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Multireference Brillouin−Wigner Coupled Cluster Singles and Doubles Study of the Singlet−Triplet Separation in Alkylcarbenes[†]

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Methylene, methylcarbene, dimethylcarbene, and methylethylcarbene were calculated by the multireference Brillouin−Wigner coupled cluster singles and doubles (MR BWCCSD) method with cc-pVDZ, cc-pVTZ, and also the cc-pVQZ basis set for methylcarbene. The calculations confirmed the trend predicted by previous calculations. In the series of methylene, methylcarbene, dimethylcarbene, and methylethylcarbene, the MR BWCCSD/cc-pVTZ singlet−triplet energy gap decreases as 10.18, 4.75, −0.82, −1.56 kcal/mol, respectively, where the minus sign means that the singlet is the ground state.

1. Introduction

Fritz Schaefer's papers on the ground-state geometry and the singlet−triplet splitting in methylene (for a review, see ref 1) are milestones in computational quantum chemistry. They marked the beginning of the "third age of quantum chemistry", in which theory by its increased credibility became a full partner with experiment. Schaefer and his collaborators also calculated methylcarbene[2,3] and dimethylcarbene.[4] We wish to express our tribute to Fritz Schaefer by our more rigorous calculations on the singlet−triplet splitting in alkyl-substituted methylenes, viz., methylcarbene, dimethylcarbene, and methylethylcarbene. We had in mind the following two objectives: Numerous derivatives of carbenes are reactive intermediates in chemical reactions (for the latest monograph, see ref 5), and a knowledge of their singlet−triplet energy gap can be useful in the elucidation of reaction mechanisms. It may also be useful to check the effect of different substituents on the singlet−triplet splitting in the parent carbene methylene by a theoretical model that was primarily developed for the treatment of systems with a quasi-degenerate electronic state.

The singlet−triplet energy gap of carbenes has been the subject of many experimental and theoretical studies. Methylene, the parent carbene, has been studied by a wide range of methods.[1,6−15] Substituted carbenes were also studied by various ab initio and density functional theory (DFT) methods. Carter and Goddard[7] performed GVB-CI and MC SCF calculations on $CH(SiH_3)$, CF_2, CCl_2CHF, and CHCl. Bolton and Schaefer[16] performed calculations of several types on nitromethylene, the CCSD(T)/TZ2P calculation being the most sophisticated. Worthington and Cramer[10] reported results of DFT calculations for CHF, CHCl, CHBr, CHI, and CF_2. Hu[12] performed DFT B3LYP and CCSD(T)/cc-pVTZ calculations on CHF, CHCl, CF_2, CFCl, CCl, $C(NO_2)H$, CH_3CH, and $C(CH_3)_2$. Recently, the singlet−triplet splitting in difluoro- and dichlorocarbenes was recalculated[17,18] with larger basis sets. The best results for alkyl-substituted carbenes obtained so far were calculated by the CCSD(T) method. The approximate inclusion of triples in the single-reference CCSD(T) seems to be adequate to account for static electron correlation by reproducing the observed singlet−triplet separation in methylene to within 1.3 kcal/mol[12] (with the cc-pVTZ basis set). However, we considered it expedient to attempt a more rigorous approach: the two-reference Brillouin−Wigner coupled cluster singles and doubles (TR BWCCSD) method developed by us[19,20] primarily for structures with a quasi-degenerate ground state.

For methylcarbene, the singlet−triplet splitting was calculated[2] to be lowered from 9 kcal/mol (in methylene) to about 4 kcal/mol. The singlet methylcarbene was predicted[3] to be a true intermediate. Dimethylcarbene and methylethylcarbene are known to be singlet carbenes.[4,10,12,22,21] More extended carbenes derived from cyclopentylidene are also predicted[24] to have singlet ground states. Further studies concerned the hydrogen migration in methylcarbene,[25] dimethylcarbene,[25,26] and methylethylcarbene[26,27] and carbon migration.

2. Theory

The multireference Brillouin−Wigner method has been described previously;[19,20] therefore, only a brief review is presented here.

Let the indices *i*, *j*, *k*... correspond to occupied orbitals, and let *a*, *b*, *c*... correspond to virtual orbitals. Furthermore, let the Greek indices μ, ν... correspond to the eigenstates of the unperturbed Hamiltonian.

