

Propargylene

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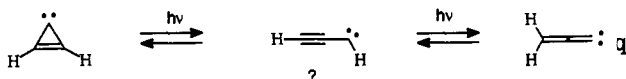
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Received December 31, 1993*

Abstract: A theoretical investigation has been performed on triplet and singlet propargylene (C_3H_2 , ethynylcarbene) using various levels of ab initio theory (MP2, MP4, QCISD, QCISD(T), and multireference CI). According to the results, and in contradiction to earlier calculations, neither the singlet nor the triplet propargylene is a carbene. Vibrational frequencies of the 1,3-diradicaloid C_2 structure of triplet propargylene are in much better agreement with experiment than those of the C_1 carbene structure. The hitherto assumed transition state (C_{2v}) of the singlet propargylene automerization is a minimum, and the singlet (like the triplet) carbene structure (C_2) is not a stationary point on the energy hypersurface at the QCISD(T)/6-31G* level. The singlet–triplet gap is much larger than previously assumed, and the rotational lines of triplet propargylene are shifted to lower frequencies compared to earlier calculation.

Introduction

There are three C_3H_2 isomers that have been thoroughly investigated by both experiment and theoretical calculations: cyclopropenylidene, propargylene, and vinylidenecarbene. Carbene-like structures have been attributed to the ground states.



Cyclopropenylidene and vinylidenecarbene are singlet ground states, and propargylene has a triplet ground state. Maier et al. have shown that the three can be interconverted in matrix by photolysis using light of different wavelengths.^{1,2} The two singlet C_3H_2 species are abundant in molecular clouds in interstellar space.^{3–6} Their characteristic rotational lines were identified by radio astronomy. Even though both singlet carbenes can be easily isomerized to propargylene by irradiation, propargylene could not be detected in space so far.

There have been numerous attempts to determine the structure of propargylene. Trapping experiments, spectra, and theoretical calculations, however, contradict.

The triplet ground state of propargylene has been identified by ESR,⁷ and a quasilinear or linear geometry was postulated on the basis of the zero-field splitting parameters. IR spectra of propargylene^{8,9} and deuterated derivatives⁹ were recorded in matrix and were interpreted in favor of a rapidly automerizing carbene-like C_1 structure. The electronic spectrum measured in the gas phase suggests a linear structure.¹⁰

* Abstract published in *Advance ACS Abstracts*, August 1, 1994.

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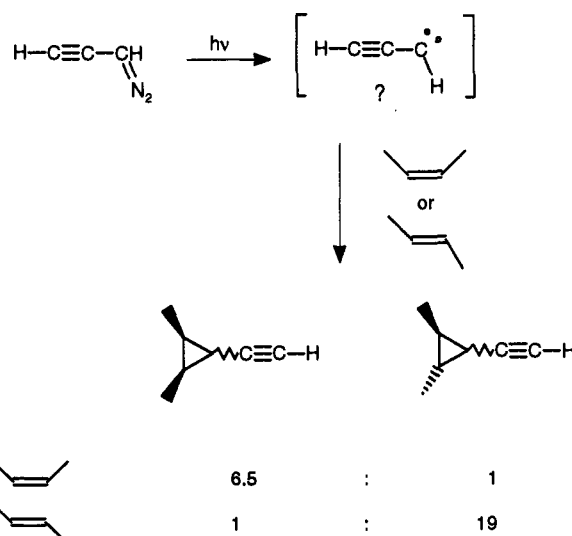


Figure 1.

Propargylene was first generated in 1960 by Skell and Klebe by photolysis of diazopropene.¹¹ Trapping reactions with *cis*- and *trans*-butene gave cyclopropanes with partial loss of stereospecificity (Figure 1). This has been interpreted as a partial spin relaxation of the generated singlet propargylene to the triplet state, the singlet carbene reacting with retention and the triplet with loss of stereochemistry of the olefin.

Trapping reactions of labeled propargylene (tritium-labeled at C1) indicate that both carbon atoms C1 and C3 have equal reactivity in the triplet state.¹² Similar observations have been made in substituted systems:¹³ Boyer and Selvarajan generated (phenylethynyl)methylene by photolyzing the corresponding ketene precursor. The trapping products with hydrocarbons, however, are derived from the isomeric (phenylethynyl)carbene.¹⁴ Similarly, (phenylethynyl)nitrene obviously rearranges to (phenylcyano)carbene before being trapped.¹⁵ Diethynylcarbenes in

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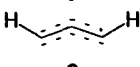
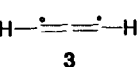
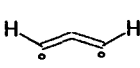



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Table 1. Single Determinant *ab Initio* Energies (in au) and Number of Imaginary Modes of Seven Different Propargylene Structures

structure	symmetry	multiplicity	6-31G*	MP2/ 6-31G*	MP4 (SDTQ) 6-31G*	PMP4 ^a (SDTQ) 6-31G*	QCISD/ 6-31G*	QCISD (T)/ 6-31G*	QCISD ^b 6-31+G*	QCISD ^b (T)/ 6-31+G**	QCISD ^b (TQ)/ 6-31+G**	ZPE QCISD/ 6-31G*
	C_s	singlet	-114.571 87 0	-144.931 47 0	-114.962 83 0		-114.961 40	<i>c</i>	-114.972 86	-114.991 77	-114.991 64	0.028 32
	C_{2v}	singlet	-114.565 18 1	-114.927 75 1	-114.961 50 1		-114.960 09 1	-114.966 19	-114.971 74	-114.992 16	-114.992 00	0.027 55
	$D_{\infty h}$	triplet	-114.629 67 4	-114.939 29 4	-114.970 99 4	-114.986 50	-114.973 04 4	-114.986 51 4	-114.995 87	-115.010 33		
	C_{2v}	triplet	-114.631 89 1	-114.939 85 2	-114.971 92 2	-114.988 14	-114.974 78 2	-114.988 52 1	-114.997 29	-115.012 01	-115.012 84	0.025 30
	C_{2h}	triplet	-114.631 14 2	-114.939 56 2	-114.971 50 2	-114.987 62	-114.974 22 2	-114.987 91 2	-114.996 78	-115.011 44		0.025 31
	C_2	triplet	-114.632 29 0	-114.939 95 1	-114.972 10 1	-114.988 37	-114.975 17 0	-114.989 01 0	-114.997 68	-115.012 47	-115.013 31	0.026 74
	C_s	triplet	<i>c</i>	-114.940 31 0	-114.972 15 0	-114.987 89	<i>c</i>	<i>c</i>	-114.996 77	-115.011 26	-115.012 01	0.026 23

