Structures and Stabilities of C_5H_2 Isomers: Quantum Chemical Studies

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Abstract: Five isomers of the carbon-rich molecule C_5H_2 are investigated computationally, using methods based on the coupled-cluster approximation. All of these structures are related to isomers of C_3H_2 via substitution of hydrogen by ethynyl or attachment of a C_2 fragment to a carbene center. The two most stable forms of C_5H_2 are linear triplet pentadiynylidene (**4**) and singlet ethynylcyclopropenylidene (**6**). Both of these isomers have been observed in the laboratory, as has a third—the cumulene carbene pentatetraenylidene (**5**)—which is predicted to lie about 15 kcal/mol above the linear triplet. Two other isomers are also studied: ethynylpropadienylidene (**7**) and 3-(didehydro-vinylidene)cyclopropene (**8**). Both are found to lie less than 25 kcal/mol above the most stable form of C_5H_2 and to possess rather large dipole moments. Predictions for the harmonic vibrational frequencies of ^{12}C and mono-^{13}C isotopomers, infrared intensities, and rotational constants are also presented. These should assist efforts to identify these molecules in the laboratory and in the interstellar medium.

Introduction

Radioastronomical studies provide compelling evidence that highly unsaturated carbenes with a large ratio of carbon to hydrogen are widely distributed in interstellar and circumstellar environments.[1] Isolation and spectroscopic study of unsaturated carbenes in terrestrial laboratories is difficult, however, because of their characteristically high reactivity. Nevertheless, some success has been achieved and detailed information about the mechanistic photochemistry and spectroscopic properties of these compounds has begun to emerge. Perhaps the most heavily studied example is provided by isomers of C_3H_2 (Scheme 1). Three forms of C_3H_2 have been identified in the laboratory: propynylidene (**1**), propadienylidene (**2**), and cyclopropenylidene (**3**).[2] The ground state of propynylidene is unquestionably a triplet, but even a qualitative determination of the molecular geometry proved to be problematic. While early experiments[3] implicated a linear geometry (**1a**), theoretical investigations suggested that the equilibrium geometry of this isomer was bent, corresponding to either a planar acetylenic

Scheme 1
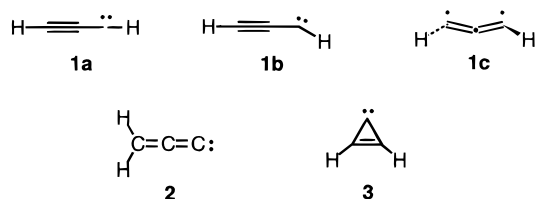
carbene (**1b**)[4] or a 1,3-diradical with C_2 symmetry (**1c**).[5] Subsequent matrix-isolation ESR and IR studies coupled with results of ab initio calculations have apparently settled this controversy in favor of the C_2 structure.[2c] In addition, photolysis of **1** in matrices produces **2** and **3**;[2a,b,6] both of these highly polar singlets have also been observed in the gas phase[7] and in the interstellar medium.[8]

A decade ago, Vrtilek et al. raised the possibility that compounds derived from stable C_3H_2 isomers by addition of carbon chains might be stable,[9] a hypothesis that was supported by subsequent calculations.[10] Although laboratory efforts did not succeed in detecting molecules of this type for several years, the sensitive technique of Fourier transform microwave spec-

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Scheme 2
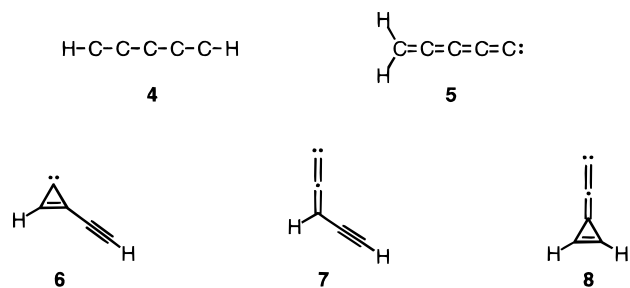
troscopy recently has been used to unambiguously identify two such isomers of C_5H_2 (Scheme 2): the cumulene carbene pentatetraenylidene (**5**)[11] (which is obtained by attaching a C_2 fragment to the carbene carbon in **2**) and, quite recently, the ring−chain compound ethynylcyclopropenylidene (**6**)[12] in which one of the hydrogen atoms of **3** is replaced by an ethynyl radical. Radioastronomical searches for **5** and **6** in interstellar clouds are now underway.[13] In other work, triplet **4** has been generated in a neon matrix and its electronic spectrum has been recorded.[14]

In addition to the three isomers of C_5H_2 that are now known from experiment, one may also envision a structure in which one of the hydrogen atoms in **2** is replaced by an ethynyl radical (**7**), and another (**8**) in which C_2 attaches to the lone pair of **3**. Recent interest in linear sp-carbon allotropes[15,16] and cyclic carbon clusters[16] gives these hypothetical isomers greater import, as well.