The reference wave function Φ belongs to the model space spanned by *N* reference configurations Φ_μ.

$$\Phi = \sum_{\mu=1}^{N} C_\mu \Phi_\mu \tag{1}$$

The wave operator Ω is defined by

$$\Psi = \Omega\Phi \tag{2}$$

where Ψ is the exact wave function.

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Let P be the projection operator onto the model space. Then Φ is an eigenfunction of the effective Hamiltonian, where the corresponding eigenvalue is the exact energy E.

$$H^{\mathrm{eff}} = PH\Omega P \tag{3}$$

$$H^{\mathrm{eff}}\Phi = E\Phi \tag{4}$$

The wave operator Ω was taken in the form of the Jeziorski–Monkhorst ansatz

$$\Omega = \sum_{\mu=1}^{N} \mathrm{e}^{T(\mu)}|\Phi_\mu\rangle\langle\Phi_\mu| \tag{5}$$

where $T(\mu)$ is the cluster operator corresponding to the μ-th Fermi vacuum. In the case of CCSD,

$$T(\mu) = T_1(\mu) + T_2(\mu) \tag{6}$$

The wave operator fulfills the Brillouin–Wigner form of the Bloch equation

$$\Omega = 1 + BV\Omega \tag{7}$$

where V is the perturbation part of the Hamiltonian and B stands for the Brillouin–Wigner resolvent

$$B = \sum_\mu \frac{1 - P}{\epsilon - E_\mu} \tag{8}$$

Here, E_μ is the energy corresponding to the wave function Φ_μ. Contributions from internal excitations are excluded from the summation.

The matrix elements of the effective Hamiltonian are given as

$$H^{\mathrm{eff}}_{\mu\nu} = \delta_{\mu\nu}H_{\mu\mu} + \langle\Phi_\nu|H_N(\mu)\,\mathrm{e}^{T(\mu)}|\Phi_\mu\rangle \tag{9}$$

From the Bloch equation, we obtain

$$(\epsilon - H_{\mu\mu})\langle\Phi_q|\mathrm{e}^{T(\mu)}|\Phi_\mu\rangle = \langle\Phi_q|\,H_N\mathrm{e}^{T(\mu)}|\Phi_\mu\rangle \tag{10}$$

where Φ_q are excited configurations from $(1 - P)$ space.

Equations for cluster amplitudes are obtained by substituting $(\Phi_\mu)_i^a$ and $(\Phi_\mu)_{ij}^{ab}$ into eq 10.

$$(\epsilon - H^{\mathrm{eff}}_{\mu\mu})\,t_i^a(\mu) = \langle(\Phi_\mu)_i^a|\,H_N\mathrm{e}^{T(\mu)}|\Phi_\mu\rangle_{\mathrm{C}} \tag{11}$$

$$\begin{aligned}(\epsilon - H^{\mathrm{eff}}_{\mu\mu})\,\tau_{ij}^{ab}(\mu) &= \langle(\Phi_\mu)_{ij}^{ab}|\,H_N\mathrm{e}^{T(\mu)}|\Phi_\mu\rangle_{\mathrm{C}} \\ &\quad + \mathscr{P}(ij)\,\mathscr{P}(ab)\,t_i^a(\mu)\langle(\Phi_\mu)_j^b|H_N\mathrm{e}^{T(\mu)}|\Phi_\mu\rangle_{\mathrm{C}}\end{aligned} \tag{12}$$

where the index C denotes that only connected parts of these contributions are included. $\mathscr{P}(ab)$ is an antisymmetrization operator and

$$\tau_{ij}^{ab}(\mu) = t_{ij}^{ab}(\mu) + t_i^a(\mu)\,t_j^b(\mu) - t_i^b(\mu)\,t_j^a(\mu) \tag{13}$$

Because MR BWCCSD is not size-extensive, it is necessary to use a size-extensivity correction. In the case of an a posteriori correction, corrected cluster amplitudes are calculated from eqs 11 and 12 in a single additional iteration with the omission of size-inextensive terms. In the case of an iterative correction, a continuous transition is carried from Brillouin–Wigner toward the Rayleigh–Schrödinger approach.[28]

TABLE 1: $\Delta E_{\mathrm{S-T}}$ of Methylene (kcal/mol)

	basis set		
method[a]	cc-pVDZ	cc-pVTZ	cc-pVQZ
CCSD	12.59	11.67	11.01
CCSD(T)	11.84	10.77	9.98
CCSDT	11.64	10.54	
MR BWCCSD ap	11.60	10.30	9.50
MR BWCCSD it	11.57	10.18	9.33

[a] MR BWCCSD calculations were performed with a posteriori (ap) and iterative (it) size-consistency corrections.

