Dimethylcarbene: A Singlet Ground State?

Claude A. Richards, Jr., Seung-Joon Kim,* Yukio Yamaguchi, and Henry F. Schaefer III

Contribution from the Center for Computational Quantum Chemistry, University of Georgia, Athens, Georgia 30602-2556

Received May 1, 1995®

Abstract: *Ab initio* molecular electronic structure theory has been used to determine the energy separation between the lowest $^3B_1$ and ^1A states of dimethylcarbene. The geometries of both states have been optimized at the self-consistent field (SCF) and the single and double excitation configuration interaction (CISD) levels of theory using the double-ζ plus polarization (DZP), the triple-ζ plus double polarization (TZ2P), and the TZ2P basis set with a set of higher angular momentum functions on the central carbon atom (TZ2P+f) basis sets. For singlet dimethylcarbene, structures have also been optimized using the two reference CISD method. Single point energies at the coupled cluster with single and double excitations (CCSD) and the CCSD with perturbative triple excitations [CCSD(T)] levels of theory were determined at the CISD equilibrium geometries with the same basis set. Harmonic vibrational frequencies and infrared (IR) intensities were determined for both states at the SCF level of theory using all three basis sets and at the CISD level of theory using the DZP and TZ2P basis sets. The energy separation between the lowest triplet state ($^3B_1$) and the lowest singlet state (^1A) for dimethylcarbene decreases with increasing basis set size and electron correlation. At the highest level of theory employed in this research, TZ2P+f CCSD(T), the singlet state is predicted to be lower in energy than the triplet state by 0.8 kcal mol^{-1}. This energy separation becomes 1.4 kcal mol^{-1} with the inclusion of zero-point vibrational energy (ZPVE) corrections.

Introduction

Carbenes are highly reactive divalent carbon intermediates that play an important role in organic chemistry.[1] They have two nonbonded electrons which can be paired (a singlet state) or unpaired (a triplet state or an open-shell singlet state). While many carbenes (:CR_2, R = X or H) have been isolated in cryogenic matrices and characterized spectroscopically,[2] few alkyl- and dialkylcarbenes have been successfully studied spectroscopically and they are even difficult to intercept with chemical traps. Alkylcarbenes are so evasive primarily because of their rapid intramolecular rearrangements, particularly the 1,2-hydrogen migrations.[3]

Ethylidene, or methylcarbene (:$CHCH_3$), is the simplest alkylcarbene which can undergo a 1,2-hydrogen migration to form ethylene. The barrier to hydrogen-migration rearrangement has been predicted via *ab initio* methods to be very small (0.6 kcal mol^{-1}) for singlet methylcarbene.[4] Even though there has been no direct observation of methylcarbene, it has been proposed as an intermediate in the photolysis of 3-methyldiazirine.[5] Recently, Seburg and McMahon,[6] while unable to observe methylcarbene spectroscopically, have succeeded in trapping singlet methylcarbene formed by the photolysis of matrix-isolated diazoethane (CH_3CHN_2) in a CO matrix. They proposed that the intersystem crossing (ISC) of the singlet methylcarbene to the triplet does not compete with the 1,2-hydrogen migration. More recently, Modarelli and Platz[7] also observed that laser flash photolysis (LFP) of the deuterated methyldiazirine, 3-methyldiazirine-d_4, produced a carbene–pyridine ylide via the interception of the singlet methylcarbene by pyridine. In 1992, Gallo reported[8] the singlet–triplet energy separation of methylcarbene to be 6.1 kcal mol^{-1}. Inclusion of the zero-point vibrational energy (ZPVE) correction reduced the energy separation by 0.9 kcal mol^{-1}, bringing their best estimate to 5 ± 1 kcal mol^{-1}. Given the small barrier to hydrogen migration rearrangement for the singlet state, intersystem crossing would not be competitive with isomerization for methylcarbene. The level of theory used in 1992 was configuration interaction with single and double excitations with Davidson's correction for unlinked quadruple excitations (CISD+Q).