^a Spin-corrected values. ^b Single-point energy calculations on QCISD/6-31G* optimized geometries. ^c Structure is not a stationary point.

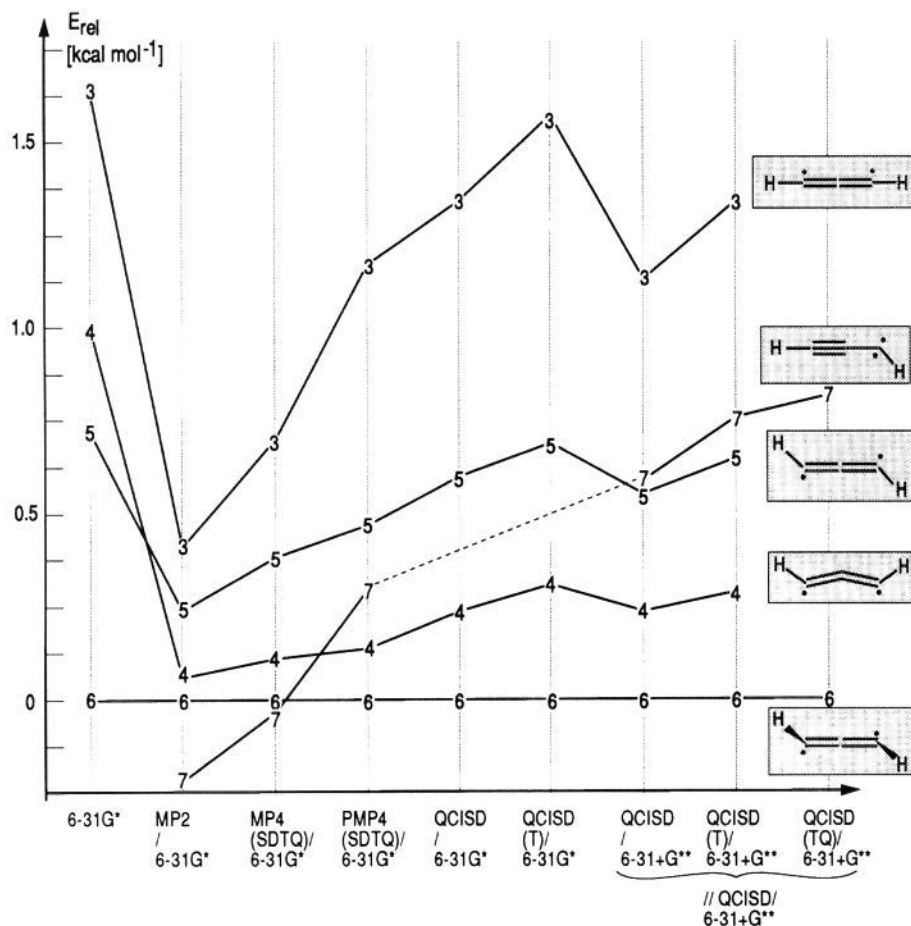
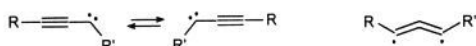


Figure 2. Relative energies of triplet propargylene structures 3–7 (in kcal/mol) at different levels of ab initio theory. The values are based on the C_2 structure 6. The carbene-like structure 7 is not a stationary point at UHF/6-31G* and at the QCISD levels. The single-point calculations QCISD/6-31+G**, QCISD(T)/6-31+G**, and QCISD(TQ)/6-31+G** of 7 are therefore based on the MP4/6-31G* optimized geometry.

the absence of trapping reagents dimerize to give all three conceivable products formally derived from 1,3-carbene shifts.¹⁶ In vinyl-substituted propargylenes, both isomeric carbenes are trapped, the ratio depending on the substituents.¹⁷

In principle, there are two alternatives that comply with these results: (1) molecules with localized carbene lone pairs that undergo a rapid 1,3-carbene shift (bond-shift) reaction or (2) 1,3-diradicaloid structures.



The propargylene problem has also been addressed by theoretical calculations. The first ab initio calculation of Hehre et al. at the (very low) STO3G level predicts a C_2 symmetrical structure.¹⁸ More recent calculations at higher levels of ab initio theory (e.g., UMP2 and UMP4), however, consistently favor a carbene-like C_s structure.^{9,19–22} Hence, this has generally been accepted as the structure of propargylene. According to our studies, however, these calculations consistently suffer from a very high spin contamination in the UHF wave function.

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Therefore, we decided to reinvestigate the structure of triplet propargylene at adequate levels of theory.

Very few theoretical investigations were performed on the singlet hypersurface of propargylene.^{21,22} No alternative to the generally and intuitively assumed ethynylcarbene structure was examined.

According to our theoretical studies, however, both the singlet and the triplet C_s structure of propargylene proved not to be minima or even stationary points on the energy surface at higher levels of theory.