3. Computational

Important reference configurations for carbenes are those that represent two electrons in the active space consisting of HOMO and LUMO orbitals ϕ_1 and ϕ_2 located on the carbenic center. Four spin-unrestricted reference configurations can be formed: $\Phi_1 = (\phi_1)^2(\phi_2)^0$, $\Phi_2 = (\phi_1)^0(\phi_2)^2$, and $\Phi_{3,4} = (\phi_1)^1(\phi_2)^1$, where the last two differ by the spin of the two electrons. However, except for systems of C_1 symmetry only two of these, Φ_1 and Φ_2, are required for the description of the singlet ground state.

MR BWCCSD calculations have been carried out only for the singlet state because the triplet state is a single-reference system. For a single-reference configuration, MR BWCCSD equations are identical to CCSD equations. For comparison, the singlet–triplet gap was also calculated by standard single-reference methods MP2, CCSD, CCSD(T), and also CCSDT for methylcarbene.

As found previously,[12,23] optimal geometries of the singlet states of methylcarbene and methylethylcarbene have C_1 symmetry. Therefore, in principle, four reference functions are needed. The importance of the singly excited reference configurations was studied by comparing energies obtained by spin-unrestricted four-reference and spin-restricted two-reference MR BWCCSD. The calculations on methylcarbene with the cc-pVTZ basis set showed that the difference was less than 1 μhartree; therefore, four-reference calculations were not attempted for other carbenes.

Both a posteriori and iterative correction on size-extensivity were used in MR BWCCSD.

Standard Dunning's correlation-consistent basis sets[29] cc-pVDZ, cc-pVTZ, and also cc-pVQZ for methylcarbene were used. For the largest system treated—methylethylcarbene—spherical Gaussians instead of a Cartesian were used.

For CCSD, CCSD(T), and MP2 calculations, the geometry was obtained with the respective method and basis set up to cc-pVTZ. Only for methylethylcarbene were the most highly polarized functions in the cc-pVTZ basis set dropped in optimization runs. Calculations in cc-pVQZ used geometries obtained by the respective method in the cc-pVTZ basis set. Calculations of singlet carbenes by MR BWCCSD were carried out at optimal CCSD geometries.

4. Results

4.1. Methylene. Methylene is included only for completeness to have consistent data for the series methylene, methylcarbene, dimethylcarbene, and methylethylcarbene. The calculated singlet–triplet energy gaps, hereafter denoted $\Delta E_{\mathrm{S-T}}$, are presented in Table 1.

4.2. Methylcarbene. The results of $\Delta E_{\mathrm{S-T}}$ for methylcarbene are given in Table 2. As found in previous studies, MP2 and CCSD methods give much higher values of the singlet–triplet

TABLE 2: ΔE_{S-T} of Methylcarbene (kcal/mol)

method[a]	basis set		
	cc-pVDZ	cc-pVTZ	cc-pVQZ
MP2[b]	9.53		
CCSD	7.40	6.26	5.31
CCSD(T)	6.96	4.53	3.81
CCSDT	6.08	4.49	
MR BWCCSD ap	6.50	4.89	4.10
MR BWCCSD it	6.40	4.75	3.94

[a] MR BWCCSD calculations were performed with a posteriori (ap) and iterative (it) size-consistency corrections. [b] MP2/cc-pVTZ and MP2/cc-pVQZ geometry optimizations of the singlet state failed because of a negative eigenvalue of the approximate Hessian.

TABLE 3: ΔE_{S-T} of Dimethylcarbene (kcal/mol)

method[a]	basis set	
	cc-pVDZ	cc-pVTZ
MP2	3.56	0.67
CCSD	2.72	0.60
CCSD(T)	1.32	−1.09
MR BWCCSD ap	1.88	−0.41
MR BWCCSD it	1.76	−0.82

[a] MR BWCCSD calculations were performed with a posteriori (ap) and iterative (it) size-consistency corrections.

