1354 J. Phys. Chem. A 2001, 105, 1354−1356

State-Specific Brillouin−Wigner Multireference Coupled Cluster Study of the Singlet−Triplet Separation in the Tetramethyleneethane Diradical

Jiří Pittner,*,† Petr Nachtigall, and Petr Čársky

J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, 18223 Prague 8, Czech Republic

Ivan Hubač‡

Department of Chemical Physics, Faculty of Mathematics and Physics, Comenius University, 84215 Bratislava, Slovakia

Received: September 13, 2000; In Final Form: December 20, 2000

The potential energy curves for the twisting of tetramethyleneethane in its lowest singlet and triplet states were calculated by the state-specific two-reference Brillouin−Wigner coupled-cluster method with single and double excitations. The calculated potential energy curves are essentially the same as those obtained by the two-determinant CCSD method, and they are also in agreement with the previously reported density functional theory results. Our data bring support for the previously suggested interpretation of experimental data on tetramethyleneethane in the gas phase and in the matrix.

1. Introduction

The ordering of lowest singlet and triplet states of the tetramethyleneethane (TME), a prototype disjoint diradical, has been a subject of debate since Paul Dowd recorded the EPR spectrum of TME.[1] The Curie Weis plot indicated that the triplet state is the ground state of TME or the singlet and triplet states are degenerate. Contrary to these experimental results, early ab initio studies of TME show that the singlet state lies below the triplet state by more than 1 kcal/mol.[2−4] This discrepancy was partially lifted when the $\sigma-\pi$ correlation was accounted for at the one- and two-reference configuration interaction (CI) level for the triplet and singlet states, respectively.[5] It was found that with the one-/two-reference CI method and triple-ζ plus double polarization basis set, the triplet state falls about 1 kcal/mol below the singlet state at the D_2 structure (torsional angle 50°). However, at the D_2 geometry the singlet state is about 1 kcal/mol below the triplet state. Even if these results were consistent with the fact that EPR signal of TME can be observed, they are in variance with experimentally measured zero field parameters. Because the EPR spectrum shows no splitting between the *x*- and *y*-lines, Dowd et al. concluded that TME has D_{2d} structure at the triplet state.[6] Using the gas-phase negative ion photoelectron spectroscopy, Clifford et al. found that the singlet state of TME is about 2 kcal/mol below the triplet state.[7] These gas-phase results are inconsistent with previous matrix isolation EPR studies.[1,8] Clifford et al.[7] suggested that this discrepancy can be due to the fact that the matrix locks the TME at the triplet equilibrium structure at which the singlet state is above the triplet state. Recently, Filatov and Shaik[9] applied the spin-restricted open-shell Kohn−Sham (ROKS) and spin-restricted ensemble-referenced Kohn−Sham (REKS) methods for the triplet and singlet states of TME, respectively. They found that at this level of theory the singlet state of TME has minimum at D_{2d} geometry, at which the triplet state is about 3 kcal/mol above the singlet. The minimum for the triplet state was found for the D_2 structure (torsional angle 50.1°). At this geometry, the singlet and triplet states are almost degenerate. Filatov and Shaik also calculated the spin−orbit coupling matrix elements between the $^3B_1$ and ^1A states as a function of torsional angle and found that spin−orbit coupling is very weak. Thus, their results are in agreement with both matrix isolation experiments of Dowd[1] and gas-phase ion photoelectron spectra of Clifford et al.[7]

We have used the newly developed state-specific multireference Brillouin−Wigner version of coupled cluster method[12−14,16] which correctly accounts for both static and dynamic correlation energy contributions. Our goal is to test the suitability of this new computational approach for description of disjoint diradicals which are very demanding for proper and consistent accounting of correlation energy for singlet and triplet states. The results of this theoretical study are compared with available experimental data and with the ROKS/REKS results of Filatov and Shaik.

2. Computational Section

Multireference coupled cluster theories (MRCC) are believed to become the method of choice for treatment of systems where both static and dynamic electron correlation is important for adequate description. In this study, we used two different MRCC approaches: (i) the two-determinantal CC method with single and double excitations (TDCCSD) developed in Bartlett's group[10] and available in the ACES II program,[11] and (ii) a newly developed state-specific multireference Brillouin−Wigner CCSD method (BWCCSD)[12,13] recently implemented into the ACES II program package[14] and corrected for size-extensivity.[15−17] Within the latter method, two closed shell reference configurations are sufficient for the description of the TME molecule, because HOMO and LUMO orbitals have different point group

---

* Corresponding author.

