Stability of Tetraoxocyclobutane Revised: Perturbation Theory and Density Functional Scheme

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The stability of the singlet and triplet states of tetraoxocyclobutane (C_4O_4, the tetramer of carbon monoxide) has been investigated at various levels of theory. Second-order perturbation favors the singlet state, whereas the triplet and open-shell singlet states are computed to be more stable using the hybrid B3LYP density functional method. High-level CCSD(T) calculations reveal the perturbation theory to be insufficient, whereas the B3LYP method provides both qualitatively and quantitatively reliable results.

It is well-known that electron correlation is most important and decisive for determining the correct structures, stability, and reactivity directly associated with the energies.[1] For studying electron correlation, various post-Hartree−Fock and density functional methods are available.[2] In some cases, however, both perturbation and density functional theories are not sufficient for estimating the correct geometry and therefore the stability, and this leads to further development of theoretical methods and understanding of modern chemistry.

One example is the boundary search between the aromatic (delocalized) and the olefinic (localized) character of the long elusive [10]annulene molecule. Both second-order perturbation (MP2) and hybrid density functional (B3LYP) theories favor the aromatic over the olefinic structure by 7−9 kcal/mol.[3,4] However, the aromatic structure does not have the experimental NMR pattern, and this disagreement raises the question whether these methods are appropriate to determine the structure and energy of [10]annulene. High correlated CCSD(T) method favors the olefinic over the aromatic structure by 3−7 kcal/mol and reveals that both MP2 and B3LYP are insufficient methods for treating the [10]annulene chemistry.[4]

In this work, we explore the stability between the singlet and the triplet states of the tetraoxocyclobutane (C_4O_4, tetramer of carbon monoxide) molecule, which is attractive in designing and searching for new high-energy-high-density materials.[5] A qualitative study of the electronic structure of C_4O_4 in D_{4h} symmetry by Gleiter et al.[6] reveals a small energy gap between the out-of-plane HOMO (a_{2u}) and the in-plane LUMO (b_{2g}), which are shown in Figure 1. Consequently, one can expect both the two singlet states [**S1**, $(b_{2g})^2(a_{2u})^0$; and **S2**, $(a_{2u})^2(b_{2g})^0$], the corresponding triplet (**T**) and open-shell (**SO**) singlet states [$(a_{2u})^1(b_{2g})^1$] to be close in energy. Therefore, the determination of the ground-state configuration is of crucial importance for this molecule.

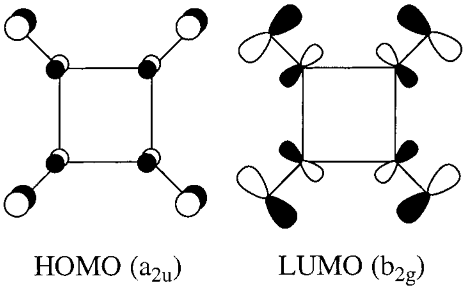

Figure 1. Schematic frontier orbitals of C_4O_4 (D_{4h}) of the **S2** configuration.

At the HF/6-31G(d) level, Gleiter et al.[6] found **S1** (0.0 kcal/mol) to be more stable than **T** (9.7 kcal/mol) and **S2** (64.6 kcal/mol). However, the correlated MP2 method changes the energies dramatically (kcal/mol), 28.4 (**T**) > 25.7 (**S1**) > 0.0 (**S2**), i.e., the most unstable **S2** at the HF level becomes the most stable at the MP2 level. They also found that **S2** at the MP2 level has a nonplanar D_{2d} rather than the expected D_{4h} symmetry.

