

Theoretical Studies of Two Key Low-Lying Carbenes of C_5H_2 Missing in the Laboratory

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Abstract

The equilibrium geometries and spectroscopic properties of two key singlet carbenes, buta-1,3-diyne carbene (**6**) and 2-methylenebicyclo[1.1.0]but-1(3)-en-4-ylidene (**9**), which have not been experimentally observed to date, are investigated using high-level coupled-cluster (CC) methods. The current theoretical study necessitates new experimental data on C_5H_2 isomers considering the relevance of these molecules to interstellar chemistry. Bent-pentadiynylidene (**4**) has been missing in the laboratory and the prime focus of our earlier theoretical work. The present theoretical study indicates that isomers **6** and **9** are also viable experimental targets. Apart from ethynylcyclopropenylidene (**2**), pentatetraenylidene (**3**), ethynylpropadienylidene (**5**), and 3-(didehydrovinylidene)cyclopropene (**8**), which are identified by Fourier transform microwave spectroscopy, the dipole moments of elusive **4**, **6**, and **9** are also non-zero ($\mu \neq 0$). The relative energies of these isomers, calculated at the CCSDT(Q)/CBS level of theory, with respect to linear triplet pentadiynylidene (**1**) reveal that they all lie within $25.1 \text{ kcal mol}^{-1}$. Therefore, geometric, energetic, aromatic, and spectroscopic parameters are reported here, which may assist the efforts of molecular spectroscopists in the future. Anharmonic vibrational calculations on isomers **6** and **9** indicate that the former is loosely bound and would be challenging to be detected experimentally. Among the undetected carbenes, **9** may be considered as a potential target molecule considering its higher polarity and aromatic nature.

Introduction

In the “H-deficient hydrocarbon” homologous series C_nH_2 , where, $n = 3, 4,$ and 6 , four carbene molecules have already been identified in the interstellar medium (ISM). They are, namely, cyclopropenylidene ($c-C_3H_2$),¹ propadienylidene (C_3H_2),² butatrienylidene (C_4H_2),³ and hexapentaenylidene (C_6H_2).⁴ Three isotopologues of C_3H_2 , the doubly deuterated $c-C_3D_2$, singly deuterated $c-C_3HD$ and one species of $c-H^{13}CC_2H$ (^{13}C off of the principal axis of the molecule),^{5–8} have also been detected in two starless cores (TMC-1C and L1544). The reason why none of the C_5H_2 isomers have been found in the ISM remains an open-ended question. On the other hand, one of the isomers of SiC_3 , which contains a transannular C–C bond (rhombohedral geometry) has been confirmed in the evolved carbon star, IRC + 10216⁹ based on laboratory rest frequencies.¹⁰ Within C_5H_2 elemental composition, the elusive aromatic carbene, 2-methylenebicyclo[1.1.0]but-1(3)-en-4-ylidene (**9**; see Figure 1), also contains a transannular C–C bond but less attention has been paid to this molecule.^{11–24} Of note, for the confirmation of four C_nH_2 carbenes in non-terrestrial environments,^{1–4} identification of the same in laboratories (terrestrial environments) is a crucial factor.^{1,11,25–27} Therefore, considering the astrochemical relevance, available laboratory astrophysics data, and enhancing our understanding of structure and bonding of various C_nH_2 isomers, where, $n = 2,$ ²⁸ $3,$ ^{1,2,24,25,29–33} $4,$ ^{3,27,34–36} $5,$ ^{11–24} $6,$ ^{4,11,34–37} $7,$ ^{12,24,38–49} $8,$ ^{34,35,39,50} $9,$ ^{12,24,38,39,41,43,51–53} etc., in this work, the electronic structures and spectroscopic properties of two additional singlet low-lying C_5H_2 isomers, buta-1,3-diyne carbene (**6**) and **9**, have been investigated in detail. Both **6** and **9**, in addition to bent-pentadienylidene (**4**),⁵⁴ are yet to be identified in the laboratory. To the best of our knowledge, high-level coupled-cluster (CC) calculations including anharmonic vibrational frequencies and spectroscopic parameters have been missing in the literature for isomers **6** and **9**.^{14,15,17–23,54–62} The theoretical work done here may assist the molecular spectroscopists in the detection and characterization of these elusive molecules in the future.

To date, five isomers of C_5H_2 have been identified in the laboratory.^{11–13,15–19,24} On the

basis of $\mathbf{1}^3\Sigma_u^- \leftarrow \tilde{X}^3\Sigma_g^-$ electronic transitions being recorded, Maier and co-workers¹² had initially claimed that the open-shell triplet isomer, linear-pentadiynylidene (**1**), has been observed. Due to lower signal-to-noise ratio for the electronic spectrum of **1**, their spectral assignments were later challenged by McMahon and co-workers.¹⁷ Isomer **1** of C_5H_2 was first unambiguously identified by the photolysis of 1-diazo-2,4-pentadiyne in a N_2 matrix.¹⁷ The electronic structure of the latter is also characterized by various (IR, EPR, UV-vis) spectroscopic techniques.¹⁷ Following this, the gas phase detection and resonant two-color two-photon ionization (R2C2PI) characterization of **1** was also reported by Maier and co-workers recently.¹⁸ McCarthy and co-workers using Fourier Transform Microwave (FTMW) spectroscopy had identified four closed-shell carbene isomers of C_5H_2 [ethynylcyclopropenylidene (**2**),¹³ pentatetraenylidene (**3**),¹¹ ethynylpropadienylidene (**5**),¹⁶ and 3-(didehydrovinylidene)cyclopropene (**8**);¹⁶ Figure 1], whose dipole moments are non-zero ($\mu \neq 0$). Among these, the cumulene carbene isomer (**3**) was reported initially.¹¹ Later, the laboratory detection of the three-membered ring-chain isomer (**2**) was also reported with both *a*- and *b*-type rotational transitions as the inertial axis dipole moment components are in two directions for this molecule.¹³ Both of these molecules (**3** and **2**) are higher homologues of propadienylidene (a cumulene carbene isomer of C_3H_2) and cyclopropenylidene, respectively. Also, the latter are known to exist in the ISM.^{1,2}