While simple dialkylcarbenes could not be generated as persistent species, several dialkylcarbenes without αC–H bonds, such as di-*tert*-butylcarbene,[9] the first direct observation of a hydrocarbon dialkylcarbene, and diadamantylcarbene,[10,11] have been characterized spectroscopically. The spectroscopic characterization of the singlet dialkylcarbene, dicyclopropylcarbene produced by the irradiation of dicyclopropyldiazirine in N_2, has been reported recently.[12] This assignment was confirmed by trapping experiments using an Ar matrix doped with CO to produce dicyclopropylketene. This was the first singlet dialkylcarbene to have been characterized spectroscopically.

Dimethylcarbene (DMC) or 2-propylidene [:$C(CH_3)_2$] is the simplest dialkylcarbene and has not been found to be persistent

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* Present address: Department of Chemistry, HanNam University, Taejon, Korea 300-791.

® Abstract published in *Advance ACS Abstracts,* September 15, 1995.

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in low-temperature matrices. In 1991, Modarelli and Platz[13] obtained evidence suggesting that DMC is a true reactive intermediate which has a finite lifetime in solution. Using LFP techniques, Modarelli, Morgan, and Platz have investigated the possible pathways of the electronically excited singlet states of dialkyldiazirines in the production of DMC. They have observed that singlet DMC was trapped by pyridine to produce the carbene−pyridine ylide and that intersystem crossing (ISC) to the triplet state was competitive with the hydrogen migration.[14]

The singlet−triplet (S−T) energy separation of DMC is of special interest as a small energy gap could provide a pathway for ISC that would be competitive with the isomerization to propylene. Previous studies indicate that the S−T energy separation decreases along the series from methylene ($:CH_2$)[15,16] to methylcarbene,[8] suggesting that the S−T energy difference of DMC is very small, perhaps less than 1 kcal/mol if the series were to progress linearly. Earlier theoretical studies on the S−T energy separation of DMC have been performed only at relatively low levels of theory and it has been predicted to be 23.8 kcal/mol (or 14 ± 2 kcal/mol based on an assumed 10 kcal/mol drop with the inclusion of 3d orbitals)[17] and 32.2 kcal/mol[18] at the STO-3G SCF level of theory. In the present paper, the energy separation between the lowest $^3B_1$ and ^1A states of DMC is investigated at significantly higher levels of theory, employing larger basis sets and including an extensive treatment of electron correlation effects.

Theoretical Approach

Three basis sets, double-ζ plus polarization (DZP), triple-ζ plus double polarization (TZ2P), and TZ2P basis augmented with an additional set of f functions on the central carbon (TZ2P+f), have been employed in this research. The DZP basis set is a standard Huzinaga[19] and Dunning[20] double-ζ set of contracted Gaussian functions augmented with a set of six Cartesian d-like polarization functions on the carbons [$\alpha_d(C) = 0.75$] and a set of p-type polarization functions on the hydrogens [$\alpha_p(H) = 0.75$]. Thus the DZP basis set may be labeled C(9s5p1d/4s2p1d) and H(4s1p/2s1p). The hydrogen s functions were scaled by 1.2. The TZ2P basis set is again the standard Huzinaga[19] and Dunning[21] triple-ζ basis set of contracted Gaussian functions augmented with two sets of Cartesian d-like polarization functions on the carbons [$\alpha_d(C) = 1.50$; 0.375] and two sets of p-type polarization functions on the hydrogens [$\alpha_p(H) = 1.50$; 0.375]. The TZ2P basis set is designated as C(10s6p2d/5s3p2d) and H(5s2p/3s2p). The third basis set, TZ2P+f, is constructed by augmenting the TZ2P basis set with a set of ten Cartesian f-like polarization functions on the central carbon atom for the DMC. The higher angular momentum polarization function orbital exponent is $\alpha_f(C) = 0.80$.