† Part of this work has been done during this author's visit at the Quantum Theory Project, University of Florida, 2301 New Physics Building, P.O. Box 118435, Gainesville, FL 32611-8435.

‡ Also at Physics Institute, Silesian University, Opava, Czech Republic.

10.1021/jp0032199 CCC: $20.00

TABLE 1: Singlet and Triplet State Energies of the TME Computed for the MP2 Optimized Geometries of the Triplet by the MRCCSD, CCSD, and MRBWCCSD Methods Employing the cc-pVDZ(6d) Basis Set[a]

tw. angle deg	E_SMRBWCCSD a.u.	E_TCCSD a.u.	ΔE kcal/mol	E_STDCCSD a.u.	E_TTDCCSD a.u.	ΔE kcal/mol
0.0	−232.606713	−232.600333	4.0	−232.607615	−232.601275	4.0
	(−232.742097)	(−232.736274)	(3.7)			
15.0	−232.607095	−232.601642	3.4	−232.607932	−232.602526	3.4
30.0	−232.607651	−232.604271	2.1	−232.608306	−232.605022	2.1
	(−232.742392)	(−232.739924)	(1.6)			
45.0	−232.607967	−232.605924	1.3	−232.608478	−232.606468	1.3
	(−232.7424732)	(−232.741370)	(0.7)			
60.0	−232.608194	−232.605868	1.5	−232.608835	−232.606175	1.7
75.0	−232.608485	−232.605104	2.1	−232.609162	−232.605236	2.5
90.0	−232.608576	−232.604722	2.4	−232.609266	−232.604792	2.8
	(−232.743389)	(−232.739828)	(2.2)			

[a] The entries in parentheses are results obtained with the cc-pVTZ′ (6d) basis set (cc-pVTZ without *d*-functions at hydrogen and *f*-functions at carbon atoms).

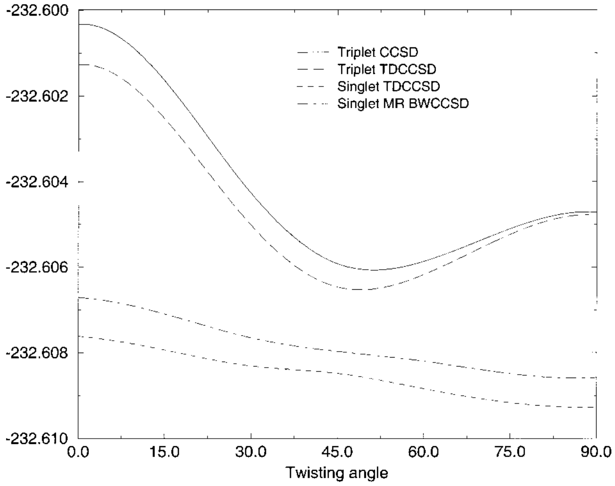

Figure 1. Potential energy curves for twisting of tetramethyleneethane, computed by the CCSD, TDCCSD, and MR BWCCSD methods.

symmetry. Because the TDCCSD method has been designed primarily for open-shell singlets, an orbital transformation has to be performed in the case of TME, which transforms the two relevant closed-shell reference configurations into open-shell ones, as described in ref 14. The calculations have been performed as follows: For each value of the twist angle, we performed a restricted geometry optimization at the MP2 level for the triplet state, using the MOLPRO package.[18] At the resulting geometries, MRCC calculations have been performed employing both aforementioned methods. The TDCCSD method computes both singlet (S) and triplet (T) state energies, while the BWCCSD calculation yields the singlet energy only. The triplet energy has been computed using the standard CCSD method, since the triplet state is well described by a single reference configuration. To compare both methods, the values of the S−T energy gap have been computed as differences of (i) TDCCSD S and T energies and (ii) BWCCSD S energy and CCSD T energy. The cc-pVDZ basis set with six Cartesian *d* functions has been employed, and only valence electrons have been correlated in this study. BWCCSD energies at some geometries were also calculated with the cc-pVTZ basis set.