Computational studies using coupled-cluster theory by Stanton and co-workers¹⁴ suggested that ethynylpropadienylidene (**5**) and 3-(didehydrovinylidene)cyclopropene (**8**) are also energetically low-lying isomers (within 1 eV) on the C_5H_2 potential-energy surface (PES). Using the charge reversal and neutralization reionization mass spectra, Bowie and co-workers had not only detected **5** but also **1** and **3** via the corresponding anion.¹⁵ Both of these theoretically suggested molecules (**5** and **8**), which are highly polar ($\mu = 4.79$ and 8.16 Debye, respectively, at the CCSD(T)/cc-pVTZ level of theory¹⁴), were also detected later using FTMW spectroscopy.¹⁶ Recently, isomers **1** and **8** have also been characterized using mass-selective threshold photoelectron spectroscopy and an adiabatic ionization energy of

8.36 ± 0.03 and 8.60 ± 0.03 eV, respectively, has been determined.¹⁹ Our previous theoretical study had focused on isomer **4** of C_5H_2 ,⁵⁴ which is yet to be experimentally identified. Here, our prime focus is on two more low-lying singlet carbenes of C_5H_2 , **6** and **9**, which are unobserved to date. Moreover, for the latter, high-level ab initio calculations including spectroscopic parameters are still missing in the literature.^{14,15,17–19,19–23,54–62} Thus, here we revisit the PES of C_5H_2 at the low-lying region. Most importantly, the motivation for the current theoretical study on these molecules stems from the fact that none of the C_5H_2 isomers have been found in the ISM so far.

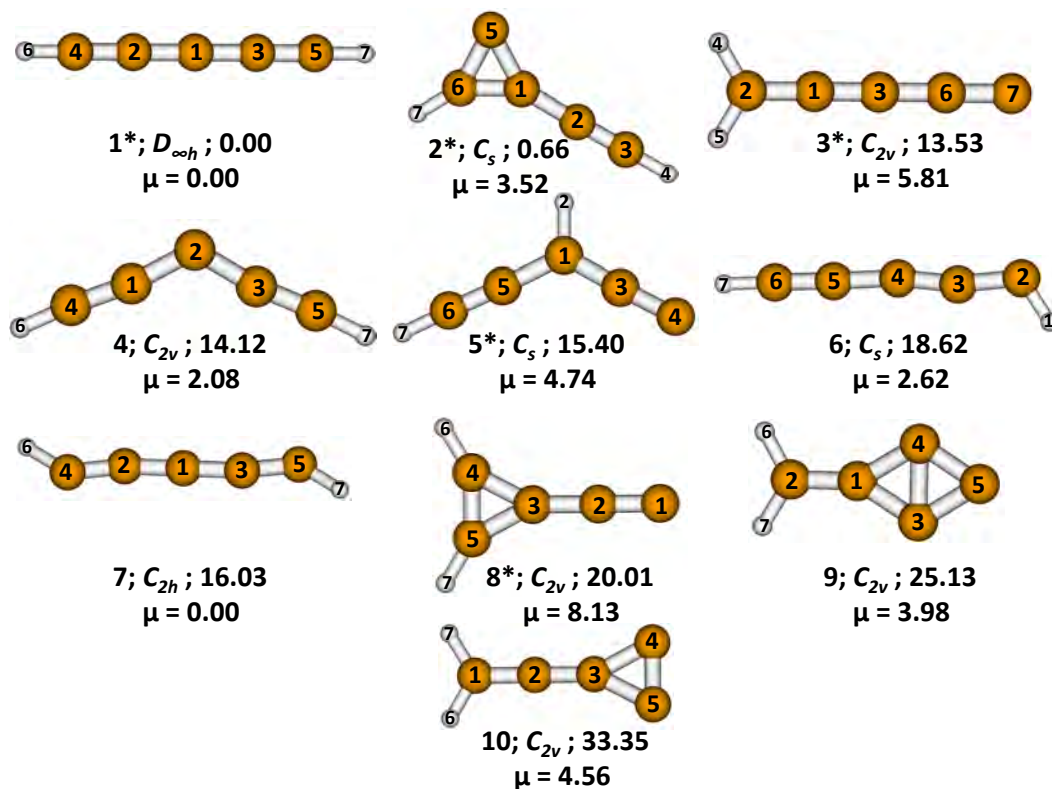


Figure 1: Isomers of C_5H_2 considered in this work. ZPVE-corrected relative energies are calculated at the CCSDT(Q)/CBS level of theory (in kcal mol⁻¹). Dipole moments (in Debye) and ZPVEs are computed at the CCSD(T)/cc-pVTZ level of theory. Experimentally detected isomers are marked with an asterisk. Isomer **1** is a triplet and all others are singlets. At the latter level, isomer **7** is a second-order saddle-point, **10** is a transition state and all others are minima. Atom numbering scheme used herein for isomers **1** to **10** are also given

Computational Details

All the isomers of C_5H_2 (**1-10**) reported in this study are optimized using second-order Møller-Plesset perturbation theory (MP2)⁶³ and coupled-cluster (CC) methods. The considered CC methods are CC with singles and doubles (CCSD),^{64,65} and CCSD with perturbative triple excitations (CCSD(T)).⁶⁶⁻⁶⁸ Dunning’s correlation consistent polarized valence double and triple zeta (cc-pVnZ; $n = D$ and T) basis sets⁶⁹ are used in these calculations. The carbon $1s$ orbitals are frozen in the post-Hartree-Fock (HF) calculations. Harmonic vibrational frequencies are calculated at the same levels of theory by analytic calculation of second derivatives⁷⁰ for all stationary points. The %TAE[(T)] diagnostics^{71,72} for all isomers of C_5H_2 have been calculated to estimate the significance of contributions from post-CCSD(T) excitations. All of the above electronic structure calculations were carried out with the CFOUR program package.⁷³