TABLE 4: ΔE_{S-T} of Methylethylcarbene (kcal/mol)

method[a]	basis set	
	cc-pVDZ	cc-pVTZ
CCSD	2.11	−0.35
CCSD(T)	0.65	−2.11
MR BWCCSD ap	1.29	−1.36
MR BWCCSD it	1.14	−1.56

[a] MR BWCCSD calculations were performed with a posteriori (ap) and iterative (it) size-consistency corrections.

gap than more advanced methods such as CCSD(T) and CCSDT. The difference between CCSD and CCSDT is between 1.3 and 1.8 kcal/mol. The entries for MP2/cc-pVTZ and MP2/cc-pVQZ are missing in Table 2 because we did not succeed in obtaining the respective optimum geometry.

Multireference treatment lowers ΔE_{S-T} because of a better description of the singlet state. Values of the singlet−triplet separation obtained by MR BWCCSD are reduced, compared to those obtained by CCSD, by 0.9 to 1.5 kcal/mol. However, CCSD(T) predictions are still closer to CCSDT results than values obtained by MR BWCCSD in all basis sets except for cc-pVDZ. This is due to the insufficient inclusion of dynamical correlation in the MR BWCCSD method, assuming that CCSDT is the right standard in this case.

The type of size-extensivity correction used in MR BWCCSD calculations has a significant effect on the results. A posteriori correction gives higher values of ΔE_{S-T} than iterative correction by approximately 0.1 to 0.16 kcal/mol.

The size of the basis set has an important effect on the values of ΔE_{S-T} for all methods used. The difference between results in cc-pVTZ and cc-pVDZ is 1.2 to 1.75 kcal/mol, and the difference between cc-pVQZ and cc-pVTZ results is 0.7 to 1 kcal/mol, where the larger basis sets yield lower values of ΔE_{S-T}.

4.3. Dimethylcarbene and Methylethylcarbene. The results are summarized in Table 3 for dimethylcarbene and in Table 4 for methylethylcarbene. Similar trends to those in the case of methylcarbene were observed. Values of ΔE_{S-T} obtained by MR BWCCSD are significantly lower than CCSD results, where the difference is 0.7−1.5 kcal for dimethylcarbene and 0.9−1.2 kcal/mol for methylethylcarbene. However, for both systems MR BWCCSD values of the singlet−triplet separation are higher than CCSD(T) values by 0.25−0.55 kcal/mol for dimethylcarbene and 0.55−0.65 kcal/mol for methylethylcarbene.

TABLE 5: Multireference Character of Singlet Carbenes Measured by the Square of the Coefficient of the Reference Configuration Φ_2

	basis set	
	cc-pVDZ	cc-pVTZ
CH_2	0.0280	0.0360
CH_3CH	0.0245	0.0232
$(CH_3)_2C$	0.0204	0.0236
$CH_3(CH_3CH_2)C$	0.0182	0.0174

5. Conclusions

The results obtained in this paper by the MR BWCCSD method are consistent with the results of previous single-reference calculations[2,4,12,23] and available experimental evidence. The two-reference nature of the carbene states decreases in the series methylene, methylcarbene, dimethylcarbene, and methylethylcarbene, as can be seen from the coefficients of the second reference configuration for these systems shown in Table 5. This behavior is also reflected in the decreasing difference between the MR BWCCSD and CCSD energies. Also, as the weight of the second reference configuration decreases, CCSD(T) and CCSDT become more successful in substituting the multireference approach by means of the approximate or rigorous inclusion of connected triples. We have every reason to believe that carbenes with bulky substituents can be safely treated with chemical accuracy by single-reference methods, provided that a sufficiently large basis set is used, and ideally, connected triples are also included. It may be concluded that the MR BWCCSD method proved to be a reliable tool for predicting the energies of structures with a quasi-degenerate electronic state. We did not claim that MR BWCCSD is a superior method for general use. For systems with a single dominant reference configuration, CCSDT or even CCSD(T) performs better. However, if the weight of another configuration becomes comparable to the weight of the leading configuration, then single-reference methods (including CCSDT) fail. A typical case of such a failure is a potential curve representing the fission of a chemical bond (cf., for example, ref 11). In general, in applications to systems with a quasi-degenerate electronic state, MR BWCCSD seems to be the method of choice. If, however, both static and dynamic electron correlation are to be accounted for accurately, then the connected T_3 clusters should be included in the MR BWCC treatment. Work in this direction is now in progress.

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