A few theoretical investigations of C_5H_2 have been reported in the literature. In separate work, both singlet[10,17] and triplet[18] states of pentadiynylidene (**4**) have been studied, with special attention given to geometries and qualitative descriptions of frontier molecular orbitals. In addition, the polar singlet isomers **5** and **6** have been investigated at the complete-active-space self-consistent-field (CASSCF) level, with an emphasis on relative stabilities and predictions of structure.[10] In that study, the cumulene carbene isomer **5** was predicted to lie about 1 kcal/mol below **6**. Rotational constants determined from the calculated equilibrium geometry of **5** at the CASSCF level have also been presented.[19] Ethynylpropadienylidene (**7**) and 3-(di-dehydrovinylidene)cyclopropene (**8**)[20] apparently have not been considered previously. In related work, isomers of the isoelectronic system C_4NH have been investigated,[21a] and selected topics involving the positive and negative ions of various isomers have been investigated.[21b,c]

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(20) Given the cumbersome nature of the systematic name for isomer **8**, a trivial name may be appropriate. To this end, we suggest "eiffelene", a name that reflects the structural similarity between this species and a prominent European landmark.

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Some experimental work has been done on substituted pentadiynylidenes. Treatment of the 3-bromo-1,4-pentadiynes (**10**) with potassium *tert*-butoxide in tetrahydrofuran and *N*-methyl-2-pyrrolidone resulted in formation of three isomeric enetetraynes **12**−**14** (Scheme 3), presumably from dimerization of pentadiynylidene intermediates (**11**).[22] The same three products result from thermolysis of the lithium tosylhydrazone salts **15** in benzene.[23] With styrene present, thermolysis of **15** leads to only one trapping product, phenylcyclopropane **16**. The ESR spectra of triplet methyl-, *tert*-butyl-, and phenylpentadiynylidene in poly(chlorotrifluoroethylene) have been observed.[3a,b] The ESR spectrum of 1,5-diphenylpenta-1,3-diynylidene (**11b**, R = Ph) in methyltetrahydrofuran at 10 K has also been observed. When the glass is warmed, **11b** apparently rearranges to 1,5-diphenylpenta-1,4-diynylidene, which possesses a nearly linear carbon backbone.[24] Results from a similar ESR study of 1,3-diphenylpropynylidene, however, suggest that a reinterpretation of the data in terms of conformational isomers may be appropriate.[25]

In this paper, high-level ab initio calculations are applied to study the structure, relative stabilities, harmonic vibrational frequencies, and infrared transition intensities of the C_5H_2 isomers pictured in Scheme 2. The work presented here will be helpful in understanding various forms of this carbon-rich system and the relationship between gross features of the C_3H_2 and C_5H_2 potential energy surfaces. In addition, estimates of the rotational constants and vibrational frequencies should facilitate experimental identification of these compounds.

Computational Methods

Three different levels of theory have been used to study the isomers of C_5H_2 that are pictured in Scheme 2. Structures were first optimized at the coupled-cluster singles and doubles (CCSD) level,[26] using the double-ζ plus polarization (DZP) basis.[27] At these geometries, harmonic vibrational frequencies were determined by analytic calculation of second derivatives[28] followed by diagonalization of the corresponding mass-weighted Hessian matrix. The force constants so obtained were then used to facilitate optimizations at higher levels of theory, specifically CCSD with the triple-ζ plus double polarization (TZ2P) basis[29] and the CCSD(T) model (which improves upon CCSD by addition of a correction that accounts for the effects of triply-excited Slater determinants[30]) with the correlation-consistent cc-pVTZ basis set of Dunning.[31] Calculations of harmonic frequencies at the two higher levels of theory [CCSD/TZ2P and CCSD(T)/cc-pVTZ] were not carried out because it is unlikely that the results will differ sufficiently from those obtained at