The W3-F12 single-point energy calculations were carried out using the CCSD(T)/cc-pVTZ equilibrium geometries. Zero-point vibrational energies (ZPVEs) are calculated at the same level of theory and scaled by a scaling factor of 0.9868 as recommended elsewhere.⁷⁴ All the CCSD(T) energy calculations involved in the W3-F12 energies were done with the Molpro program package⁷⁵ while the post-CCSD(T) calculations were carried out with the MRCC program.^{76,77} For the three ring isomers (**2**, **8**, and **9**), the aromatic stability has been estimated by computing nucleus independent chemical shift (NICS)^{78,79} values with the B3LYP hybrid-functional⁸⁰⁻⁸² using the 6-311+G(d,p) basis set.^{83,84} NICS values reported here have been calculated at 1Å above the plane of the rings. These calculations were done with the Gaussian 16 program.⁸⁵

Anharmonic Vibrational Calculations

The anharmonic vibrational calculations are carried out using the PVSCF program⁸⁶ and are based on the vibrational self-consistent field (VSCF) approach.⁸⁷⁻⁸⁹ The normal modes

are represented in curvilinear coordinates, resulting in a very compact representation of the potential energy operator.⁹⁰ The PES is expanded in a multimode expansion, that is $V = \sum_i V^{1D}(\mathbf{Q}_i) + \sum_{i,j} V^{2D}(\mathbf{Q}_i, \mathbf{Q}_j) + \sum_{i,j,k} V^{3D}(\mathbf{Q}_i, \mathbf{Q}_j, \mathbf{Q}_k) + \dots$ for normal modes \mathbf{Q} and modes i, j, k . As such, the potential contains contributions from the 1D anharmonicity (the deviation of the potential well from a harmonic oscillator along the coordinate of that mode), the 2D anharmonicity (anharmonic mode-mode coupling), and higher-order (3D, 4D, ...) coupling terms. By using a curvilinear coordinate representation instead of rectilinear normal-mode coordinates, the potential can be truncated after the second order already without too much loss of accuracy,⁹⁰ providing substantial savings in computing time as the costly higher-order couplings can be neglected. Post-VSCF methods are used and include vibrational mode-mode correlation through vibrational configuration interaction (VCI).^{91,92} In our VCI implementation, a statewise calculation is carried out, in that for each vibrational mode, its corresponding VSCF wave function is first optimized and then a VCI calculation is performed for each of the modes separately. This has the advantage that the reference wave function that is used to generate the VCI basis is more optimal, leading to a faster convergence of the VCI wave function with respect to the level of excitation that is included. Note that the VCI states that are then obtained for each of the modes are not necessarily orthogonal to all of the other vibrational modes, as they are based on a different reference wave function. For the VCI calculations carried out here, all one- and two-mode excitations are taken into account for each of the modes, up to a quantum number of six (vibrational level).^{90,92} For very delocalized vibrational modes, a higher level of excitations in the VCI expansion may become necessary. All potentials for the anharmonic vibrational calculations were calculated using ORCA⁹³ and the B3LYP hybrid-functional,⁸⁰⁻⁸² with Dunning’s cc-pVTZ basis set⁶⁹ and atom-pairwise dispersion correction with Becke-Johnson damping⁹⁴ (D3BJ). The choice of electronic structure method for the PES results as a compromise between accuracy and computational demand, as 240 single-point energies need to be calculated for both isomer **6** and **9** for the 1D anharmonicity, and 26,880 points for the anharmonic

mode-mode coupling. The vibrational spectra were then generated using the peak positions and harmonic intensities, and applying a Lorentzian broadening with 5 cm^{-1} and 50 cm^{-1} to demonstrate the effect of the finite lifetimes of the vibrational states on the spectra.

Results and Discussion

For all the C_5H_2 isomers (**1-10**) reported in this study, the component breakdown of the W3-F12 energies as well as the final relativistic, all-electron, CCSDT(Q)/CBS relative energies on the electronic PES (ΔE_e) and at 0 K (ΔE_0) are collected in Table 1. Relative energies obtained from previous theoretical works^{14,18,20} are also given for comparison. The atom numbering scheme adopted here for isomers (**1-10**) is given in Figure 1. The electronic structure and spectroscopic parameters of isomer **4** had been discussed in detail in an earlier work by us⁵⁴ and therefore these details are not repeated here. The optimal geometry parameters obtained at different levels for isomers **6** and **9** are listed in Tables 2 and 3, respectively. Valence structures possible for the latter are given in Figure 2 along with bond lengths obtained at the fc-CCSD(T)/cc-pVTZ level of theory. The rotational and centrifugal distortion constants, inertial axis dipole moment components, and absolute dipole moments obtained at the latter level for isomers **6** and **9** are given in Table 4. Harmonic vibrational frequencies, anharmonic vibrational frequencies, and the isotopic shifts (^{12}C - ^{13}C and ^1H - ^2D) in harmonic vibrational frequencies for isomers **6** and **9** are listed in Tables 5 and 6, respectively. Isomer **7** is a second-order saddle point whereas isomer **10** (vinylidenecycloprop-1-yne) is a transition state at all six levels of theory employed here. It is noted here that isomer **10** has been reported as a local minimum at the M06-2X/cc-pVTZ level of theory in a previous theoretical study.¹⁸

Table 1: Component Breakdown of the W2-F12 and W3-F12 Relative Energies Along with the Final W2-F12 and W3-F12 Values at the Bottom of the Well (ΔE_e) and at 0 K (ΔE_0). All Values are Given Relative to Isomer 1 in kcal mol⁻¹