More recently, Schleyer et al.[7] found that **S2** in D_{4h} symmetry is a true minimum on the potential energy surface at the hybrid B3LYP/6-311+G(d) density functional level of theory and exhibits cyclic electron delocalization due to partial occupancy of the C−C σ-bonds. At the same level of theory, we found that the triplet state (**T**) in D_{4h} symmetry is not only an energy minimum,[8] but also more stable than both **S2** and **S1** by 10.2 and 13.3 kcal/mol, respectively, and, therefore, no more attention to **S1** will be paid further. In contrast to **S2**, **T** does not exhibit cyclic electron delocalization.[9] The fourth possibility of electron configuration is the open-shell singlet state (**SO**). At B3LYP/6-311+G(d), **SO** is computed to be more stable than **S2** by 8.1 kcal/mol but less stable than **T** by 2.2 kcal/mol. However, MP2/6-311+G(d) shows that **SO** is less stable than both singlet (**S2**) and triplet (**T**) states by 21.3 and 4.4 kcal/mol. Thus, the ground state configuration depends strongly on the computational methods employed. Because no experimental references for this molecule are available for judgment, these contradictory data questioned the reliability of these two methods. Therefore, we carried out systematic optimizations and high-level MP4SDTQ, QCISD(T), and CCSD(T) single-point energy calculations on both the MP2 and the B3LYP geometries by using the Gaussian

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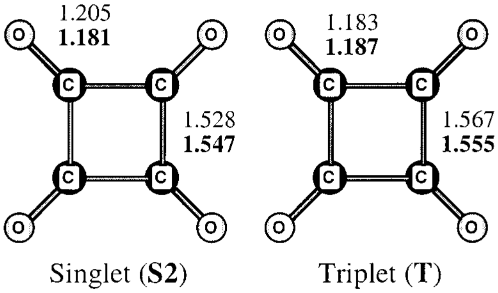
TABLE 1: Energy Difference (Δ*E*, kcal/mol) between the Singlet (S2) and Triplet (T) states of Tetraoxocyclobutane (C_4O_4)[a]

level of theory[b]	Δ*E*(**T**-**S2**)
MNDO//fopt	33.8
AM1//fopt	27.4
PM3//fopt	34.9
HF/6-311G(d)//fopt	−52.9
HF/6-311+G(d)//fopt	−52.1
MP2/6-31G(d)//fopt	+17.0
MP2/6-311+G(d)//fopt	+16.9
B3LYP/6-31G(d)//fopt	−11.2
B3LYP/6-311+G(d)//fopt	−10.2
B3P86/6-311+G(d)//fopt	−9.0
B3PW91/6-311+G(d)//fopt	−9.2
B3LYP/aug-cc-pvTZ//sp[c]	−9.9
MP2/aug-cc-pvTZ//sp[c]	+15.7
MP2/6-31G(d)//sp[c]	+13.0
MP3/6-31G(d)//sp[c]	−26.4
MP4SDTQ/6-31G(d)//sp[c]	+18.9
QCISD(T)/6-31G(d)/sp[c]	−7.7
CCSD(T)/6-31G(d)//sp[c]	−8.0
MP4SDTQ/6-31G(d)//sp[d]	+25.3
QCISD(T)/6-31G(d)//sp[d]	−6.0
CCSD(T)/6-31G(d)//sp[d]	−6.5
B3LYP/6-311+G(d)//fopt (**SO**)[e]	−2.2[h]
MP2/6-311+G(d)//fopt (**SO**)[e]	−4.4[h]
CCSD(T)/6-31G(d)//sp (**SO**)[f]	−1.0[h]
CCSD(T)6-31G(d)//sp (**SO**)[g]	+2.3[h]

[a] See text. [b] fopt: full geometry optimization. [c] Using the B3LYP/6-311+G(d) geometries. [d] Using the MP2/6-311+G(d) geometries.[e] For open-shell singlet state (**SO**). [f] Using the B3LYP/6-311+G(d) geometry for open-shell singlet state (**SO**). [g] Using the MP2/6-311+G(d) geometry for open-shell singlet state (**SO**). [h] Δ*E*(T-50).



Singlet (**S2**) Triplet (**T**)

Figure 2. Optimized C−C and C−O bond lenghts (Å) in C_4O_4: MP2/6-311+G(d) in plain and B3LYP/6-311+G(d) in bold.

98 program.[10] The main data are summarized in Table 1 and the total energies are given in the Supporting Information.

Figure 2 summarizes the C−C and C−O bond lengths for both **S2** and **T** optimized at the MP2/6-311+G(d) and B3LYP/6-311+G(d) levels of theory. At both levels, the C−C bond length of **S2** is slightly shorter than that of **T**. However, the C−C bond for **S2** at MP2 is shorter than that at B3LYP (1.528 vs 1.547 Å), whereas for **T** MP2 favors longer C−C bond than B3LYP (1.567 vs 1.555 Å). The elongation of the C−C bond is more pronounced at MP2 (0.039 Å) than at B3LYP (0.008 Å). Can this geometrical change be responsible for the energetic differences?