Theoretical Approach

Singlet carbenes and, moreover, highly unsaturated systems give rise to notorious problems in single determinant ab initio calculations, since higher configurations significantly contribute to the overall wave function. To account for the large correlation energies, we performed calculations using different methods for treating electron correlation: (1) single determinant calculations with perturbational treatments of the correlation energy using the Møller–Plesset approach²³ (MP2 and MP4); (2) quadratic configuration interaction with single and double excitations and perturbational treatment of triple and quadruple excitations²⁴ (QCISD(T) and QCISD(T,Q)); and (3) multireference CI calculations (MRD-CI).^{25,26} The description of the basis sets follows the notation of Binkley, Pople, and Hehre.²⁷ GAUSSIAN92²⁸ and CADPAC²⁹ were

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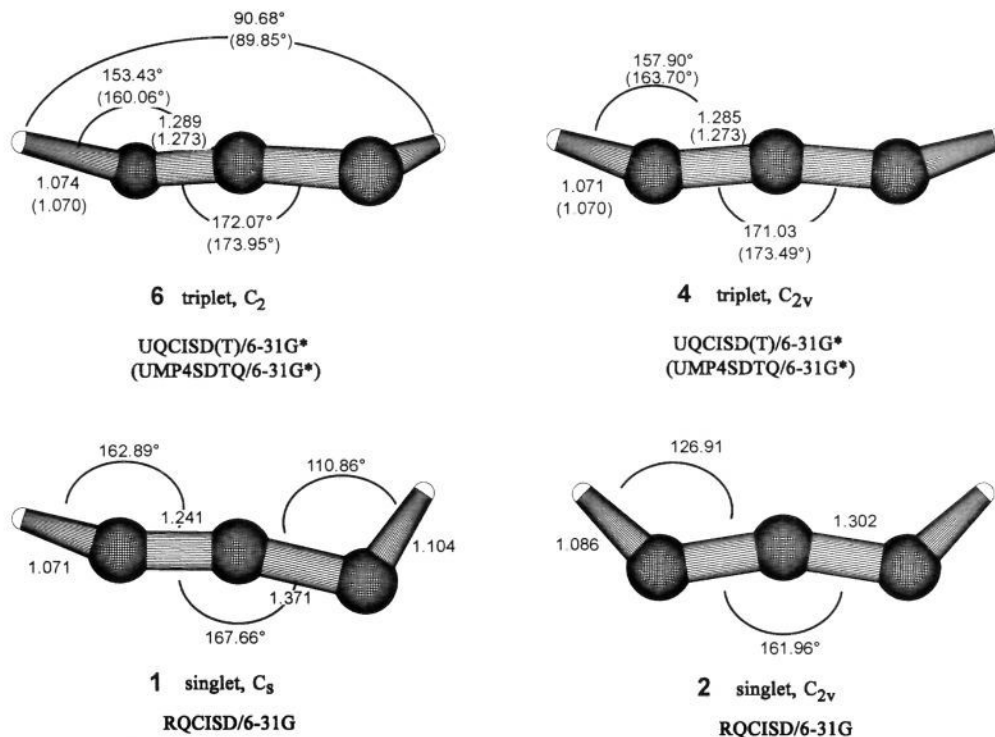


Figure 3. Ab initio calculated geometries of propargylene structures 1, 2, 4, and 6. UMP4SDTQ/6-31G* values are given in parentheses.

Table 2. Results and Details of MRD-CI Calculations of Structures 6, 7, 1, and 2

basis set/ structure	symmetry	multiplicity	no. of reference functions	size of CI matrix ^a	E_{MRD} (au)	C^2 ^b	E_{FCI}^c (au)
6-31G*							
6	C_2	triplet	8	17 863	-114.935 75	0.892	-114.971 16
7	C_{2v}	triplet	9	17 863	-114.941 24	0.901	-114.973 09
6-311G**							
6	C_2	triplet	10	17 837	-114.991 52	0.895	-115.028 04
7	C_{2v}	triplet	12	17 811	-114.992 94	0.895	-115.029 63
6-311G(2p,2d)							
6	C_2	triplet	6	17 969	-115.007 94	0.884	-115.052 32
7	C_{2v}	triplet	10	17 941	-115.006 79	0.899	-115.043 00
6-31G*							
1	C_s	singlet	6	17 134	-114.919 03	0.892	-114.953 28
2	C_{2v}	singlet	9	17 884	-114.924 36	0.897	-114.956 65

^a Number of symmetry adapted configuration state functions that have been selected at the threshold energy of 2×10^{-5} au. ^b Contributions of the references space to the total MRD-CI expansion. ^c Extrapolated full CI values (see refs 25, 26).

used for single reference and Peyerimhoff's MRD-CI program³⁰ for multireference CI calculations. The number of reference configurations for different structures was 6–12 to generate 17 811–18 969 symmetry-adapted configuration-state functions.

Results and Discussion

Triplet Propargylene. A reinvestigation of the triplet propargylene calculations recently performed at the UHF, UMP2, and UMP4 levels revealed a very high spin contamination of the UHF wave function. At the UMP2/6-31G* and UMP4/6-31G* levels, we found values for $\langle S^2 \rangle$ of 2.365 and 2.386 (the expectation value for $\langle S^2 \rangle$ of a pure triplet is 2.0). If Schlegel's spin-projection method³¹ is used for annihilation of the spin contamination (PMP4/6-31G*), the singlet–triplet gap of propargylene increases from 5.8 to 15.7 kcal/mol. Consequently, the results published

for UHF, UMP2, and UMP4 methods are not reliable and were reinvestigated. The quadratic configuration interaction method (QCI) is less sensitive toward spin contamination³² and was therefore applied using different levels of excitation. In order to obtain a consistent picture, we systematically increased the basis set as well as the level of correlation treatment from UHF, UMP2, UMP4, QCISD, and QCISD(T) to QCISD(TQ) and optimized seven conceivable structures (1–7) of propargylene of different symmetry on the singlet and triplet hypersurfaces. We performed 59 geometry optimizations and obtained 30 stationary points. Each was checked by harmonic frequency analysis. Single-point energy calculations on the six stationary points at the QCISD/6-31G* level and the triplet structure 7 at the UMP4/6-31G* level were performed on the QCISD, QCISD(T), and QCISD(TQ) levels with a 6-31+G** basis. The absolute energies and the number of imaginary frequencies are given in Table 1. Figure 2 gives a graphical representation of the results. The relative energies of the triplet structures are plotted as a function of the theoretical level used for computation. The geometries of the two most stable singlet and triplet species are depicted in Figure 3.