Theory ^k	Comp.	2	3	4	5	6	7	8	9	10
W2-F12	HF	-18.77	4.88	2.66	1.89	6.48	11.91	1.98	20.01	29.59
W2-F12	CCSD	13.77	9.01	11.40	10.87	11.10	9.17	13.75	2.77	4.80
W2-F12	(T)	1.73	-2.74	-0.65	-0.32	-1.55	-3.08	0.11	-2.50	-3.41
W2-F12	Inner-shell	0.60	0.84	0.51	0.86	0.48	0.42	0.76	1.58	1.28
W2-F12	Scalar rel.	-0.06	-0.11	-0.07	-0.12	-0.06	-0.05	-0.07	-0.17	-0.14
W3.2	T-(T)	-0.06	-0.38	-0.59	-0.31	4.01	-0.96	-0.12	0.40	0.02
W3.2	(Q)	0.48	-0.33	-0.22	0.11	-2.26	-1.03	0.36	-0.08	-0.32
W2-F12	CCSD(T)/CBS ^a	-2.73	11.89	13.85	13.19	16.45	18.37	16.53	21.71	32.12
W3-F12	CCSDT(Q)/CBS ^b	-2.31	11.18	13.04	12.94	18.20	16.38	16.77	22.03	31.83
	ZPVE ^c	2.97	2.35	1.08	2.46	0.42	-0.35	3.24	3.10	1.52
W2-F12	CCSD(T)/CBS ^d	0.24	14.24	14.94	15.64	16.87	18.02	19.77	24.81	33.64
W3-F12	CCSDT(Q)/CBS ^e	0.66	13.53	14.12	15.40	18.62	16.03	20.01	25.13	33.35
Other ^f	ae-CCSD(T)/cc-pVTZ ^g	2.01	13.82	N/A	16.78	N/A	N/A	21.14	N/A	N/A
Other ^h	M06-2X/cc-pVTZ	-0.60	18.02	N/A	20.67	N/A	N/A	17.78	N/A	34.46
Other ⁱ	CCSD(T)/cc-pVQZ//B3LYP/6-311G(d,p) ^j	-1.50	11.90	13.80	13.50	15.50	N/A	17.70	N/A	N/A

^a Relativistic, all-electron CCSD(T)/CBS relative energies at the bottom of the well (ΔE_e). ^b Relativistic, all-electron CCSDT(Q)/CBS relative energies at the bottom of the well (ΔE_e). ^c fc-CCSD(T)/cc-pVTZ harmonic ZPVEs scaled by a factor of 0.9868. ⁷⁴ ^d

Relativistic, all-electron CCSD(T)/CBS relative energies at 0 K (ΔE_0). ^e Relativistic, all-electron CCSDT(Q)/CBS relative energies at 0 K (ΔE_0). ^f Non-relativistic, all-electron

CCSD(T)/cc-pVTZ relative energies at 0 K (ΔE_0) taken from ref.¹⁴ ^g Note that the ZPVEs were calculated at the ae-CCSD/DZP level of theory. ^h Relative energies at 0 K (ΔE_0) taken from ref.¹⁸ ⁱ Relative energies at 0 K (ΔE_0) taken from ref.²⁰ ^j Note that the ZPVEs were calculated at the B3LYP/6-311G(d,p) level of theory. ^k Values for isomers **2**, **3**, **4**, **5**, and **8** are taken from our earlier work⁵⁴

Energetics

The best relativistic, all-electron CCSDT(Q)/CBS ΔE_0 values relative to isomer **1** are: 0.66 (**2**), 13.53 (**3**), 14.12 (**4**), 15.40 (**5**), 18.62 (**6**), 16.03 (**7**), 20.01 (**8**), 25.13 (**9**), and 31.83 (**10**) kcal mol⁻¹. These values predict the same isomer ordering as the all-electron CCSD(T)/cc-pVTZ values of Stanton and co-workers.¹⁴ Nonetheless, isomers **4**, **6**, **7**, **9**, and **10** were not considered in their study. Our relative energies are systematically larger (Table 1). In particular, the CCSDT(Q)/CBS values are larger by 1.35 (**2**), 0.29 (**3**), 1.38 (**5**), and 1.13 (**8**) kcal mol⁻¹ compared to the CCSD(T)/cc-pVTZ values.¹⁴ Considering the magnitude of the relative energies, the difference between the two sets of values is particularly pronounced for isomer **2**, which we predict is closer in energy to the global minimum geometry, isomer **1** (i.e., 0.66 vs. 2.01 kcal mol⁻¹, Table 1). The differences in relative energy between our values and those reported in ref.¹⁴ for isomers **1-3**, **5**, and **8** could be attributed to three main differences: (i) our best values are calculated at the relativistic, all-electron CCSDT(Q)/CBS level of theory (vs. the all-electron CCSD(T)/cc-pVTZ level of theory in ref.¹⁴); (ii) here we use an ROHF-based wavefunction for isomer **1** vs a UHF based wavefunction used in ref.;¹⁴ and (iii) Our ZPVE corrections are calculated at the fc-CCSD(T)/cc-pVTZ level of theory (vs. an ae-CCSD/DZP level of theory used in ref.¹⁴).

At the CCSDT(Q)/CBS level of theory (including fc-CCSD(T)/cc-pVTZ ZPVE corrections) the linear isomer (**1**) with a triplet ($\tilde{X}^3\Sigma_g^-$) ground electronic state is the most stable C₅H₂ isomer (Table 1). However, Maier and co-workers¹⁸ reported the singlet ground electronic state (\tilde{X}^1A') of isomer **2** is the most stable geometry at the M06-2X/cc-pVTZ level of theory. Comparison of our best relativistic, all-electron CCSDT(Q)/CBS relative ΔE_0 energies with the M06-2X/cc-pVTZ values¹⁸ reveals that M06-2X does not predict the correct isomer order. To be precise, M06-2X predicts that isomer **2** is the most stable isomer and that isomer **1** lies higher in energy by 0.60 kcal mol⁻¹. Moreover, it predicts that isomer **8** is more stable than isomer **5** and nearly isoenergetic with isomer **3**. Also, isomer **10** was predicted to be a minimum at the M06-2X/cc-pVTZ level of theory whereas our

CC results indicate that this particular geometry is a transition state. This reveals that M06-2X is not a reliable functional for calculating these relative energies. Likewise, relative energies obtained at the CCSD(T)/cc-pVQZ//B3LYP/6-311G(d,p) level of theory predicts that isomer **2** is more stable than **1** by 1.50 kcal mol⁻¹.²⁰ The poor performance of density functional theory (DFT) for similar relative energies has been previously noted in the case of C₇H₂ isomers, in particular for the low-lying non-linear isomers^{42,44–46} (see also Ref.⁹⁵ for a comprehensive survey of the performance of a wide range of DFT methods for challenging structural relative energies). We note that we have tried to optimize the geometry of isomer **1** in the singlet electronic state (\tilde{X}^1A_g) at the fc-CCSD(T)/cc-pVTZ level of theory, however, this optimization resulted in multiple imaginary frequencies (see Supporting Information for further details).