On the basis of the semiempirical methods, **S2** is more stable than **T** by 27−35 kcal/mol (Table 1). At the HF level, however, **T** becomes more stable than **S2** by 51−55 kcal/mol using various basis sets, as found by Gleiter et al.[6] At the MP2/6-311+G(d) level, **S2** is 16.9 kcal/mol lower in energy than **T**,[11] and the energy difference due to second-order perturbation is 69.0 kcal/mol. In contrast, B3LYP/6-311+G(d) favors **T** over **S2** by 10.2 kcal/mol, and the correlation energy at this level is 42 kcal/mol.

Faced with this contradictory data, both MP2 and B3LYP single-point energy calculations with the Dunning's[12] correlation consistent basis set including diffuse functions (aug-cc-pvDZ and aug-cc-PVTZ) were carried out on the B3LYP/6-311+G(d) geometries. We found nearly the same energetic data, and no decisive results regarding the stability could be achieved (Table 1). Therefore, the dependence of basis sets can be ruled out. Moreover, different functionals (B3P86, B3PW91) instead of B3LYP provide also the same energetic order.

High-order perturbation (MP4SDTQ) calculations were carried out on the B3LYP/6-311+G(d) geometries. Alike for [10]annulene,[4] the perturbation series strongly oscillates, HF (−55 kcal/mol); MP2 (17 kcal/mol), MP3 (−26 kcal/mol) and MP4SDTQ (19 kcal/mol), indicating these energies to be unreliable for this molecule.

In addition, we performed the QCISD(T) single-point energy calculations on the MP2 and B3LYP geometries. In both cases, QCISD(T) favors **T** over **S2** by 6.0 (MP2 geometries) or 7.7 kcal/mol (B3LYP geometries). This indicates high-level electron correlation rather than slight changes of the metrical parameters is responsible for the energetic order.

More decisive results are obtained at the CCSD(T) level of theory.[13] Indeed, the triplet state (**T**) is more stable than the singlet state (**S2**) by 6.5 (MP2 geometries) or 8.0 kcal/mol (B3LYP geometries). It is also interesting to point out that the open-shell singlet state (**SO**) is slightly more stable than **T** (2.3 kcal/mol, MP2 geometries), but less stable than **T** (1.0 kcal/mol, B3LYP geometries) at the same level, indicating **T** and **SO** to be very closely in energy and to exhibit possible energetic and magnetic interaction. This brands C_4O_4 as advanced material with interesting properties.

In conclusion, perturbation theory is inadequate to describe the electronic structures and energies of tetraoxocyclobutane. On the other hand, the hybrid B3LYP density functional method is sufficient for both structures and energies. It turns out that high-level electron correlation rather than the size of the basis set is responsible for the contradictory data between MP2 and B3LYP methods.

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Supporting Information Available: Total electronic energies (au) calculated at various levels of theory are summarized in Table S1. This material is available free of charge via Internet at http://pubs.acs.org.

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(8) At B3LYP/6-311+G(d), one set of degenerate modes for the asymmetrical ring deformation (1673 cm^{-1}) with high IR intensity (750)

and two sets of modes for the symmetrical ring deformation (1830, 1850 cm^{-1}) were computed. All frequencies were scaled by 0.97.

(9) The NICS (Nucleus Independent Chemical Shifts, Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; van Eikema Hommes, N. J. R. *J. Am. Chem Soc.* **1996**, *118*, 6317) value at the ring center of the triplet state is only −5.3 ppm, which is much smaller that the value of −32.0 ppm for the singlet state, see ref 7.

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(13) One referee raised the question on the weight of the reference determinant on the MP and CCSD(T) solutions, which shows the measure of the single-reference of the wave function. G98 uses intermediate normalization on all of its post-HF correlation methods, so the weight of the reference is held at 1.0 and then the norm of the expansion vectors, which is greater than 1.0, can be used as a measure of the importance of A0. The weight of the reference can be see directly as 1.0/Norm(A) as the suitable quantity. The Norm(A) of MP2 and CCSD(T) are 1.19 and 1.17, which correspond to a coefficient of about 0.85 for the HF reference.