In order to include electron correlation effects, the configuration interaction with single and double excitations (CISD), the coupled cluster method with all single and double excitations (CCSD), and CCSD with perturbative triple excitations [CCSD(T)] methods were employed. The CCSD and CCSD(T) single point energies are obtained at their respective CISD geometries with the same basis set. The three lowest molecular orbitals are kept doubly occupied and the three highest virtual orbital are deleted in all correlated procedures. A total of 201 129 configurations in C_{2v} symmetry for the $^3B_1$ state of DMC and 327 757 configurations in C_2 symmetry for the ^1A state of DMC were included in the correlation procedure with the TZ2P+f basis set. The Davidson procedure for correcting the energy of unlinked quadruple excitations[22] is also taken into account and the associated energies are denoted by CISD+Q.

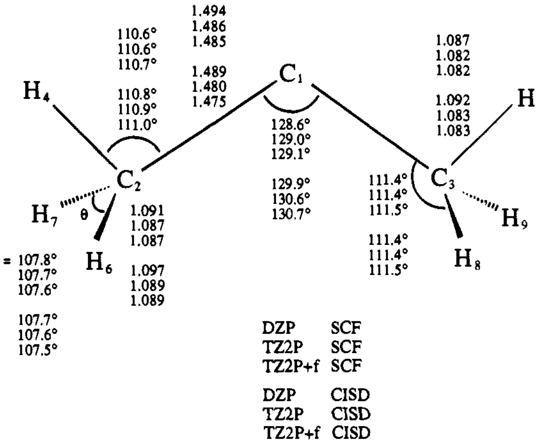

Figure 1. Predicted geometries for the lowest triplet state ($^3B_1$) of dimethylcarbene. Bond lengths are in Å and bond angles are in deg.

The structures of the lowest triplet state ($^3B_1$) and the lowest singlet state (^1A) of DMC are optimized using analytic gradient techniques[23] at the self-consistent field (SCF)[24] and single and double excitation configuration interaction (CISD)[25,26] levels of theory. The geometry of the ^1A state of DMC is also determined with the two-configuration SCF (TCSCF) and the two-reference CISD (TC-CISD) methods. The CI coefficients of the two configurations are 0.983 and −0.186 at the TZ2P+f TCSCF level.

Harmonic vibrational frequencies and infrared (IR) intensities for both states of DMC are evaluated for each basis set by analytic second energy derivative technique at the SCF level of theory,[27−29] while they were determined for the DZP and TZ2P basis sets via central finite differences of gradients[25,26] at the CISD level of theory. All computations were carried out with the PSI-2[30] suite of codes developed in our laboratory.

Results and Discussion

A. Geometry. The optimized geometries at the SCF and CISD levels of theory for the lowest triplet state ($^3B_1$) and the lowest singlet state (^1A) of dimethylcarbene are shown in Figures 1 and 2, respectively. The triplet state of DMC has C_{2v} symmetry as is shown in Figure 1. All the bond distances of the triplet state of DMC decrease in going from the DZP basis set to the TZ2P basis set at both the SCF and the CISD levels of theory. In going from the TZ2P basis set to the TZ2P+f basis set, only the C−C bond length decreases. This is to be expected, as the additional basis functions are located

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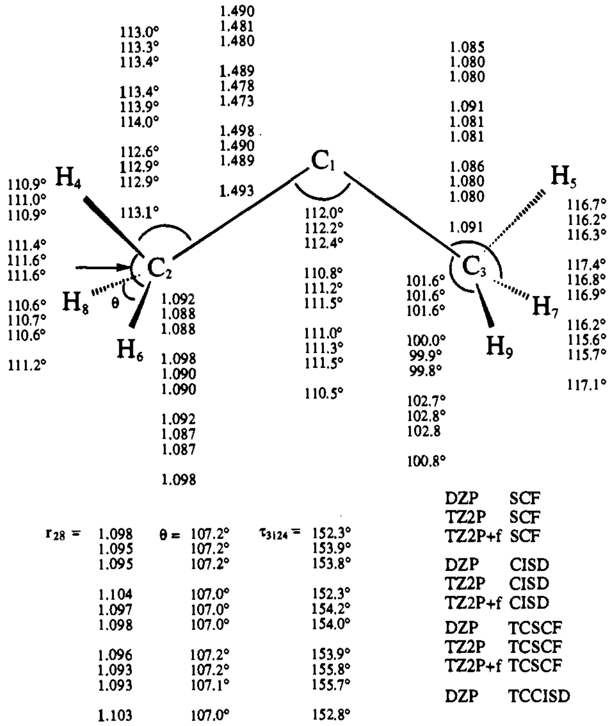