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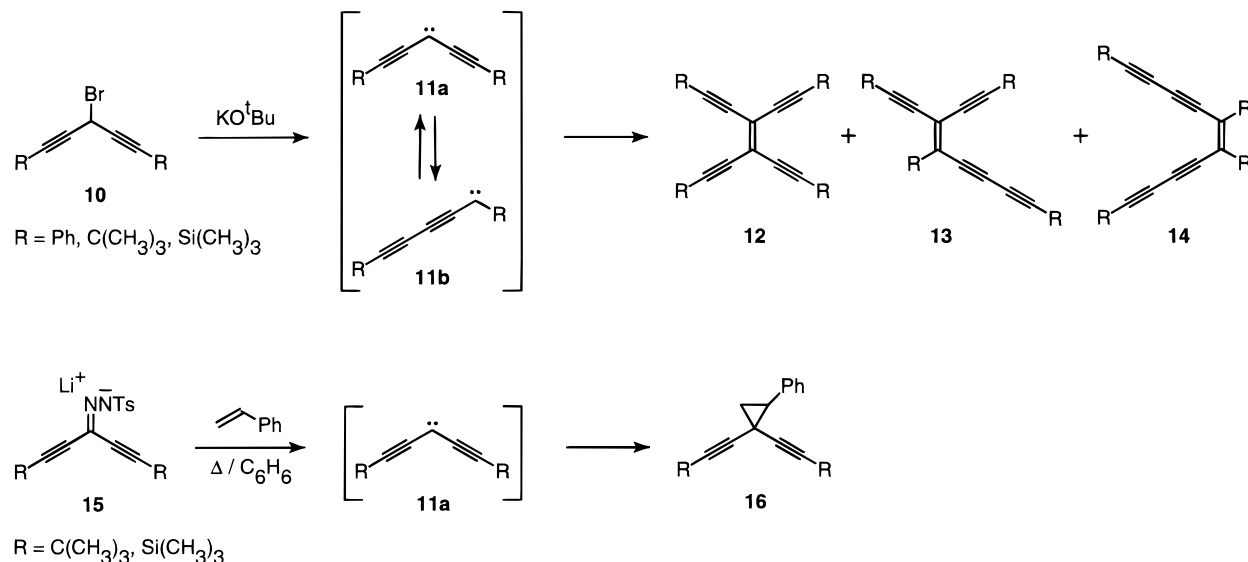
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Scheme 3

R = Ph, C(CH$_3$)$_3$, Si(CH$_3$)$_3$

10 → KO^{t}Bu → [**11a** ⇌ **11b**] → **12** + **13** + **14**

15 (Li$^+$ $^-$NNTs) → $\triangle$ / C$_6$H$_6$, with $=$Ph → [**11a**] → **16** (Ph)

R = C(CH$_3$)$_3$, Si(CH$_3$)$_3$

the CCSD/DZP level to justify the added computational expense. Indeed, it is the isotopic shifts, rather than the absolute position of harmonic frequencies, that have proven most useful in assigning the infrared spectra of matrix-isolated C$_3$H$_2$ isomers,[2b,d] and these should be adequately approximated by the calculations presented here.

Spherical representations of d- and f-type polarization functions were used in all calculations. Accordingly, for C$_5$H$_2$, the DZP, TZ2P, and cc-pVTZ basis sets contain 85, 138, and 178 contracted Gaussian functions, respectively. The CCSD(T)/cc-pVTZ optimizations of C$_5$H$_2$ isomers were the most expensive calculations performed. For the C_s structures, each cycle of optimization required about one day of cpu time on a DEC-AlphaStation 500/333. All calculations were performed with a local version of the ACESII program system.[32]

Results and Discussion

A. Structures and Properties of Individual Isomers. Equilibrium geometries of isomers **4**−**8** calculated at the CCSD/DZP, CCSD/TZ2P and CCSD(T)/cc-pVTZ levels of theory are documented in Tables 1−5 along with the corresponding CCSD/DZP harmonic vibrational frequencies, infrared intensities, dipole moments, and rotational constants calculated from the optimized structures.