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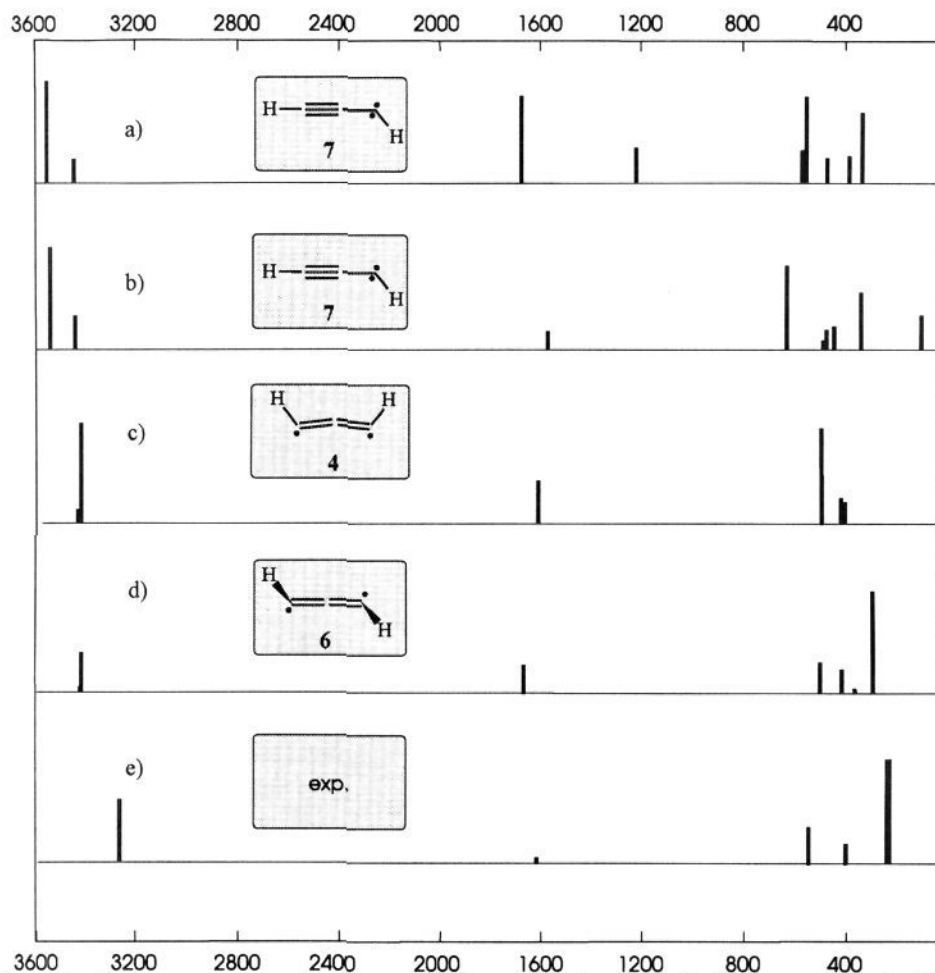


Figure 4. Ab initio calculated IR spectra of propargylene structures and experimental spectrum of triplet propargylene. Positions and heights of bars indicate frequency and relative intensity of absorption bands. (a) UMP2/6-31G** harmonic frequencies of C_s structure 7 (ref 9). (b) Spectrum of a corrected by an anharmonic model (ref 9). (c) QCISD/6-31G* harmonic frequencies of the triplet C_{2v} structure (uncorrected). (d) QCISD/6-31G* harmonic frequencies of the triplet C_2 structure (uncorrected). (e) Experimental spectrum.

Based on the results given in Table 1 and Figure 2, the following conclusions can be drawn. The hitherto assumed triplet C_s structure 7 is not a stationary point at the UHF (6-31G*) nor at the QCI levels (QCISD/6-31G*, QCISD(T)/6-31G*). It seems to be an artifact of the Møller–Plessett treatment. The linear structure 3 that has been predicted by ESR and UV has four imaginary frequencies and therefore also is ruled out as a plausible candidate for triplet propargylene. The C_{2h} structure 5, for which consistently two imaginary frequencies were found at all levels, also is unlikely. The global minimum at all levels except UMP2 and UMP4 was the C_2 structure 6. The C_{2v} structure 4 was found to be the transition state of the racemization of the two conceivable enantiomeric C_2 structures, according to the frequency analysis. However, the activation barrier is only 0.3 kcal/mol on the QCISD(TQ)/6-31+G** level, and, including zero-point energy, the order of stability is reversed, the C_{2v} structure being 0.6 kcal/mol more stable than the C_2 structure. Thus, no classical structure can be assigned to propargylene. Based on our results, it appears to be a superposition of two enantiomeric C_2 structures (the nuclear density function is delocalized over the two minima on the potential energy hypersurface).