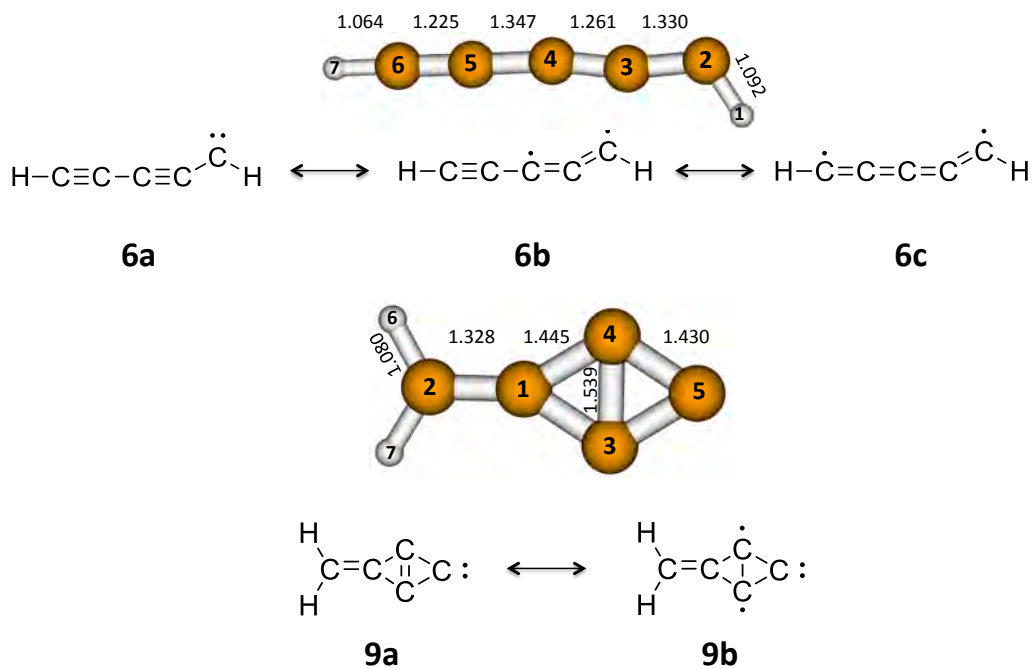


Figure 2: Possible resonance structures for isomers **6** and **9**. The bond lengths (in Å) calculated at the fc-CCSD(T)/cc-pVTZ level of theory are also given

buta-1,3-diyne (6)

Figure 2 shows three valence resonance structures (**6a**, **6b**, and **6c**) for isomer **6**. Considering the triple bond distance of the C_5C_6 bond (see Table 2 and also Figure 2) and an intermediate bond distance between a double and triple bond of the C_3C_4 bond and the double bond distance of the C_2C_3 bond obtained at all levels, we conclude that valence structure **6b** is dominant. The nearly equal to 180 degree bond angles obtained for $C_4C_5C_6$ and $C_5C_6H_7$ at all levels supports our conclusion further.

Table 2: Optimal Geometry Parameters (Å and Degree) of Isomer 6 Calculated at Different Levels

	cc-pVDZ		cc-pVTZ		
	MP2	fc-CCSD ^a	MP2	fc-CCSD	fc-CCSD(T)
R(H_1C_2)	1.1101	1.1116	1.0918	1.0928	1.0922
R(C_2C_3)	1.3592	1.3620	1.3330	1.3385	1.3297
R(C_3C_4)	1.2605	1.2614	1.2478	1.2446	1.2612
R(C_4C_5)	1.3677	1.3736	1.3484	1.3552	1.3467
R(C_5C_6)	1.2382	1.2320	1.2222	1.2137	1.2253
R(C_6H_7)	1.0771	1.0781	1.0626	1.0623	1.0641
$\theta(H_1C_2C_3)$	113.81	112.70	116.45	114.58	117.52
$\theta(C_2C_3C_4)$	168.70	169.24	170.28	171.55	168.68
$\theta(C_3C_4C_5)$	175.43	173.18	177.29	177.56	171.74
$\theta(C_4C_5C_6)$	179.45	179.10	179.64	179.75	178.67
$\theta(C_5C_6H_7)$	179.90	179.51	179.99	179.98	179.09

^a At the fc-CCSD(T)/cc-pVDZ level of theory, isomer **6** rearranges to isomer **4**

The rotational constants (A_e , B_e , and C_e) obtained at the fc-CCSD(T)/cc-pVTZ level of theory from the equilibrium geometries of isomers **6** and **9** (Table 4) indicate that these molecules are asymmetric tops. However, considering the minimal difference between B_e and C_e , they both can also be considered as “nearly prolate symmetric tops”. The centrifugal distortion constants (D_J , D_K , D_{JK} , etc.) are also computed for these yet to be observed molecules to aid the efforts of microwave spectroscopists. The theoretical values reported here do not include the effects of corrections from the zero-point vibrational motion whereas the experimentally measured values are vibrationally averaged rotational constants (A_0 , B_0 ,

and C_0). Moreover, the calculations for **6** and **9** lack the effect of core-valence correlation in their optimal geometries at the CCSD(T)/cc-pVTZ level of theory.⁹⁶ Apart from these two effects, basis set effects and higher-level treatment of electron correlation effects on the equilibrium geometries may significantly improve the rotational constants,^{97,98} which would be helpful for the accurate simulation to search for the rotational transitions of **6** and **9**; however, such an endeavor is beyond the scope of the present work. While the inertial axis dipole moment components are in two directions (μ_a and μ_b) for isomer **6**, it is in only one direction for **9**. Therefore, for the latter only one type of rotational transition is possible whereas for the former both *a*- and *b*-type rotational transitions are possible. The total dipole moments of **6** and **9** are 2.62 and 3.98 Debye, respectively, at the CCSD(T)/cc-pVTZ level of theory. Although isomer **8** is the highly polar carbene among the C_5H_2 isomers,^{14,16} the dipole moments of **6** and **9** make these molecules potential candidates, in principle, for FTMW spectroscopic observations.

