonding MOs ($3b_1$) and the out-of-phase combination ($2a_2$) are nearly degenerate in energy.[14] This is reflected in the fact that the two dominant configurations, $|...2a_2^2\rangle$ and $|...3b_1^2\rangle$, in the CI wave functions for

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[8] Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657. The bond lengths for **2** that were found with this basis set were all within 0.02 Å of those optimized with the 3-21G basis set (Lahti, P. Ph.D. Thesis, Yale University, 1985).

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[11] CI calculations were perfomed with MELD, developed at the University of Washington by E. R. Davidson and co-workers.

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[13] For these CI calculations two reference configurations were used for the $^1A_1$ states. The triplet RHF MOs and singlet TCSCF MOs were transformed to K orbitals (Feller, D.; Davidson, E. R. *J. Chem. Phys.* **1981**, *74*, 3977), which were used, respectively, for the CI calculations on $^3B_2$ and $^1A_1$. Test computations on **1** showed that K orbitals from a TCSCF calculation on $^1A_1$ gave the same singlet and triplet CI energies as the K orbitals from an RHF calculation on $^3B_2$, but for **2**, **3**, and **5** the TCSCF derived K orbitals gave lower $^1A_1$ CI energies than did the K orbitals from the triplet RHF calculations.

[14] The orbital energies of $2a_2$ and $3b_1$ from an RHF calculation on $^3B_2$ differ by 5 kcal/mol, with $2a_2$ lower in energy.

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Table I. Calculated Singlet and Triplet Energies in **1**, **2**, **3**, and **5**

diradical	calculation	$^1A_1$ energy[a]	$^3B_2$ energy[a]	ΔE[b]
1	SV[c] SDTQ CI[d]	−269.6267	−269.6243	1.5
1	SV[c] MRSD CI[e]	−269.6473	−269.6447	1.6
1	SVP[f] SDTQ CI[d]	−269.7212	−269.7189	1.4
2	SV[c] SDTQ CI[d]	−305.4255	−305.4210	2.8
2	SV[c] MRSD CI[e]	−305.4583	−305.4538	2.8
2	SVP[f] SDTQ CI[d]	−305.5470	−305.5434	2.3
3	SV[c] SDTQ CI[d]	−285.6244	−285.6128	7.3
3	SV[c] MRSD CI[e]	−285.6556	−285.6448	6.8
5	SV[c] SDTQ CI[h]	−152.7952	−152.7688	16.6
5	SVP[g] SDTQ CI[h]	−152.8786	−152.8461	20.4

[a] Energy in hartrees. [b] Singlet–triplet energy difference in kcal/mol. [c] Split-valence basis set. [d] SDTQ CI in the space of the conceptual minimal π basis set. [e] Multi-reference SD CI calculation in the full π space. [f] Split-valence basis set with polarization functions on heavy atoms. [g] Split-valence basis set with polarization functions on all atoms. [h] SDTQ CI in the full π space.

$^1A_1$ have nearly equal weight. The ratio of the squares of their coefficients is 0.87 in the SDTQ CI wave function (0.88 in the MRSD CI), with the latter configuration having the larger weight.

Despite the near degeneracy of the nonbonding MOs, a singlet ground state is calculated for **1**. This result contrasts with the triplet ground state that has been computed for **4**[15] and for cyclopentane-1,3-diyl[16] and that has been found experimentally for the latter diradical.[17] The singlet ground state that is calculated for **1** is due to the fact that this diradical contains two allylic π systems that are joined at the inactive carbons. In the lowest singlet state of **1** dynamic spin polarization gives opposite spins at these two carbon atoms, thus allowing more π bonding between them than in the triplet state, where the spins at these atoms are the same.[2,3]

Evidence that this effect is responsible for the singlet ground state predicted for **1** at the CI level comes from RHF and two-configuration (TC) SCF calculations, which correlate only the nonbonding electrons. The RHF energy of −269.5401 hartrees for the $^3B_2$ state of **1** is 0.9 kcal/mol lower than the TCSCF energy of $^1A_1$. The reversal of the ordering of these two states at the CI level comes from inclusion of correlation between the bonding and nonbonding electrons. This additional electron correlation produces the dynamic spin polarization in **1** that is responsible for the predicted violation of Hund's rule in this diradical.

When CH_2 in **1** is replaced by a better π donor group, O in **2** and NH in **3**, the $3b_1$ nonbonding MO is destabilized relative to $2a_2$. This destabilization is due to the fact that the π orbital of the donor group mixes in an antibonding way into $3b_1$ but does not mix with $2a_2$. Because of the lower energy of $2a_2$, the electron population in this MO in the lowest singlet state increases with the strength of the donor group. This increase is reflected in the fact that the ratio of the squares of the CI coefficients for the two dominant configurations in the $^1A_1$ wave function goes from 0.87 (0.88) in **1** to 1.76 (1.84) in **2** and to 2.74 (2.87) in **3**.

