energy difference, which gives support to experimental observation and proposal that 2,5′-methyl substituents suppress 1–3 misinsertion.[10]

As to isotactic polymerization, methyl groups on the Cp rings favor one specific conformation of polymer chain end over the others by a margin of several (~6) kcal/mol. This fixed conformation of the polymer chain end in turn favors one primary insertion transition state over the other having opposite site stereochemistry by several (7–9) kcal/mol. This *indirect* stereocontrol mechanism, as illustrated in Scheme IV, is essentially same as that very recently proposed by Corradini and collaborators.[12,13] However, their proposal is based on a guess of transition state, which looks more like our olefin π-complex. As discussed for regioselectivity, the steric requirement of the π-complex is very different from that of the transition state. It is essential that one uses a reasonable transition state structure for comparison of steric energy.

A word of caution is in order even with regard to our transition state model. We have used without modification the main feature of the transition state structure determined for $(SiH_2Cp_2)ZrCH_3^+ + C_2H_4$, the catalyst with unsubstituted Cp rings and with CH_3 as the polymer chain end and the unsubstituted ethylene, and optimized the geometrical parameters of only the substituents on Cp groups, the chain end CH_3, and CH_3 of the olefin. The transition state structure should actually depend on the substituents. This must be the next step of improving our model. Efforts of optimizing the transition state structure in the MO–MM mixed approach have been made,[16] but some arbitrariness in such studies has been pointed out.[34]

Our model for syndiotactic polymerization is essentially the same as that for isotactic polymerization: the indirect control mechanism. We have suggested that SiR_2(FluCp) may be a good ligand for syndiotactic polymerization of propylene and 4-methyl-1-pentene.

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Advancing the Search for Cyclopropenylidenecarbene, the Exocyclic Ring Isomer of Diacetylene

Charlene L. Collins,[†,‡,||] Cynthia Meredith,[§,||] Yukio Yamaguchi,[||] and Henry F. Schaefer III*,[||]

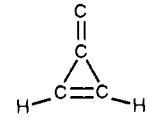
Contribution from the Department of Physics and Astronomy and Center for Computational Quantum Chemistry, University of Georgia, Athens, Georgia 30602. *Received April 23, 1992*

Abstract: Ab initio molecular electronic structure theory is used to determine the structure, harmonic vibrational frequencies, infrared (IR) intensities, rotational constants, and dipole moment of cyclopropenylidenecarbene ($:C{=}CC_2H_2$). These properties are investigated using double-ζ plus polarization (DZP) and triple-ζ plus double polarization function (TZ2P) basis sets at the self-consistent-field (SCF), configuration interaction with single and double excitations (CISD), and coupled cluster with single and double substitutions (CCSD) levels of theory. Based on the IR intensity profile and the large dipole moment (~5 D), we predict that this molecule is a good candidate for an astronomical search and for identification in the laboratory.

Introduction

As the quest for larger, more complex molecules in the interstellar medium continues, reliable information on some exotic species is needed. Carefully chosen theoretical methods provide accurate predictions of the physical observables of these species, thereby expediting the search.

Structural isomers of diacetylene (HC_4H) are currently of interest to astrophysicists. Although the nonpolar diacetylene has not yet been observed in the interstellar medium (ISM), Cernicharo, Gottlieb, Guēlin, Killian, Thaddeus, and Vrtilek have used a millimeter-wave spectral survey in the ISM to detect one isomer, butatrienylidene ($:C{=}C{=}C{=}CH_2$),[1] lying 43 kcal mol^{-1} (1.9 eV) above diacetylene.[2] Another isomer, cyclopropenylidenecarbene,



has been estimated to lie 81 kcal mol^{-1} (3.5 eV) above diacetylene and contains a three-membered carbon ring.[1] At present, it has neither been observed in the interstellar medium nor identified in the laboratory.