Table 3: Optimal Geometry Parameters (Å and Degree) of Isomer 9 Calculated at Different Levels

	cc-pVDZ			cc-pVTZ		
	MP2	fc-CCSD	fc-CCSD(T)	MP2	fc-CCSD	fc-CCSD(T)
R(C ₁ C ₂)	1.3385	1.3365	1.3440	1.3243	1.3206	1.3284
R(C ₁ C ₄)	1.4596	1.4548	1.4612	1.4436	1.4381	1.4447
R(C ₄ C ₃)	1.5745	1.5427	1.5641	1.5488	1.5168	1.5385
R(C ₄ C ₅)	1.4445	1.4366	1.4472	1.4279	1.4186	1.4295
R(C ₂ H ₆)	1.0917	1.0929	1.0945	1.0781	1.0782	1.0801
$\theta(C_2C_1C_4)$	147.36	147.98	147.64	147.56	148.17	147.83
$\theta(C_1C_4C_5)$	114.34	115.51	114.93	114.71	115.85	115.27
$\theta(C_1C_4C_3)$	57.36	57.98	57.64	57.56	58.17	57.83
$\theta(C_1C_2H_6)$	119.89	120.07	120.03	119.92	120.11	120.05

A fully anharmonic vibrational analysis of isomer **6** reveals that two of the vibrational modes, modes 7 and 9, which are the out-of-plane bend of C₄ and H₁ wag, and the H₂ wag, are bound by a very shallow potential and are likely to connect isomer **6** to one (or more) of the other isomers such as isomer **4** (see Figure 3). The harmonic and anharmonic

Table 4: Rotational and Centrifugal Distortion Constants (in MHz), and Inertial Axis Dipole Moment Components (in Debye; \perp^r Representation) of Isomers **6 and **9** of C_5H_2 Calculated at the CCSD(T)/cc-pVTZ Level of Theory^a**

constant	6	9
A_e	575100.98	31658.89
B_e	2265.22	4569.62
C_e	2256.33	3993.24
μ_a	2.22	-3.98
μ_b	1.38	-
$ \mu $	2.62	3.98
D_J	0.1487×10^{-3}	0.4743×10^{-3}
D_K	13182.30	0.1168
D_{JK}	-1.5279	0.5492×10^{-2}
d_1	-0.6751×10^{-5}	-0.7106×10^{-4}
d_2	-0.7035×10^{-7}	-0.1217×10^{-4}

^a Centrifugal distortion constants are from the S-reduced Hamiltonian for **6** and **9** considering the fact that they are approaching close to the prolate limit.

vibrational transition frequencies, as well as the harmonic intensities have been used to generate vibrational spectra as shown in Figure 4. It is very noticeable that the most intense mode, mode 10, shifts to lower frequencies (760 cm^{-1} to 406 cm^{-1}). However, the spectrum for isomer **6** should be viewed more from a qualitative point of view, as several of the vibrational modes reside in very shallow potential wells and represent reactive rather than vibrational coordinates. Through the anharmonic mode-mode coupling, these loosely bound modes affect the other vibrational modes in the molecule, and our anharmonic vibrational analysis indicates that this isomer is very short-lived – and may undergo isomerization faster than the vibrational period, at least for the low-frequency modes. Therefore, we do not report low-frequency modes in Table 5; and the high-frequency vibrations are only reported tentatively, as these are coupled to very loosely bound modes.

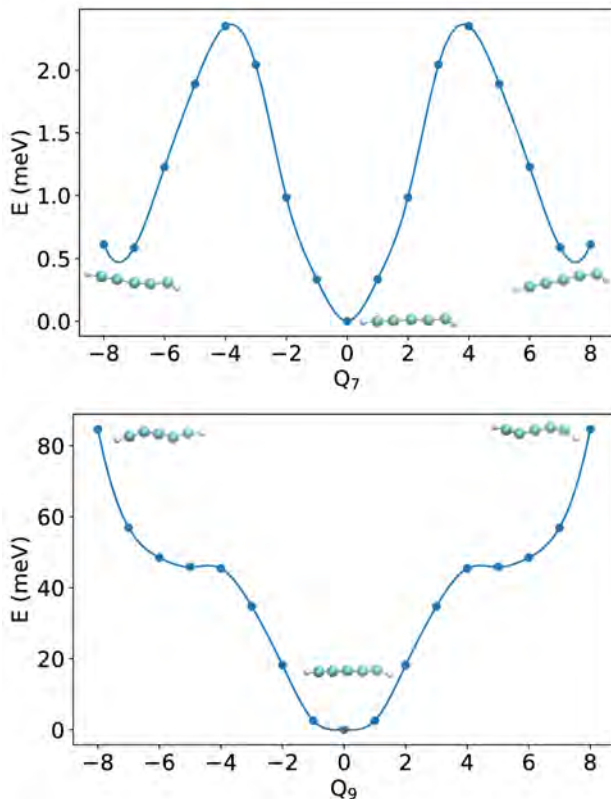


Figure 3: Potential along vibrational mode 7 (top) and mode 9 (bottom) of isomer **6**. Mode 7 is very loosely bound, and mode 9 is very shallow, so that this isomer is expected to be short-lived.