However, the correlation effects are too large to undoubtedly exclude the C_s structure 7, based on results from single determinant calculations. More adequate for the problem are multiconfiguration SCF and multireference configuration interaction methods. We chose the latter method because it includes dynamical electron correlation and compared the energies of the C_2 structure 6 and the C_s structure 7 at different basis set levels. The number of

reference configurations in the MRD-CI treatment^{25,26} was between 6 and 12, and the number of symmetry-adapted configuration-state functions generated was in the range of 17 811–17 969. The calculations are based on the UMP4/6-31G* optimized geometries of 6 and 7, the highest level at which both structures are stationary points in the single determinant treatments. The MRD-CI energies were extrapolated to full configuration (E_{FCI}) values using the perturbation method of Peyerimhoff et al.^{25,26} Table 2 clearly indicates that with increasing basis set level, the C_2 structure is energetically favored. At the highest (6-311G(2d,2p)) level, the C_2 structure 6 is 5 kcal/mol more stable than the C_s structure 7. This is in qualitative agreement with our single determinant calculations and rules out the hitherto tentatively assumed carbene-like structure 7 for propargylene.

A final discrimination should be possible by comparing computed and experimental observables of the different propargylene structures: Maier et al. measured the IR spectra of propargylene, C_3H_2 , and the deuterated derivatives C_3HD and C_3D_2 in matrix.⁹ Even using an anharmonicity treatment for correcting the harmonic frequencies of the C_s structure 7, the authors obtained only a moderate agreement of the computed and the recorded IR spectra. Alternative structures were not considered. In Figures 4–6 and Tables 3–5, the calculated harmonic vibrational modes of the propargylene structure candidates 4, 6, and 7 are compared with the experimental IR spectra.

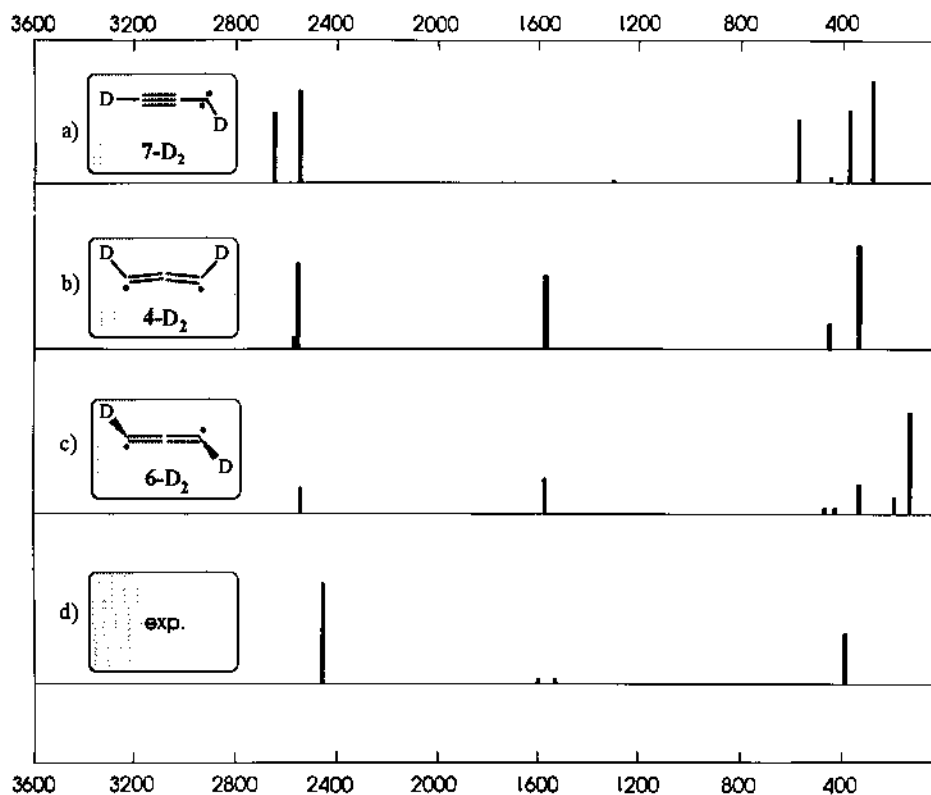


Figure 5. Ab initio calculated IR spectra of deuterated propargylene structures and experimental spectrum. Positions and heights of bars indicate frequency and relative intensity of absorption bands. (a) UMP2/6-31G** harmonic frequencies of C_s structure (ref 9). (b) QCISD/6-31G* harmonic frequencies of the C_{2v} structure. (c) QCISD/6-31G* harmonic frequencies of the C_2 structure. (d) Experimental spectrum (ref 9).

Table 3. Ab Initio Calculated Harmonic Frequencies and IR Intensities for Triplet Propargylene Structures 7, 4, and 6 and the Observed Spectrum of Matrix Isolated Propargylene

		UMP4/6-31G* anharmonicity corrected ^a		UQCISD/6-31G*		UQCISD/6-31G*		exptl			
mode	ν (cm ⁻¹)	ν (cm ⁻¹)	relative intensity	mode	ν (cm ⁻¹)	relative intensity	mode	ν (cm ⁻¹)	relative intensity	ν (cm ⁻¹)	relative intensity
A'' wag	343	344	0.70	A_2	-297		$B \rightarrow C_s^b$	296	1.00	245/248 ^c	1.00
A' bend	389	485	0.28	B_2	-89		$A \rightarrow C_{2h}$	361	0.06	401/403 ^c	0.18
A'' wag	477	636	0.26	A_1	409	0.22	$A \rightarrow C_{2v}$	414	0.23	550	0.35
A' bend	561	477	0.84	B_1	424	0.26	B	426	0.00		
A' bend	575	448	0.32	A_1	500	0.94	$A \rightarrow D_{mh}$	502	0.31		
A' C-C ν	1226	1361	0.34	A_1 C-C ν	1272	0.00	A C-C ν	1267	0.00		
A' C-C ν	1679	1576	0.87	B_2 C-C ν	1620	0.43	B C-C ν	1625	0.28	1650	0.04
A' C-H ν	3452	3448	0.25	B_2 C-H ν	3450	1.00	B C-H ν	3420	0.39		
A' C-H ν	3561	3549	1.00	A_1 C-H ν	3442	0.16	A C-H ν	3426	0.05	3265	0.61

^a Reference 9. ^b Distortion in direction to the C_s structure. ^c Splitting caused by matrix effects (see ref 9).