Figure 2. Predicted geometries for the lowest singlet state (^1A) of dimethylcarbene. Bond lengths are in Å and bond angles are in deg.

exclusively on the central carbon. The C−C−C bond angle at the TZ2P+f CISD level was found to be 130.7°, which is close to the value of 131.3° reported by Gallo and Schaefer[8] for triplet methylcarbene. This angle is significantly smaller than those found experimentally for the triplet states of diadamantylcarbene (152°, ref 10) and di-*tert*-butylcarbene (143°, ref 9). Such larger C−C−C bond angles would be expected for those extremely bulky substituents. The remaining three bond angles, the C−C−H (in plane), the C−C−H (out of plane), and the H−C−H angles, are relatively insensitive to the level of theory used. The largest deviation between different theoretical methods is only 0.4° for the C−C−H (in plane) bond angle.

The singlet state of DMC was found to be of C_2 symmetry, as is depicted in Figure 2. In the singlet state the methyl groups are rotated about the C−C bond by approximately 26° from the C_{2v} conformation. The rotation of the methyl groups also increases the interaction of a hydrogen on each of the methyl groups with the unoccupied p orbital on the central carbon so that they can donate electron density to the p orbital in a manner similar to the p donation described by Mueller *et al.*[31] This hyperconjugation of the two methyl groups stabilizes the singlet state relative to the triplet state. The rotation of the methyl groups reduces the repulsion between the sp^2 orbital on the carbene carbon and the hydrogens of the methyl groups. The sp^2 orbital on the carbene carbon is occupied by a lone pair in the singlet state and takes up more space. The C_2 conformation also reduces the repulsion between the hydrogens of the two methyl groups as they are brought together by the smaller C−C−C bond angle preferred by the singlet state. The singlet bond angle at the carbene carbon with the TZ2P+f CISD method was found to be 111.5°. The rotation of the methyl groups is not opposed by the half-occupied p orbital on the central carbon as it would be in the triplet case.

B. Harmonic Vibrational Frequencies and Infrared (IR) Intensities. The harmonic vibrational frequencies and infrared intensities for the triplet and singlet states at the SCF level of theory are presented in Tables A and B (supporting information), and those for the two states at the CISD level of theory are presented in Tables 1 and 2. The predicted SCF and CISD harmonic vibrational frequencies are expected to be about 10% and 5% higher than the experimental values.[32-35] Their real vibrational frequencies confirm that both structures correspond to potential minima.

Table 1. Harmonic Vibrational Frequencies (in cm^{-1}), Infrared Intensities (in km mol^{-1}), and Zero-Point Vibrational Energies (ZPVE, in kcal mol^{-1}) for the $^3B_1$ State of Dimethylcarbene at the CISD Level of Theory

			basis set	
mode	sym	approx assign	DZP	TZ2P
ω_1	a_1	CH str	3218(30)	3186(20)
ω_2	a_1	CH str	3099(22)	3076(27)
ω_3	a_1	Me bend	1535(3)	1537(4)
ω_4	a_1	Me bend	1463(1)	1456(1)
ω_5	a_1	Me rock	1182(4)	1170(2)
ω_6	a_1	CC s-str	873(3)	853(3)
ω_7	a_1	CCC bend	321(1)	319(1)
ω_8	a_2	CH str	3163(0)	3120(0)
ω_9	a_2	Me bend	1518(0)	1522(0)
ω_{10}	a_2	Me rock	988(0)	987(0)
ω_{11}	a_2	torsion	98(0)	126(0)
ω_{12}	b_1	CH str	3163(66)	3119(59)
ω_{13}	b_1	Me bend	1529(13)	1533(13)
ω_{14}	b_1	Me rock	1096(1)	1094(<1)
ω_{15}	b_1	torsion	148(4)	152(4)
ω_{16}	b_2	CH str	3217(11)	3185(11)
ω_{17}	b_2	CH str	3093(38)	3072(33)
ω_{18}	b_2	Me bend	1524(7)	1527(6)
ω_{19}	b_2	Me bend	1459(2)	1447(1)
ω_{20}	b_2	CC a-str	1328(1)	1301(1)
ω_{21}	b_2	Me rock	968(<1)	966(<1)
ZPVE			50.0	49.7