In the lowest triplet state of **1**–**3**, however, the electron occupancy of these two orbitals remains about equal. Consequently, lifting the near degeneracy of the two nonbonding MOs in **1** is expected to increase the singlet–triplet splitting. The better the electron donor group is, the larger the singlet–triplet energy gap is anticipated to be. This expectation is borne out by the data in Table I.

Because the nonbonding allylic MOs in **1**–**3** have only half as much density adjacent to X as the nonbonding MOs in **4**–**6**, π donation from X to the b_1 nonbonding MO should be considerably smaller in **1**–**3** than in **4**–**6**. Consequently, replacement of the CH_2 in **1** and **4** by a better donor group like O should have a smaller effect on selectively stabilizing the lowest singlet state in **2** than in **5**.

To verify that this was in fact the case, we performed CI calculations on **5**[18] for comparison with those on **2**. The geometry of **5** was taken from a previous π MCSCF optimization of the $^1A_1$ state.[18e] Because we anticipated that strong donation from oxygen in **5** could cause the singlet and triplet to have significantly different C–O bond lengths, the optimal C–O bond length for each state was found by SDTQ CI calculations in the full π space at several C–O bond lengths, using the Dunning SV basis set. Quadratic fitting gave 1.341 Å as the optimal C–O bond length for the singlet state, 1.378 Å for the triplet, and a singlet–triplet energy separation at these geometries of 16.6 kcal/mol.

Since the C–O bond length in the $^1A_1$ state of **2** was also expected to be shorter than that in the $^3B_2$ state, we reoptimized these bond lengths with the SV basis set by carrying out SDTQ CI calculations for each state. The optimized C–O bond lengths found were respectively 1.364 and 1.378 Å. As expected, the difference of 0.014 Å between the optimized singlet and triplet C–O bond lengths in **2** is considerably less than the 0.037 Å in **5**. Also as anticipated, calculating the singlet–triplet splitting in **2** at the optimized C–O bond length for each state, rather than at the $^3B_2$ UHF geometry, increased this energy difference slightly, from 2.8 to 4.1 kcal/mol with SDTQ CI. The $^1A_1$ CI energy at the CI optimized geometry was 0.0033 hartrees lower than that given in Table I.[19]

In order to test the effect of including polarization functions, the SDTQ π CI calculations on **1**, **2**, and **5** were repeated with d orbitals on C and O. For the calculations on **5** p orbitals on H were also included. The computed singlet–triplet splitting decreased slightly in **1** and **2** but increased by 3.8 kcal/mol in **5**.[20] Presumably, inclusion of polarization functions has a substantial effect on the singlet–triplet energy difference calculated for **5**, because these functions improve the description of the strong C–O π bonding[21] that is present in the singlet state of **5**.

The very large ratio of 5.05 (6.13 with the inclusion of polarization functions) for the squares of the CI coefficients of the two most important configurations in the $^1A_1$ wave function for **5**[22] is indicative of the significant delocalization of the lone pair on oxygen in **5**. From comparison of either the ratio of the square of the CI coeffcients or the singlet–triplet energy gap in **2** with those in **1** and **5**, it is clear that **2** is better regarded as a weakly perturbed derivative of planar tetramethyleneethane, like **1**, rather than as a carbonyl ylide like **5**. Nevertheless, the experimental verification that, as predicted, **1** too has a singlet ground state would provide a more unequivocal example of a violation of Hund's rule in a disjoint diradical.

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Supplementary Material Available: UHF optimized geometries for **1**–**3** (3 pages). Ordering information is given on any current masthead page.

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(19) At the UHF 3-21G geometry for $^3B_2$ the SDTQ CI energies for $^1A_1$ and $^3B_2$ were each 0.0011 hartree lower than the energies given in Table I at the UHF STO-3G geometry for $^3B_1$.

(20) SDTQ CI optimization of the C–O bond lengths in **5** gave values that were 0.03 Å smaller for both the singlet and triplet state with the SVP basis set than with the SV. However, the singlet–triplet energy splitting was essentially the same at both sets of geometries. The SVP energies for **5** in Table I are those at the geometries optimized with this basis set. The SVP energies for **2** were obtained at the UHF STO-3G geometry of $^3B_2$.

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(22) In contrast to the case with **5**, when polarization functions are included in the calculations on **1** and **2**, the ratios of the squares of the CI coefficients decrease slightly, to 0.82 for **1** and to 1.69 for **2**.