A.1. Pentadiynylidene (4). Molecular orbital considerations reveal that the highest occupied and lowest unoccupied orbitals of linear **4** have π_u and π_g symmetries respectively; the former contains two electrons in the neutral. Thus, Hund's rule predicts that the ground electronic state of this isomer will be a triplet, a conclusion that is supported by some preliminary calculations[33] and is consistent with laboratory ESR studies of substituted pentadiynylidenes.[3a,b,24] In this report, our focus is on the ground electronic state of each isomer of C$_5$H$_2$; the singlet state of **4** will consequently not be considered. Geometries optimized at the three levels of theory are rather similar, exhibiting the usual contraction and expansion of internuclear distances that accompany basis set expansion and inclusion of higher-level correlation effects to the CCSD model,[26] respectively. The distance between the central carbon and that adjacent to it is somewhat less than typically found in single bonds between sp

Scheme 4

H$-$C≡C$-$C̈$-$C≡C$-$H ⟷ H$-$Ċ=C=C=C=Ċ$-$H

H$-$C≡C$-$C≡C$-$C̈(H)
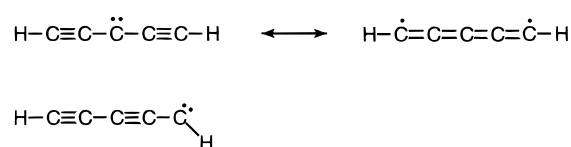
carbon atoms (1.38 Å),[34] while the significantly shorter outer carbon−carbon distance is intermediate between typical double and triple bond distances.[35] Qualitatively, this behavior can be rationalized as a competition between two resonance structures. One of these might be described as diethynylcarbene, while the other is a 1,5-cumulenic diradical (Scheme 4). Participation of the first resonance structure clearly raises the question of whether this isomer is linear, or rather behaves like its C$_3$H$_2$ analog **1** and adopts an equilibrium geometry with lower symmetry.

A definitive answer to the question raised at the end of the preceding paragraph cannot be supplied here. While linear **4** is stable with respect to bending distortions at the CCSD/DZP level, the small π_u frequency of 40 cm^{-1} shows that the corresponding restoring force is exceedingly feeble. Moreover, lower-level calculations carried out with second-order many-body perturbation theory (MBPT(2)) and quadratic configuration interaction (QCISD) with the 6-31G* basis predict a V-shaped C_{2v} geometry obtained from linear **4** via distortion along the aforementioned π_u bending mode.[33] However, density functional calculations concur with the CCSD/DZP results and point to a linear structure.[33] In any event, energy differences between linear and optimized distorted structures found in the MBPT-(2) and QCISD calculations are extremely small, showing that theory unanimously predicts a structure that certainly will have dynamical $D_{\infty h}$ symmetry. A strongly bent structure corresponding to triplet butadiynylcarbene (Scheme 4) was also considered at the CCSD/DZP level. However, optimizations starting with a bond angle of ca. 130° for H$_1$−C$_2$−C$_3$ (see Figure 1) lead back to the linear structure, suggesting that the bent structure does not represent a minimum on the triplet potential energy surface.

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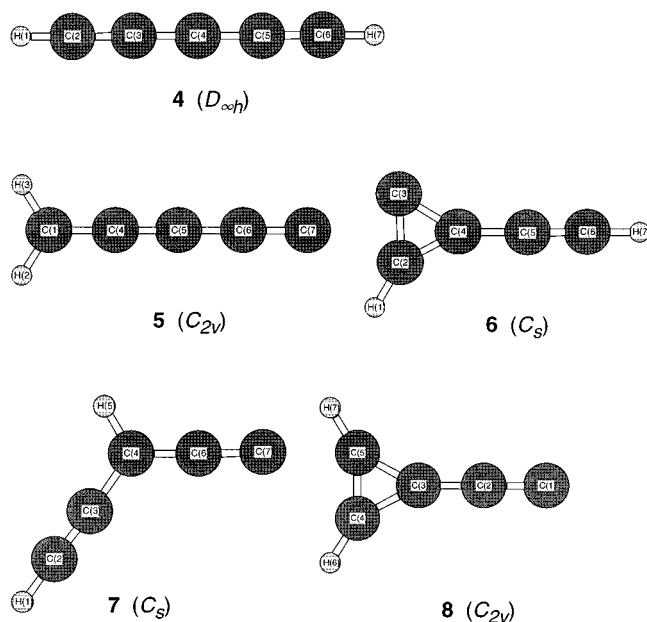
C₅H₂ Isomers

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Figure 1. Computed structures (CCSD(T)/cc-pVTZ) and atom numbering for C_5H_2 isomers **4**−**8**.