The best overall agreement of theory with experiment is observed for the C_2 structure 6, which also was found to be the energetically most stable. However, a more symmetrical C_{2v} structure 4 cannot be definitively excluded. If we accept the assumption that propargylene is a superposition of two C_2 structures with no classical geometry, then lower frequencies should be less reliably predicted than those with higher wavenumbers. Thus, the excellent quantitative agreement of bending and torsional frequencies of 6 in Figure 4d and e may be fortuitous. A carbene-like structure 7, however, is undoubtedly ruled out. For a C_s structure, two C-H stretching vibrations of different wavelengths and nonzero intensity should be observed, because both C-H bonds have different bond lengths and force constants. It is not to be expected that an anharmonicity treatment

should dramatically change that (see Figure 4a and b). Structures 4 and 6, with symmetry-equivalent C-H bonds, also exhibit two C-H stretching modes: a symmetrical (transforming as totally symmetric irreducible representations within the point group C_2 or C_{2v}) and an antisymmetrical vibration. The symmetrical stretching vibration, however, is almost IR inactive because there is very little mixing with bending and torsional modes. For the same reason, both symmetrical and antisymmetrical modes are very similar in energy (see Figure 4c and d). The IR spectrum in matrix shows only one absorption in the C-H stretching region. This is compatible only with structures 4 and 6 and not with 7.

For monodeuterated propargylene C_3HD as well, a single C-H and C-D stretching absorption was found in matrix IR. If

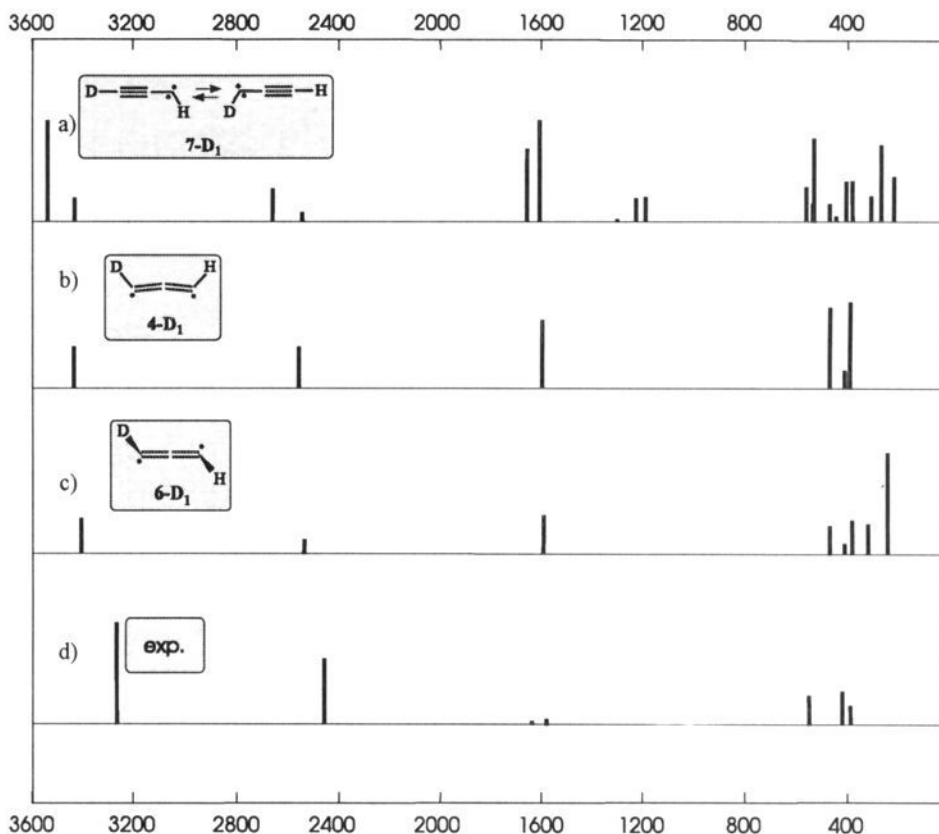


Figure 6. Ab initio calculated IR spectra of monodeuterated propargylene structures and experimental spectrum. Positions and heights of bars indicate frequency and relative intensity of absorption bands. (a) UMP2/6-31G* harmonic frequencies of a 1:1 mixture of both isomeric C_s structures. (b) QCISD/6-31G* harmonic frequencies of the C_{2v} structure. (c) QCISD/6-31G* harmonic frequencies of the C_2 structure. (d) Experimental spectrum (ref 9).

Table 4. Ab Initio Calculated Harmonic Frequencies and IR Intensities for Dideuterated Triplet Propargylene Structures 4, 6, and 7 and the Observed Spectrum of Dideuterated, Matrix Isolated Propargylene

 C_s 7 UMP2/6-31G*		 C_{2v} 4 UQCISD/6-31G*		 C_2 6 UQCISD/6-31G*		exptl	
ν (cm^{-1})	relative intensity	ν (cm^{-1})	relative intensity	ν (cm^{-1})	relative intensity	ν (cm^{-1})	relative intensity
275	1.00	331	1.00	226	1.00	386.7	0.50
365	0.74	389	0.06	284	0.20		
440	0.04	447	0.28	330	0.32		
565	0.64			408	0.10		
				451	0.10		
1294	0.02	1207	0.00	1204	0.00	1532.0	0.05
		1565	0.72	1568	0.38	1606.2	0.04
2541	0.71	2556	0.84	2545	0.27	2457.7	1.00
2646	0.94	2572	0.16	2559	0.05		

^a Reference 9.