In 1981, Andrade, Chandrasekhar, and Schleyer obtained an ab initio geometry and energy for this ring isomer at the 6-31G*/SCF level of theory.[3] Although the theoretical results were illuminating, spectroscopists and astrophysicists require more accurate descriptions of the structural and physical properties of their target species. In the present work, high level ab initio methods are used to predict a reliable equilibrium geometry, harmonic vibrational frequencies, infrared (IR) intensities, rotational constants, and the dipole moment of cyclopropenylidenecarbene.

Theoretical Methods

This study investigates the salient physical features of cyclopropenylidenecarbene, using two basis sets and three theoretical methods. The basis set designated DZP is the standard Huzinaga–Dunning double-ζ basis contracted as C(9s5p/4s2p), H(4s/2s),[4,5] augmented by po-

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[†] Arnold Christian Wahl Graduate Fellow.

[‡] Department of Physics and Astronomy.

[§] Charles A. Coulson Graduate Fellow.

[||] Center for Computational Quantum Chemistry.

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Table I. Predicted Harmonic Vibrational Frequencies[a] and Infrared Intensities[b] of Cyclopropenylidenecarbene

			DZP			TZZP
symm species	no	assignment	SCF	CISD	CCSD	SCF
a_1	ω_1	CH str	3510	3448	3376	3497
			(11)	(10)	(9)	(11)
	ω_2	C_1C_2–C_3C_4 str	1952	1899	1835	1945
			(1)	(9)	(17)	(<1)
	ω_3	C_1C_2 + C_3C_4 str	1647	1621	1579	1641
			(23)	(81)	(107)	(26)
	ω_4	HCC i/p bend	1081	1032	1002	1080
			(<1)	(<1)	(2)	(<1)
	ω_5	C–C str	913	870	836	903
			(<1)	(<1)	(<1)	(<1)
a_2	ω_6	CH o/p bend	929	824	749	926
			(0)	(0)	(0)	(0)
b_1	ω_7	CH o/p bend	754	678	624	759
			(67)	(62)	(60)	(62)
	ω_8	ring deformation	449	396	360	449
			(9)	(9)	(8)	(6)
b_2	ω_9	CH str	3457	3395	3325	3444
			(26)	(25)	(20)	(25)
	ω_{10}	HCC i/p bend	1125	1045	1003	1132
			(21)	(19)	(18)	(21)
	ω_{11}	C–C str	974	877	810	950
			(1)	(<1)	(<1)	(<1)
	ω_{12}	i/p C_3C_4 bend	252	198	179	251
			(4)	(4)	(3)	(6)

[a] In cm^{-1}. [b] In km mol^{-1}. Infrared intensities given in parentheses.

Table II. Predicted Rotational Constants and Dipole Moments of Cyclopropenylidenecarbene

	rotational constants, cm^{-1}			dipole moment,
level of theory	A_e	B_e	C_e	D
DZP SCF	1.120	0.279	0.223	5.01
DZP CISD	1.099	0.274	0.219	4.81
DZP CCSD	1.081	0.269	0.215	4.69
TZ2P SCF	1.140	0.282	0.226	5.12
TZ2P CISD	1.127	0.278	0.223	4.98
TZ2P CCSD	1.110	0.273	0.219	4.88

larization functions with orbital exponents $\alpha_p(H) = 0.75$ and $\alpha_d(C) = 0.75$. For the DZP basis set, the hydrogen s functions are scaled by a standard factor of 1.2. The other basis set, designated TZ2P, is the Huzinaga–Dunning triple-ζ basis contracted as C(10s6p/5s3p), H(5s/3s),[6] augmented by two sets of polarization functions with orbital exponents $\alpha_p(H) = 0.375, 1.5$ and $\alpha_d(C) = 0.375, 1.5$. Sets of six Cartesian d-like functions are used throughout. Geometries are fully optimized in C_{2v} symmetry at all levels of theory using the gradient technique of Pulay.[7] Residual Cartesian and internal coordinate gradients are in all cases less than 10^{-6} au. Self-consistent-field (SCF) gradients and second derivatives are evaluated analytically.[8,9] For the correlated methods—namely, configuration interaction with single and double excitations (CISD)[10] and coupled cluster with single and double substitutions (CCSD)[11]—gradients are obtained analytically and second derivatives are computed by central finite differences of analytic gradients. Note that the vibrational frequencies thus determined are harmonic and therefore should not be directly compared with experimentally determined fundamental (anharmonic) frequencies.