Table 1. Results for Triplet Pentadiynylidene (**4**)[a]

Structure and Rotational Constants			
parameter	CCSD/DZP	CCSD/TZ2P	CCSD(T)/cc-pVTZ
$r(H_1C_2)$	1.0726	1.0616	1.0594
$r(C_2C_3)$	1.2554	1.2360	1.2365
$r(C_3C_4)$	1.3309	1.3146	1.3079
A	2197	2257	2270

Harmonic Frequencies and Infrared Intensities			
mode	symmetry	frequency	intensity
ω_1	σ_g	3473.3	−
ω_2	σ_g	1926.1	−
ω_3	σ_g	737.1	−
ω_4	σ_u	3467.2	184.2
ω_5	σ_u	1578.8	1.0
ω_6	σ_u	1503.2	11.2
ω_7	π_g	433.1	−
ω_8	π_g	323.2	−
ω_9	π_u	439.4	173.4
ω_{10}	π_u	268.6	16.7
ω_{11}	π_u	39.5	11.3

[a] Bond lengths (Å), bond angles (degrees), dipole moment (Debye), harmonic frequencies (cm⁻¹), infrared intensities (km/mol), and rotational constants calculated from the equilibrium structure (MHz). Atom numbering is shown in Figure 1.

A likely source of difficulty in predicting the lowest π_u bending mode in **4** is the rather severe spin contamination of the unrestricted Hartree−Fock (UHF) determinant used in both this study and ref 33. At the SCF level, the expectation value of S^2 is about 2.8, significantly higher than the value of 2 that corresponds to an electronic triplet state. The MBPT(2) treatment of correlation is not adequate for such a highly contaminated reference function. While QCISD should fare somewhat better, coupled-cluster methods provide a more satisfactory treatment of orbital relaxation.[36] Indeed, the first spin contaminant is fully removed at the CCSD level,[37] and rigorous expectation values of S^2 calculated for UHF-CCSD wave functions are typically very close to nominally exact values, even when badly contaminated reference states are used.[38] In the present case, the value of $\langle S^2 \rangle$ at the CCSD/DZP optimized geometry is 2.03. Hence, spin contamination does not appear to be a problem at this level of theory.

Although the nonpolar structure **4** is clearly not a candidate for radioastronomical observation, laboratory detection in matrix-isolation experiments has already been reported[14] and is likely to play a role in future mechanistic studies. To this end, the harmonic vibrational frequencies given in Table 1 should serve as a guide for identifying features in the infrared spectrum that can be attributed to **4**. The strongest modes are predicted to be the out-of-phase CH stretch and the highest π_u bending vibrations; these should be found above 3000 and ca. 400 cm⁻¹, respectively. Also useful for confirming experimental assignments are ¹²C−¹³C isotopic shifts; these are documented in Table 6 for **4** as well as for the other isomers considered below.

A.2. Pentatetraenylidene (5). Pentatetraenylidene is fourth in the series of cumulene carbenes H_2C_n that begins with vinylidene ($n = 2$). Although vinylidene has a sub-nanosecond lifetime,[39] higher members of the series are more stable. Propadienylidene ($n = 3$),[8] butatrienylidene ($n = 4$),[40] and hexapentaenylidene ($n = 6$)[11,41] have been identified in interstel-

lar clouds. It has been suggested[1,2d] that electronic transitions in cumulene carbenes might be responsible for some of the mysterious diffuse interstellar bands that have vexed the astrophysics community for decades.[42] Thus, there is great interest in this family of molecules.

Equilibrium geometries predicted by the three levels of theory again display the usual trends for **5**. From the results in Table 2, one sees a rather small extent of bond alternation in the carbon framework which diminishes in magnitude toward the carbene end of the molecule. It is interesting that the C_{2v} structure is stable with respect to asymmetric distortion in **5**, as the analogous cumulenic ketene OCCCCH₂ adopts a decidedly nonlinear structure.[43] Rotational constants calculated from the CCSD(T)/cc-pVTZ equilibrium geometry (B_e) agree rather well with those corresponding to the CASSCF structure of Maluendes and McLean.[19] For the two principal moments of inertia perpendicular to the carbon framework, agreement with experiment is essentially perfect. For the A rotational constant, the theoretical values lie appreciably higher than the measured value of 277 600 MHz. Superficially, this is puzzling because the corresponding equilibrium moment of inertia is determined solely by the hydrogen atom positions and these are not expected to pose a difficult problem for theory. Hence, it is unlikely that errors in the CCSD(T)/cc-pVTZ equilibrium structure are large enough to account for the difference. A more likely rationalization is that the experimental rotational constant, which is a vibrationally averaged value (B_0), contains a significant contribution from effects of zero-point motion. This possibility is qualitatively consistent with the very shallow potential that governs bending of the carbon chain in this molecule; harmonic frequencies for two of these modes are calculated at <150 cm⁻¹. Moreover, similarly large discrepancies between theory and