Table 2. Harmonic Vibrational Frequencies (in cm^{-1}), Infrared Intensities (in km mol^{-1}), and Zero-Point Vibrational Energies (ZPVE, in kcal mol^{-1}) for the ^1A State of Dimethylcarbene at the CISD Level of Theory

			basis set	
mode	sym	approx assign	DZP	TZ2P
ω_1	a	CH str	3234(15)	3212(9)
ω_2	a	CH str	3144(61)	3103(70)
ω_3	a	CH str	3071(14)	3042(8)
ω_4	a	Me bend	1561(2)	1558(1)
ω_5	a	Me bend	1466(1)	1465(3)
ω_6	a	Me bend	1400(7)	1394(10)
ω_7	a	Me rock	1213(4)	1196(<1)
ω_8	a	CC s-str	966(<1)	958(1)
ω_9	a	Me rock	711(<1)	719(<1)
ω_{10}	a	CCC bend	447(<1)	445(<1)
ω_{11}	a	torsion	258(5)	250(4)
ω_{12}	b	CH str	3232(26)	3210(23)
ω_{13}	b	CH str	3146(25)	3106(22)
ω_{14}	b	CH str	3066(1)	3036(2)
ω_{15}	b	Me bend	1557(9)	1554(13)
ω_{16}	b	Me bend	1466(6)	1468(6)
ω_{17}	b	Me bend	1414(59)	1402(48)
ω_{18}	b	CC a-str	1232(16)	1219(15)
ω_{19}	b	Me rock	1041(11)	1031(12)
ω_{20}	b	Me rock	763(14)	747(16)
ω_{21}	b	torsion	219(6)	231(5)
ZPVE			49.5	49.1

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Table 3. Absolute Energies (in hartrees) and Relative Energies (in kcal mol^{-1}) of the Lowest Triplet and Singlet States of Dimethylcarbene

	absolute energies		rel energies[a]
method	$T_0(^3B_1)$	$S_0^{SC}(^1A)$	$\Delta E(T_0-S_0^{SC})$
DZP SCF	−117.024 476	−116.999 057	−16.0 (−15.4)
TZ2P SCF	−117.040 678	−117.017 618	−14.5 (−13.8)
TZ2P+f SCF	−117.041 989	−117.018 776	−14.6 (−13.9)
DZP CISD	−117.404 615	−117.394 158	−6.6 (−6.1)
TZ2P CISD	−117.456 313	−117.448 466	−4.9 (−4.3)
TZ2P+f CISD	−117.468 810	−117.461 832	−4.4 (−3.8)
DZP CISD+Q	−117.448 394	−117.442 070	−4.0 (−3.5)
TZ2P CISD+Q	−117.505 787	−117.502 259	−2.2 (−1.6)
TZ2P+f CISD+Q	−117.519 758	−117.517 251	−1.6 (−1.0)
DZP CCSD	−117.451 376	−117.446 268	−3.2 (−2.7)
TZ2P CCSD	−117.509 654	−117.507 311	−1.5 (−0.9)
TZ2P+f CCSD	−117.523 785	−117.522 383	−0.9 (−0.3)
DZP CCSD(T)	−117.462 377	−117.459 381	−1.9 (−1.4)
TZ2P CCSD(T)	−117.525 467	−117.525 710	0.2 (0.8)
TZ2P+f CCSD(T)	−117.540 416	−117.541 648	0.8 (1.4)

[a] Relative energies in parentheses include zero-point vibrational energy (ZPVE) corrections. The zero-point vibrational energy corrections to the SCF energies are based on the vibrational frequencies determined at their respective equilibrium geometries while the ZPVE corrections for the correlated levels of theory are based on the single-configuration CISD frequencies using the DZP and TZ2P basis sets.