2-methylenebicyclo[1.1.0]but-1(3)-en-4-ylidene (**9**)

Like SiC_3 ,⁹ the electronic structure of **9** contains a transannular C–C bond. At all levels, the C_1C_2 bond length exhibits double bond characteristics. The C_1C_4 (C_1C_3) and C_4C_5 (C_3C_5) bond lengths are intermediate between a double and single-bond. The most interesting bond length for **9** is the C_3C_4 distance of 1.539 Å, which is a typical C–C single bond length. The diradical valence structure seems to be the dominant one (**9b** in Figure 2) considering these bond lengths. The singlet-triplet energy gap was also estimated, and the singlet electronic state is 63.26 kcal mol⁻¹ more stable than the triplet electronic state at the UB3LYP/6-311+G(D,P) level of theory. The NICS (1Å) value was found to be -10.53 ppm at the B3LYP/6-311+G(d,p) level of theory. For two other cyclic systems within C_5H_2 , **2** and **8**, the values were estimated to be -11.36 and -9.99 ppm, respectively, at the latter level of

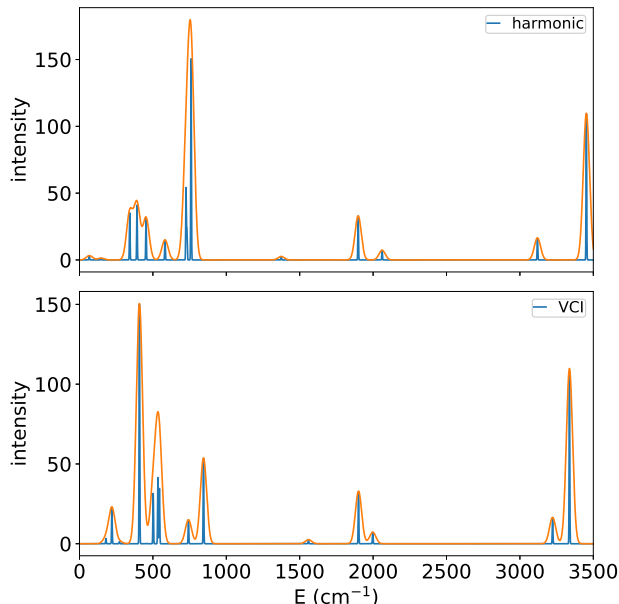


Figure 4: Harmonic (top) and VCI (bottom) vibrational spectrum of isomer **6**, using harmonic intensities and a Lorentzian broadening of 5 cm^{-1} (blue) and 50 cm^{-1} (orange). It is notable that the intense peak at 760 cm^{-1} (mode 10) shifts down to 406 cm^{-1} . However, the spectra should be viewed from a more qualitative point of view as some of the modes in this isomer are extremely shallow and very loosely bound, so that these resemble a mixture of reactive and vibrational coordinate.

theory. The negative value indicates that these molecules are aromatically stabilized. The value obtained for isomer **9** is slightly larger than isomer **8**. However, NICS is a response property whereas energetic stability is a ground-state property. For isomer **9**, two vibrational modes (modes 11 and 13), which should be readily identifiable are the C_2C_1 stretch (1396 cm^{-1}) and the C_5C_4 (C_5C_3) stretch (1795 cm^{-1}). The isotopic shifts in harmonic vibrational frequencies are also pronounced for these two modes.

The anharmonic vibrational calculations on isomer **9** further confirm that this isomer is stable. All vibrational modes are comparatively strongly bound especially in comparison with isomer **6**. Modes 8, 10, 12 and 14 exhibit the most shallow potentials; these modes are bound by 0.5 eV and contain seven bound states in the limited region of the PES that was explored. Further following these modes along may reveal the height of potential barriers to other isomers, but as a result of the anharmonic calculations, these barriers must be higher

Table 5: Harmonic Vibrational Frequencies ω and VCI Frequencies ν (cm^{-1}), IR intensities (km mol^{-1}) and Isotopic Shifts ($^{12}\text{C} - ^{13}\text{C}$ and $^1\text{H} - ^2\text{D}$) in Harmonic Vibrational Frequencies (cm^{-1}) for the Ground Electronic State (\tilde{X}^1A_1) of Isomer 6 Calculated at the fc-CCSD(T)/cc-pVTZ Level of Theory^a

Mode	Isomer 6				$^{12}\text{C} - ^{13}\text{C}$					$^1\text{H} - ^2\text{D}$	
	symm.	ω	ν	intensity	C(2)	C(3)	C(4)	C(5)	C(6)	H(1)	H(7)
1	a'	67	–	3	0	0	2	0	0	1	2
2	a''	146	–	1	2	1	1	0	1	0	5
3	a''	321	–	0	0	5	0	5	1	6	12
4	a'	342	–	35	1	2	2	4	3	21	33
5	a'	392	–	42	1	6	0	2	1	20	28
6	a'	453	–	32	0	0	1	4	0	1	44
7	a''	582	–	15	0	3	12	5	0	9	16
8	a'	726	–	54	13	3	1	4	5	99	132
9	a''	732	–	23	0	0	0	1	6	3	12
10	a'	760	–	151	4	5	0	2	3	28	4
11	a'	1374	<i>1560</i>	3	16	13	16	0	6	29	12
12	a'	1898	<i>1901</i>	33	1	34	36	0	1	15	6
13	a'	2061	<i>1997</i>	7	1	1	2	50	21	1	93
14	a'	3119	<i>3223</i>	17	10	0	0	0	0	816	473
15	a'	3453	<i>3338</i>	110	0	0	0	1	16	0	333

^a VCI frequencies based on potentials from B3LYP/cc-pVTZ calculations. Anharmonic frequencies for this isomer can only be reported for the high-frequency modes, and these still have to be considered from a more qualitative viewpoint and are shown in italics.