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Table 2.   Results for Pentatetraenylidene (**5**)[a]

Structure, Rotational Constants and Dipole Moment

parameter	CCSD/ DZP	CCSD/ TZ2P	CCSD(T)/ cc-pVTZ	experiment[b]
$r(C_1C_4)$	1.3369	1.3185	1.3219	
$r(C_4C_5)$	1.2864	1.2676	1.2655	
$r(C_5C_6)$	1.3165	1.2988	1.2988	
$r(C_6C_7)$	1.3082	1.2861	1.2879	
$r(C_1H_2)$	1.0917	1.0806	1.0803	
θ $(C_4C_1H_2)$	120.83	120.99	121.00	
dipole moment	5.584	5.792	5.829	
A	285294	292176	292397	277600
B	2239	2304	2303	2305
C	2221	2286	2285	2286

Harmonic Frequencies and Infrared Intensities

mode	symmetry	frequency	intensity
ω_1	a_1	3178.1	0.8
ω_2	a_1	2179.8	664.7
ω_3	a_1	1938.7	270.8
ω_4	a_1	1523.1	9.6
ω_5	a_1	1361.5	16.0
ω_6	a_1	753.3	0.9
ω_7	b_1	910.6	36.1
ω_8	b_1	526.6	5.2
ω_9	b_1	251.5	5.1
ω_{10}	b_1	129.8	1.9
ω_{11}	b_2	3279.4	0.1
ω_{12}	b_2	1031.1	0.2
ω_{13}	b_2	410.6	1.5
ω_{14}	b_2	225.3	6.1
ω_{15}	b_2	137.6	0.0

^{a} Bond lengths (Å), bond angles (degrees), dipole moment (Debye), harmonic frequencies (cm^{-1}), infrared intensities (km/mol), and rotational constants calculated from the equilibrium structure (MHz). Atom numbering is shown in Figure 1. ^{b} From ref 11.

experiment occur for both propadienylidene and butatrienylidene,[44] and the bending modes of both of these species also have small harmonic frequencies with correspondingly large amplitudes of vibration.

Finally, it should be noted that the two high-frequency CC stretching modes in **5** will be readily observable in matrix spectra, as both are predicted to have intensities in excess of 250 km/mol. None of the other species studied in this work is expected to exhibit two strong absorptions in this region of the spectrum (1800−2200 cm^{-1}), and the relative intensities and isotopic shifts (see Table 6) calculated for these modes should provide a reliable diagnostic for laboratory identification of **5**.

A.3. Ethynylcyclopropenylidene (6). The third form of C_5H_2 that has been observed is ethynylcyclopropenylidene (**6**). This species, which is structurally related to the most stable isomer of C_3H_2, has been detected in a diacetylene−neon discharge and studied by Fourier-transform microwave spectroscopy.[12] Qualitative considerations suggest that replacement of hydrogen in **3** by the ethynyl radical provides a slightly increased potential for delocalization and charge separation. That this simple picture is consistent with theory is seen when calculated structures of **3** and **6** are compared. At the CCSD-(T)/cc-pVTZ level, the nominal double-bond lengths are 1.324 and 1.331 Å, respectively. In cyclopropenylidene, the two equivalent CC single bond distances are 1.422 Å,[2d] while those in **6** are 1.394 and 1.433 Å. The shorter of the two is that opposite the ethynyl substituent [$r(C_2-C_3)$ according to the

(44) For a discussion, see ref 19.

(45) Stanton, J. F., unpublished calculation.

(46) The ranges given in the text are somewhat below the calculated CCSD/DZP frequencies, which accounts for both anharmonic contributions and our estimate of the difference between calculated and exact harmonic frequencies.