For the $^3B_1$ state of DMC, five CH_3 stretching and one bending mode are predicted to show relatively large IR intensities (> 10 km/mol). The IR intensities generally decrease with both an increase in the size of basis set and the inclusion of electron correlation effects. This reflects the general shortening of bond lengths with basis set augmentation and the opening of the C−C−C angle as well as the shortening of the C−C bond lengths with correlated levels of theory.

For the ^1A state of DMC, three CH_3 stretching and one CH_3 bending modes are predicted to present comparatively large IR intensities (> 20 km/mol). Again, the IR intensities generally decrease both with an increase in basis set size and with the inclusion of electron correlation effects, reflecting the general shortening of bond lengths with larger basis sets and the shortening of the C−C bond lengths with electron correlation. The C−C−C bending vibrational modes are predicted to have relatively small IR intensities for both states.

C. Energetics. The absolute and relative energies for the lowest triplet and singlet states of DMC are displayed in Tables 3 and 4. The energy separation decreases with an increase in the size of the basis set. The inclusion of correlation effects further decreases the energy separation between the two states. At the highest level of theory employed in this study, TZ2P+f CCSD(T), the energy separation is found to be 0.8 kcal/mol, with the singlet state lower in energy than the triplet. Inclusion of the zero-point vibrational energy (ZPVE) corrections to the energy differences brings the value for the singlet−triplet energy separation to 1.4 kcal/mol, with the singlet state again lying lower.

Table 4. Absolute Energies (in hartrees) and Relative Energies (in kcal mol^{-1}) of the Lowest Triplet and Singlet States of Dimethylcarbene[a]

	absolute energies		rel energies[b]
method	$T_0(^3B_1)$	$S_0^{TC}(^1A)$	$\Delta E(T_0-S_0^{TC})$
DZP SCF/TCSCF	−117.024 476	−117.017 143	−4.6 (−4.1)
TZ2P SCF/TCSCF	−117.040 678	−117.036 777	−2.4 (−1.8)
TZ2P+f SCF/TCSCF	−117.041 989	−117.038 507	−2.2 (−1.6)
DZP CISD/TC-CISD	−117.404 615	−117.400 716	−2.4 (−1.9)
DZP CISD+Q/TC-CISD+Q	−117.448 394	−117.445 254	−2.0 (−1.5)

[a] In this table only, the singlet state is described by two-configuration SCF wave functions or by two-reference CISD wave functions.
[b] Relative energies in parentheses include zero-point vibrational energy (ZPVE) corrections.

Concluding Remarks

The energy separation between the singlet and triplet states of dimethylcarbene has been studied using *ab initio* SCF, CISD, CCSD, and CCSD(T) levels of theory. The triplet state of DMC was found to have an equilibrium structure with C_{2v} symmetry, while the singlet state of DMC has a C_2 symmetry equilibrium geometry. In the singlet state the methyl groups were rotated about the C−C bonds by approximately 26° from the C_{2v} configuration. At the highest level of theory employed in this research, TZ2P+f CCSD(T), the energy separation between the lowest triplet and singlet states is predicted to be only 1.4 kcal mol^{-1}. This is consistent with the experimental observations of Modarelli *et al.*:[14] intersystem crossing would be expected to be competitive with both isomerization (1,2-hydrogen migration) and intermolecular reactions. This small energy separation between the two states would make both states accessible even at low temperatures and account for the effect of triplet scavengers in decreasing the yields of chemical trapping experiments.

Acknowledgment. The authors thank Dr. Buyong Ma and Dr. J. R. Thomas for their very helpful discussions. This research was supported by the Office of Basic Energy Sciences, Division of Chemical Sciences, Fundamental Interactions Branch, Grant DE-FG05-94ER14428.

Supporting Information Available: Tables of harmonic vibrational frequencies, infrared intensities, and zero-point vibrational energies for the $^3B_1$ and ^1A states of dimethylcarbene at the SCF level of theory (2 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA9514003