propargylene were a fast equilibrating structure of C_s symmetry (7-D₁ in Figure 6a), then all lines should be doubled. Again, structures 4 and 6 show a much better agreement with experiment. The doublet appearing in the C–C stretching region (1579.2, 1639.7 and 1532.0, 1606.2 cm^{-1}) in the mono- and dideuterated propargylene spectra (Figures 5d and 6d) is probably due to Fermi splitting.³³

The discovery of cyclopropenylidene and vinylidene carbene (propadienylidene) in space suggests that propargylene, the third stable C_3H_2 species, should also be present, because it can be generated by irradiation of both isomers.^{1,2} Three astronomically observed rotational lines were tentatively assigned to propargylene.²⁰ A comparison with ab initio (MP3/6-31G*) calculated

rotational frequencies, however, showed a deviation of more than 2%, and the assignment was neither confirmed nor completely ruled out.²⁰ It was obvious to assume that in this case as well, the high spin contamination of the UHF wave function led to an inaccurate geometry and thus caused the discrepancy in the rotational constants.³⁴ Table 6 comprises the MP3/6-31G* results of DeFrees and McLean and our own calculations at the more reliable QCISD/6-31G* and QCISD(T)/6-31G* levels. Structures 4 and 6 are asymmetric top molecules, but they can be treated as near prolate symmetric tops because the rotational constants B and C are almost equal. The characteristic rotational energy levels were calculated using eq 1, where A , B , and C are

(34) DeFrees and McLean also point out that the deviations might be due to an insufficient treatment of the correlation energy, see ref 20.

(33) Maier, G., private communication.

Table 5. *Ab Initio* Calculated Harmonic Frequencies and IR Intensities for Monodeuterated Triplet Propargylene Structures 4, 6, and 7 and the Observed Spectrum of Monodeuterated, Matrix Isolated Propargylene

C _s 7-D ₁ UMP2/6-31G*		C _{2v} 4-D ₁ UQCISD/6-31G*		C ₂ 6-D ₁ UQCISD/6-31G*		exptl	
ν (cm ⁻¹)	relative intensity	ν (cm ⁻¹)	relative intensity	ν (cm ⁻¹)	relative intensity	ν (cm ⁻¹)	relative intensity
214	0.46	384	0.87	247	1.00	390/393	0.18
264	0.79	406	0.19	325	0.33	416.8	0.36
303	0.28	464	0.81	384	0.36	547.5	0.33
375	0.39	1237	0.00	422	0.17	1579.2	0.06
401	0.39	1595	0.68	472	0.33	1639.7	0.04
442	0.04	2565	0.42	1233	0.00	2469.2	0.68
466	0.18	3438	1.00	1599	0.40	3270.5	1.00
528	0.84			2552	0.14		
531	0.18			3423	0.36		
557	0.34						
1180	0.24						
1220	0.24						
1603	1.00						
1652	0.73						
2545	0.10						
2658	0.32						
3433	0.23						
3438	1.00						

Table 6. *Ab Initio* Calculated Rotational Constants and Rotational Transitions (GHz) (without Zero-Point Vibration and Centrifugal Corrections) for Propargylene Structures 7, 6, and 4

structure	level	A	B	C	5 ₀₅ → 4 ₀₄	4 ₀₄ → 3 ₀₃	1 ₀₁ → 0 ₀₀
	7 MP3/6-31G* ^a	2484.1	10.244	10.202	102.2	81.8	20.4
	6 MP3/6-31G* ^a	2484.2	10.297	10.288	102.9	82.3	20.6
	UQCISD/6-31G*	1517.4	10.088	10.076	100.8	80.7	20.16
	UQCISD(T)/6-31G*	1420.3	10.056	10.045	100.5	80.3	20.10
	4 UQCISD/6-31G*	2095.9	10.093	10.044	100.7	80.5	20.13
	UQCISD(T)/6-31G*	2027.4	10.060	10.010	100.3	80.3	20.07
astronomical ^a					100.60	80.48	20.12

^a The astronomically observed rotational lines were tentatively assigned to a C₃H₂ species (ref 20).

the rotational constants and $W_{J_r}(b_p)$ the reduced energies that are expressed as an expansion of b_p (eq 2). K_{-1} is the limiting prolate index of the level, and the coefficients C_i were taken from the literature.^{35,36}

$$E = \frac{1}{2}(B + C)J(J + 1) + [A - \frac{1}{2}(B + C)]W_{J_r}(b_p) \quad (1)$$

$$W_{J_r}(b_p) = K_{-1}^2 + C_1 b_p + C_2 b_p^2 + C_3 b_p^3 + \dots \quad (2)$$

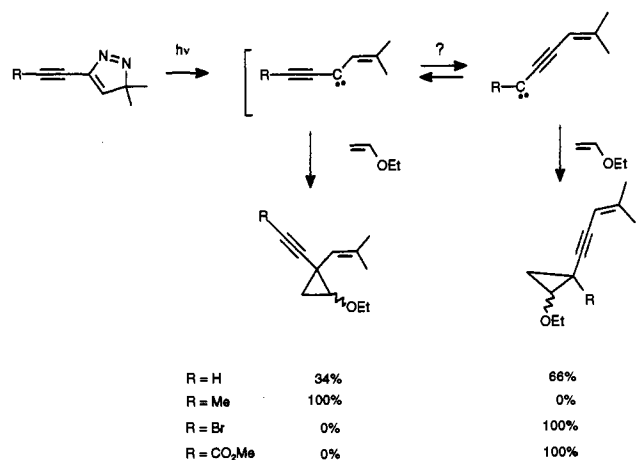
At the QCI levels, the calculated rotational transitions now agree very well with three astronomical lines that were tentatively assigned to a C₃H₂ species. The error of >2% at MP3 decreased to <0.2% at the QCI levels. However, these lines already were unambiguously assigned to the cyanomethyl radical CH₂CN (²B₁).³⁷ To prove the existence of propargylene in space, therefore, additional lines have to be calculated or measured and matched with astronomical microwave spectra.