3. Results and Discussion

The results of our calculations are summarized in Table 1, and the graphs of the potential energy (PE) curves obtained by the MRBWCCSD and TDCCSD methods are plotted in Figure 1.

Independent of the method employed, the PE curve of the singlet state has the minimum at 90 degrees, while the triplet PE curve has minimum at 49.0 or 51.4 degrees, for the single reference ROHF−CCSD and two-determinantal MRCCSD, respectively, which is only a marginal difference.

The singlet−triplet gaps have been computed as the difference between the singlet and triplet energies obtained by the two-determinantal CCSD method on one hand, and as the difference between the ROHF−CCSD energy of triplet and MR BWCCSD energy of the singlet, on the other hand. In the former case, the gap acquires its minimum value of 1.25 kcal/mol for the twisting angle of 46.7 degrees, whereas the latter approach yields 1.24 kcal/mol at 49.3 degrees. Figure 1 shows that the MR BWCCSD and TDCCSD PE curves are essentially the same. This brings additional evidence to our previous findings[16,17] that the deficiency of the MRBWCCSD theory − its size-inextensivity − may be eliminated by an a posteriori correction.[15,16]

In the whole range of twisting angles, the triplet state is higher in energy than the singlet state, again independent of the method. Since the geometry optimizations (for each particular value of twisting angle) have been performed for the triplet state, introducing thus a bias in the opposite direction, we come to the conclusion that the ground state of the TME diradical is singlet, in agreement with the experimental data on free radicals obtained by Ellison.[19]

The disagreement of this finding with the Paul Dowd EPR experiment[1] motivated us to recalculate the energies at twisting angle of 0, 30, 45, and 90 degrees with the cc-pVTZ′ basis set (see Table 1). The singlet−triplet energy gap at 45° was reduced from 1.3 kcal/mol to 0.7 kcal/mol, whereas the gap at 90° remained almost unchanged. It may be assumed that, on further basis set extension, the S−T energy gap at 45° would become even smaller. These results can also explain the differences between ROKS/REKS and CASPT2 S−T gaps at 45° twisting angle obtained by Filatov and Shaik[9]. The 6-311G** basis set used by these authors is not sufficient for CASPT2 (results are biased toward singlet), whereas DFT is not so sensitive to the quality of the basis set. It is therefore conceivable that the twisted D_2 structure, enforced by the matrix environment, might have a triplet ground state, in agreement with experimental observation.[1] It is, however, interesting to note that the BWCCSD energy of the singlet state, even in the cc-pVTZ′ basis set, decreases monotonically between 0° and 90°, in contrast to the DFT results[9], which exhibit a little maximum near the crossing with the PE curve of the triplet state.

4. Conclusions

The main results achieved in this paper can be summarized as follows: (1) The potential curves obtained for the singlet and triplet state of tetramethyleneethane are in accord with the results reported by Filatov and Shaik.[9] In this way the theoretical interpretation of experimental evidence on tetramethyleneethane, based on the DFT calculations, was confirmed by a rigorous MO approach based on the coupled cluster theory. (2) As with other molecules studied so far,[14,16,17] the state-specific BWCCSD theory provides energies that are close in absolute value to those obtained by the two-determinant CCSD method.[10] (3) For any twist angle, the singlet state is predicted to be below the triplet state. On extending the basis set from cc-pVDZ to cc-pVTZ′, the S−T gap at the optimum triplet geometry is reduced from 1.3 kcal/mol to 0.7 kcal/mol. However, it is not certain that on further basis set extension the triplet state will become lower in energy than the singlet state and that the reported crossing of singlet and triplet DFT potential curves[9] is realistic. In our opinion, a firm interpretation of the observed triplet state of matrix-isolated TME would need more rigorous calculations. In particular, we think that besides the basis set extension, the (approximate) inclusion of triple excitations into the MR BWCC method may have an important influence on the S−T gap at the optimum triplet geometry.