Table 6: Harmonic Vibrational Frequencies ω and VCI Frequencies ν (cm^{-1}), IR Intensities (km mol^{-1}) and Isotopic Shifts ($^{12}\text{C} - ^{13}\text{C}$ and $^1\text{H} - ^2\text{D}$) in Harmonic Vibrational Frequencies (cm^{-1}) for the Ground Electronic State (\tilde{X}^1A_1) of Isomer 9 Calculated at the fc-CCSD(T)/cc-pVTZ Level of Theory^a

Mode	Isomer 9				$^{12}\text{C} - ^{13}\text{C}$				$^1\text{H} - ^2\text{D}$	
	symm.	ω	ν	intensity	C(1)	C(2)	C(3) ^b	C(5)	H(7) ^b	
1	b_1	252	–	2	3	2	1	3	5	
2	b_2	330	–	1	3	2	2	2	20	
3	b_1	590	–	4	11	0	5	3	20	
4	b_2	617	598	(-12)	45	6	0	6	5	20
5	a_2	708	703	(-13)	0	0	2	0	109	
6	a_1	783	780	(-22)	0	3	11	4	9	18
7	b_1	877	917	(14)	46	0	8	0	0	53
8	b_2	953	<i>930</i>		6	3	0	15	5	29
9	a_1	1046	1065	(3)	7	0	4	17	0	82
10	b_2	1065	<i>1055</i>		1	9	8	0	0	18
11	a_1	1396	1358	(-57)	69	1	0	11	27	82
12	a_1	1454	<i>1435</i>		1	3	4	2	2	48
13	a_1	1795	1786	(-37)	27	46	18	2	0	15
14	a_1	3181	<i>3052</i>		2	0	6	0	0	799
15	b_2	3282	3134	(-128)	0	0	14	0	0	47

^a VCI frequencies based on potentials from B3LYP/cc-pVTZ calculations. Anharmonic frequencies for this isomer that have to be considered from a more qualitative viewpoint are shown in italics. Frequencies for weakly bound modes/modes strongly coupled to weakly bound modes are excluded from the table as these are unreliable. Deviations for reliable anharmonic frequencies to the corresponding harmonic frequencies at the same level of theory are shown in parentheses. ^b Due to symmetry, C(3) and C(4); H(6) and H(7) are equivalent.

than 0.5 eV. Modes 12 and 14 resemble the H₂C scissoring (bending) and symmetric C-H stretching modes. The vibrational harmonic and anharmonic spectra, using the harmonic intensities, are shown in Figure 5 and are quite similar, with the exception of a small shoulder appearing in the low-energy region of the spectrum. The anharmonic frequencies in Table 6 are given together with the deviation to the harmonic frequencies at the same level of theory, for reliable modes. Frequencies for unreliable modes that couple very strongly to shallow modes are not given (this affects the three lowest frequency modes), and tentative modes are displayed in italics.

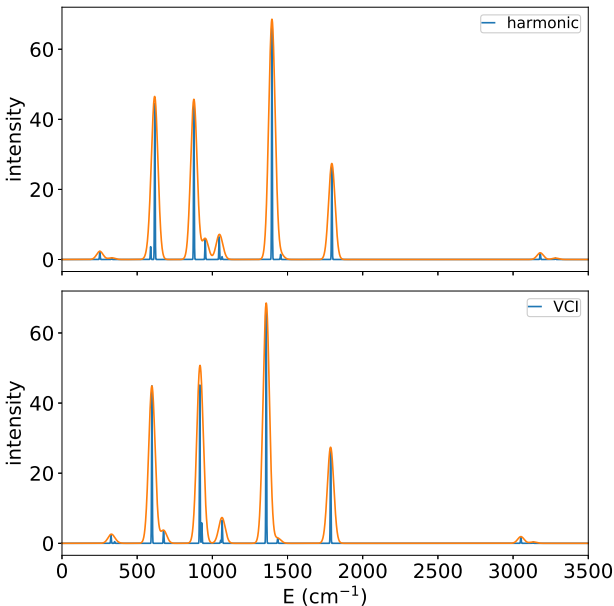


Figure 5: Harmonic (top) and VCI (bottom) vibrational spectrum of isomer **9**, using harmonic intensities and a Lorentzian broadening of 5 cm⁻¹ (blue) and 50 cm⁻¹ (orange). Except for the appearance of an additional shoulder in the low-energy region, the harmonic and anharmonic spectra are quite similar

Conclusions

One of the pertinent questions in interstellar chemistry is why none of the C₅H₂ isomers have been identified in the ISM so far? Detection of molecules in the ISM often depends on their identification in the laboratory. Therefore, another important question is, are all low-

lying isomers of C_5H_2 have been identified in the laboratory? Here, the low-energy region of the C_5H_2 PES has been revisited at the CCSDT(Q)/CBS level of theory to help address answering these questions. To this end, this theoretical study suggests that three low-lying isomers (**4**, **6**, and **9**) are still missing in the laboratory. At the CCSDT(Q)/CBS level of theory, these three isomers lie at 14.12, 18.62, and 25.13 kcal mol⁻¹ above isomer **1**. The absolute dipole moments of these isomers are 2.08, 2.62, and 3.98 Debye, respectively, at the fc-CCSD(T)/cc-pVTZ level of theory. Therefore, in principle, they are suitable molecules for FTMW spectroscopic and radio-astronomical studies. The low barrier to linearity (16.5 meV at the UCCSD(T)/aug-cc-pVDZ level of theory) may pose challenges in the identification of **4**⁵⁴ in the laboratory. Similar reasons may be attributed for **6** as well. Also, the anharmonic vibrational calculations further point towards isomer **6** being short-lived with several vibrational modes that are very loosely bound, one of these by only three meV (0.07 kcal mol⁻¹). While the local topology of the potential may look different if constructed using a higher-level method such as CCSD(T), it is unlikely that the character of these modes changes substantially. We therefore predict that isomer **6** is reactive and more difficult to detect experimentally than isomer **4**. However, considering the high polarity and aromatic nature, we believe that isomer **9** is a potential target molecule for laboratory identification. In principle, identification of these three isomers in the laboratory becomes mandatory for answering the question whether C_5H_2 isomers exist in the ISM. We hope that our theoretical efforts here may assist and encourage further experimental studies for the identification of isomer **9** in the laboratory.

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Supporting Information Available

The Cartesian coordinates of the optimized geometries, total electronic energies, zero-point vibrational energies, and %TAE[(T)] values calculated at different levels for C₅H₂ isomers are given in the supporting information. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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