In the CISD and CCSD methods, only the valence electrons are explicitly correlated—that is, the four lowest occupied (C 1s-like) molecular orbitals are held doubly occupied (frozen cores) and the four highest lying virtual (C 1s*-like) orbitals are excluded (deleted virtuals) from the CISD and CCSD procedures. Otherwise, all single and double excitations from the SCF reference configuration are included. The highest level of theory, TZ2P/CCSD, includes 119 452 single and double excitations in the optimization. All correlated methods use a single configuration SCF wavefunction as the reference configuration.

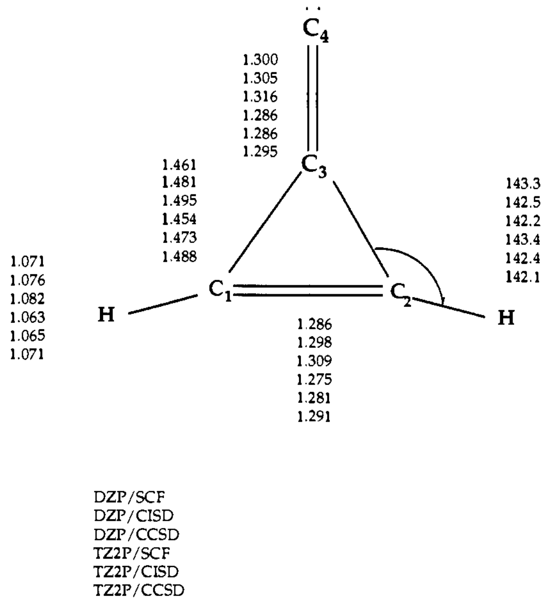

Figure 1. Equilibrium structures of cyclopropenylidenecarbene at six levels of theory (bond lengths in Å).

Results and Discussion

Figure 1 depicts the optimized equilibrium geometries at six levels of theory for cyclopropenylidenecarbene. Table I contains predictions for the harmonic vibrational frequencies and IR intensities at all but the highest levels of theory (TZ2P/CISD and TZ2P/CCSD), and Table II displays theoretical estimates of the rotational constants and dipole moment at all levels of theory.

In general, the geometries show the typical trends of bond lengths decreasing with larger basis set size and increasing with higher correlation level.[12-14] The H–C_2–C_3 angle decreases

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slightly with higher levels of theory.

From the internuclear distance, a qualitative description of a bond can be determined. For example, the C_1–C_2 and C_3–C_4 distances are predicted to be 1.291 and 1.295 Å, respectively, at the TZ2P/CCSD level of theory. Although slightly shorter than the prototypical C–C double bond length of ethylene, $r_e = 1.330$ Å,[15] each is characterized as a double bond. The distance between the C_1 and C_3 nuclei is determined to be 1.488 Å at this level of theory. Since this is close to the typical value of the C–C single bond length for cyclopropane, $r_0 = 1.510$ Å,[16] the C_1–C_3 linkage is considered to be a single bond.

The harmonic vibrational frequencies shown in Table I are consistent throughout the levels of theory investigated. However, the CH out-of-plane a_2 bend (ω_6) becomes lower in frequency than the C–C a_1 stretch (ω_5) when electron correlation is included. According to the normal coordinate analysis, the C_1–C_2 and C_3–C_4 double bond stretchings are found to couple strongly (almost 50/50 mixing) with each other. The values of 1899 and 1621 cm^{-1} (DZP/CISD) for the combinations of these stretches fall within the range of double bond harmonic stretching vibrational frequencies.