Acknowledgment. This work has been supported by the COST D9 action (Grant No. D9/0001/97 and Grant No. OC D9.10 of the Czech Ministry of Education) and by the Slovak Grant Agency for Science (Grant No. 1/4197/97). One of us (I.H.) acknowledges also the support by the Grant Agency of the Czech Republic (Grant No. 202/98/1028). One of us (J.P.) acknowledges the support by the Grant Agency of the Czech Republic (Grant No. 203/99/D009). He also thanks Professor R. J. Bartlett for kind hospitality during his stay at the Quantum Theory Project, University of Florida. We thank Professor R. J. Bartlett for providing us with the source code of the program ACES II, and members of his group, especially Dr. A. Perera, for kind assistance.

References and Notes

(1) Dowd, P. *J. Am. Chem. Soc.* **1970**, *92*, 1066.

(2) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4587.

(3) Du, P.; Borden, W. T. *J. Am. Chem. Soc.* **1987**, *109*, 930.

(4) Nachtigall, P.; Jordan, K. D. *J. Am. Chem. Soc.* **1992**, *114*, 4743.

(5) Nachtigall, P.; Jordan, K. D. *J. Am. Chem. Soc.* **1993**, *115*, 270.

(6) Dowd, P.; Chang, W.; Partian, C. J.; Zhang, W. *J. Phys. Chem.* **1993**, *97*, 13408.

(7) 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. 2* **1998**, 1015.

(8) Dowd, P.; Chang, W.; Paik, Y. H. *J. Am. Chem. Soc.* **1986**, *108*, 7416.

(9) Filatov, M.; Shaik, S. *J. Phys. Chem. A* **1999**, *103*, 8885.

(10) Balková, A.; Bartlett, R. J. *Chem. Phys. Lett.* **1992**, *193*, 364. Szalay, P. G.; Bartlett, R. J. *J. Chem. Phys.* **1994**, *101*, 4936.

(11) ACES II is a program product of Quantum Theory Project, University of Florida. Stanton, J. F.; Gauss, J.; Watts, J. D.; Nooijen, M.; Oliphant, N.; Perera, S. A.; Szalay, P. G.; Lauderdale, W. J.; Gwaltney, S. R.; Beck, S.; Balkova, A.; Bernholdt, D. E.; Baeck, K.-K.; Rozyczko, P.; Sekino, H.; Huber, C.; Bartlett, R. J. Integral packages included are vmol (Almloef, J.; Taylor, P. R.); vprops (Taylor, P. R.); and abacus (Helgaker, T.; Jensen, H. J. Aa.; Joergensen, P.; Olsen, J.; Taylor, P. R.).

(12) Hubač, I. In *New Methods in Quantum Theory*; NATO ASI Series; Tsipis, A.; Popov, V. S.; Herschbach, D. R.; Avery, J. S.; Kluwer: Dordrecht, 1996; pp 183−202.

(13) Mášik, J.; Hubač, I. In *Quantum Systems in Chemistry and Physics: Trends in Methods and Applications*; McWeeny, R., Maruani, J., Smeyers, Y. G., Wilson, S., Eds.; Kluwer Academic: Dordrecht, 1997; pp 282−308.

(14) Pittner, J.; Nachtigall, P.; Čársky, P.; Mášik, J.; Hubač, I. *J. Chem. Phys.* **1999**, *110*, 10275.

(15) Hubač, I.; Wilson, S. *J. Phys. B* **2000**, *33*, 365.

(16) Hubač, I. Pittner, J.;Čársky, P. *J. Chem. Phys.* **2000**, *112*, 8779.

(17) Sancho-García, J. C.; Pittner, J.; Čársky, P.; Hubač, I. *J. Chem. Phys.* **2000**, *112*, 8785.

(18) MOLPRO is a package of ab initio programs written by Werner, H.-J.; Knowles, P. J. with contributions from Almlöf, J.; Amos, R. D.; Berning, A.; Cooper, D. L.; Dee gan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Elbert, S. T.; Hampel, C.; Lindh, R.; Lloyd, A. W.; Meyer, W.; Nicklass, A.; Peterson, K.; Pitzer, R.; Stone, A. J.; Taylor, P. R.; Mura, M. E.; Pulay, P.; Schütz, M.; Stoll, H.; Thorsteinsson, T.

(19) 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.