Singlet Propargylene. Even though singlet propargylene is about 14 kcal/mol less stable than the triplet ground state

(35) Gordy, W.; Cook, R. L. *Microwave Molecular Spectra*; Interscience: New York, 1970; p 186.

(36) Schwendeman, R. H. *A Table of Coefficients for the Energy Levels of a Near Symmetric Top*; Department of Chemistry, Harvard University: Cambridge, MA, 1958.

(37) Saito, S.; Yamamoto, S.; Irvine, W. M.; Ziurys, L. M.; Suzuki, H.; Ohishi, M.; Kaifu, N. *Astrophys. Lett.* 1988, 334, L113.

**Figure 7.** Trapping reactions of vinyl-substituted propargylenes.

(predicted at the QCISD(T,Q)/6-31+G**//QCISD/6-31G* level, see table 1), there is evidence that, at least in substituted systems, there are trapping reactions in which the singlet might be the reactive spin state (see, for instance, Figure 7¹⁷). At the Hartree-Fock, MP2, and MP4 levels, singlet propargylene is predicted to be a carbene with C_v symmetry that undergoes a fast automerization (symmetry-allowed bond-shift reaction³⁸) via a

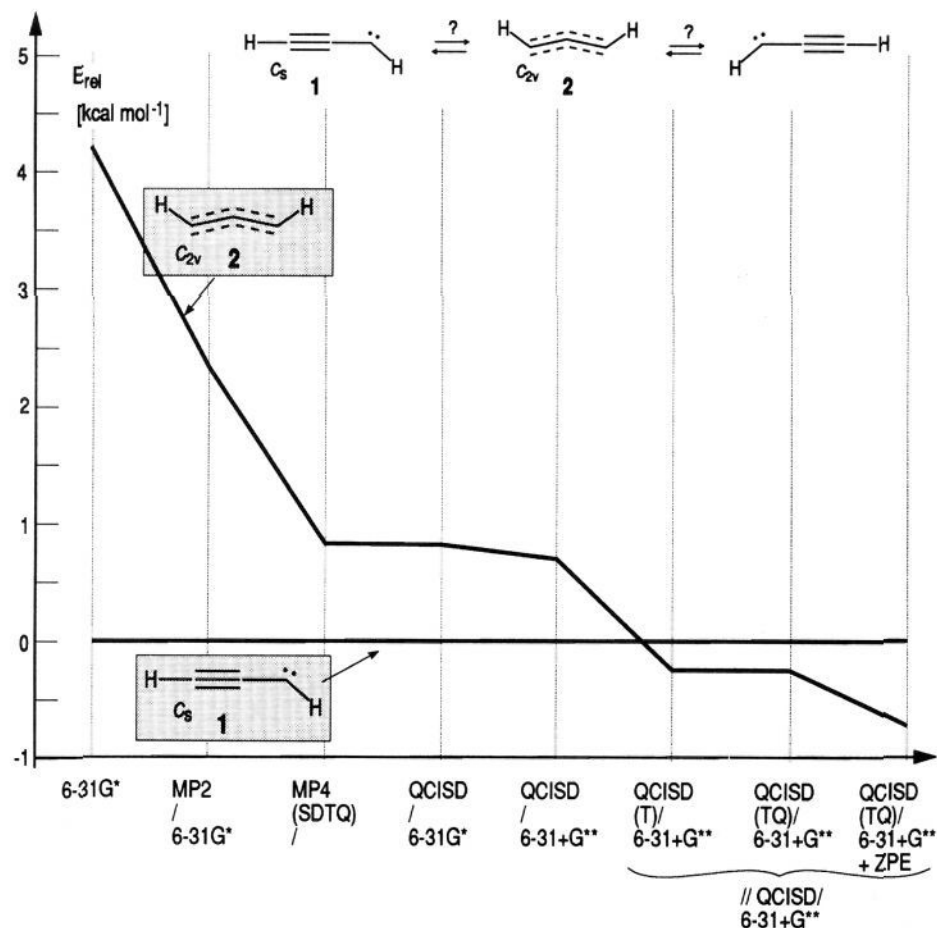


Figure 8. Relative energies of singlet propargylene structures **1** and **2** (in kcal/mol) at increasing levels of ab initio theory. The values are based on the C_s structure **1**. At HF/6-31G*, MP2/6-31G*, MP4(SDTQ)/6-31G*, and QCISD/6-31G*, the carbene structure **1** is a minimum, and **2** is the transition state of the automerization reaction of **1**. At higher levels of correlation treatment, structure **1** is not a stationary point, and **2** is a minimum.

C_{2v} symmetric transition state (see Table 1, first two rows, and Figure 8). However, an increase of the basis set level as well as improvement of the correlation treatment favors the C_{2v} structure. At the QCISD(T)/6-31+G** level, **2** is no longer a transition state but a minimum on the singlet energy hypersurface. The energy difference at the QCISD(TQ)/6-31+G**+ZPE level is 0.71 kcal/mol. A MRD-CI calculation with a 6-31G* basis confirms the single determinant calculations (see Table 2). The C_{2v} symmetrical structure **2** is predicted to be 2.1 kcal/mol more stable than the C_s structure. Thus, propargylene on the singlet hypersurface as well is predicted not be a classical carbene.

(38) For a review, see: Herges, R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 255.

Conclusions

Both QCI single determinant and MRD-CI calculations predict that propargylene does not have a classical carbene structure, neither in the triplet nor in the singlet state. In both spin states, the nonbonding electrons are symmetrically delocalized over the carbon atoms. Triplet propargylene is a 1,3-diradical (structure **4** or **6**), and singlet propargylene could be described as a frozen (coarctate³⁸) transition state of a symmetry-allowed bond-shift reaction (structure **2**). Ab initio calculated and experimental IR spectra of **4** and **6** are in good agreement with experiment.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for support.