The infrared intensities remain reasonably consistent as well, with the exception of the $C_1C_2 + C_3C_4$ a_1 stretch (ω_3). While the SCF wavefunctions predict moderate intensities for the ω_3 mode, correlated methods indicate that this mode exhibits the strongest intensity. In addition, the CH out-of-plane b_1 bend (ω_7) has a relatively strong intensity.

An encouraging sequence of events occurred in the mid 1980s when ab initio studies[17] aided the laboratory identification[18] and, subsequently, the astronomical observation[19] of cyclopropenylidene (:CC_2H_2). In the experimental study several band frequencies, including the CH out-of-plane b_1 bend ($\nu = 789$ cm^{-1}), were matched with theoretical frequencies (b_1 bend, $\omega = 854$ cm^{-1} and $I = 53$ km mol^{-1}, DZP/SCF) to identify this molecule. The success of this search supports our prediction that the CH out-of-plane b_1 bend (ω_7) may be used to identify cyclopropenylidenecarbene (:$C{=}CC_2H_2$). Theoretical investigations of a related structure, silacyclopropenylidene (:SiC_2H_2),[20,21] indicate that it has several detectable modes. The CH out-of-plane b_1 bend of :SiC_2H_2 is particularly intense (740 cm^{-1} and 67 kcal mol^{-1}, TZ2P/CISD),[20] a finding that is similar to our results for :$C{=}CC_2H_2$. Due to its large IR intensity, the previously mentioned $C_1C_2 + C_3C_4$ stretch ω_3 at 1621 cm^{-1} (DZP/CISD) is another attractive choice.

The theoretical estimates given in Table II indicate that the dipole moment is approximately 5 D, a value significantly higher than that of either cyclopropenylidene (3.3 D)[22] or silacyclopropenylidene (1 D).[20] In cyclopropenylidenecarbene, the distance (along the C_2 axis) between the hydrogens and the lone pair is much greater than in the other two systems, contributing to these differences. The values of each rotational constant remain within a range of 0.041 cm^{-1} throughout the levels of theory. Our recommended equilibrium rotational constants are those from the highest level of theory, namely, $A_e = 1.110$, $B_e = 0.273$, and $C_e = 0.219$ cm^{-1} (TZ2P/CCSD).

Conclusions

With large basis sets and high-level theoretical methods, the structure and physical properties of the exocyclic ring isomer of diacetylene, cyclopropenylidenecarbene (:$C{=}CC_2H_2$), are predicted. Several of the vibrational frequencies appear to have IR intensities strong enough for detection. Moreover, cyclopropenylidenecarbene has a large dipole moment, raising the hope that experimental and astronomical investigations will soon meet with success.

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Communications to the Editor

Palladium-Catalyzed Tandem Cyclization of 4,6- and 5,7-Diene Amides. A New Route toward the Pyrrolizidine and Indolizidine Alkaloids

Pher G. Andersson* and Jan-E. Bäckvall*

Department of Organic Chemistry
University of Uppsala, Box 531
S-751 21 Uppsala, Sweden

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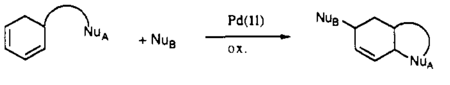
A few years ago we developed several palladium-catalyzed 1,4-oxidations of conjugated dienes which allow the regio- and stereoselective addition of nucleophiles to the 1- and 4-positions of the 1,3-diene.[1,2] These reactions, which proceed via (π-allyl)palladium intermediates, were recently extended to intramolecular variants which give access to a number of heterocyclic systems (eqs 1 and 2).[3,4]



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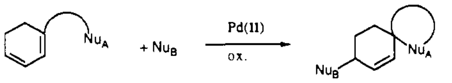

(2)

A further extension of the intramolecular reaction would be to use a nucleophile with the ability of making a 2-fold attack

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