Table 3.   Results for Ethynylcyclopropenylidene (**6**)[a]

Structure, Rotational Constants and Dipole Moment

parameter	CCSD/ DZP	CCSD/ TZ2P	CCSD(T)/ cc-pVTZ	experiment[b]
$r(H_7C_6)$	1.0738	1.0617	1.0591	
$r(C_5C_6)$	1.2246	1.2044	1.2088	
$r(C_4C_5)$	1.4211	1.4060	1.3940	
$r(C_3C_4)$	1.4514	1.4304	1.4326	
$r(C_2C_4)$	1.3444	1.3270	1.3307	
$r(C_2H_1)$	1.0864	1.0739	1.0730	
θ $(H_1C_2C_4)$	148.32	148.67	148.58	
θ $(C_4C_5C_6)$	179.04	179.08	178.87	
θ $(H_7C_6C_5)$	179.86	179.88	179.96	
θ $(C_3C_4C_5)$	148.81	148.25	148.28	
θ $(C_2C_4C_5)$	149.42	148.67	148.58	
dipole moment	3.499	3.567	3.535	
A	33483	34587	34640	34638
B	3332	3418	3428	3425
C	3030	3110	3120	3114

Harmonic Frequencies and Infrared Intensities

mode	symmetry	frequency	intensity
ω_1	a'	3478.9	68.4
ω_2	a'	3298.9	1.1
ω_3	a'	2194.0	10.3
ω_4	a'	1743.7	6.7
ω_5	a'	1290.4	52.7
ω_6	a'	1130.1	8.9
ω_7	a'	943.9	2.7
ω_8	a'	690.2	1.9
ω_9	a'	604.3	51.6
ω_{10}	a'	474.2	2.1
ω_{11}	a'	178.1	5.3
ω_{12}	a''	880.5	18.0
ω_{13}	a''	696.4	31.3
ω_{14}	a''	507.3	0.8
ω_{15}	a''	204.0	0.8

^{a} Bond lengths (Å), bond angles (degrees), dipole moment (Debye), harmonic frequencies (cm^{-1}), infrared intensities (km/mol), and rotational constants calculated from the equilibrium structure (MHz). Atom numbering is shown in Figure 1. ^{b} From ref 12.

numbering in Figure 1] which carries a double bond in the polar resonance structure. The dipole moment of **6** predicted at the same level of theory is 3.54 D, which is slightly greater than the CCSD(T)/cc-pVTZ value of 3.38 D obtained for **3**.[45]

Rotational constants calculated from both the CCSD/TZ2P and CCSD(T)/cc-pVTZ equilibrium geometries are in excellent agreement with experiment. The near coincidence of measured B_0[12] and calculated B_e values at the latter level of theory is no doubt in part due to fortuitous cancellation of zero-point vibrational averaging and residual inadequacies in the theoretical treatment as they affect B_e. Nevertheless, our survey of the relative energies of C_5H_2 isomers, along with predictions of the structure, dipole moment, and rotational constants of **6** played a pivotal role in spurring the experimental search for this species by microwave spectroscopy.[12] For the most part, the harmonic vibrational frequencies of **6** listed in Table 3 reflect the structural trends discussed above. The three carbon−carbon stretching modes in the three-membered ring are 1743, 1290, and 1130 cm^{-1}, respectively, which are intermediate between the single and double CC bond stretching frequencies in cyclopropene.[47] While all of the other species studied here are expected to have at least one very strong absorption in the fingerprint region of the IR spectrum, none of the CCSD/DZP intensities for **6** exceeds 70 km/mol. Differentiation of this species in the matrix from isomers **7** and **8** may be difficult due to similarities in their predicted harmonic frequencies that in turn reflect the

(47) Yum, T. Y.; Eggers, D. F. *J. Phys. Chem.* **1979**, *83*, 501.

C₅H₂ Isomers

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Table 4. Results for Ethynylpropadienylidene (**7**)[a]

Structure, Rotational Constants and Dipole Moment

parameter	CCSD/DZP	CCSD/TZ2P	CCSD(T)/cc-pVTZ
$r(H_1C_2)$	1.0740	1.0621	1.0595
$r(C_2C_3)$	1.2255	1.2053	1.2105
$r(C_3C_4)$	1.4395	1.4244	1.4128
$r(C_4H_5)$	1.0952	1.0837	1.0836
$r(C_4C_6)$	1.3513	1.3334	1.3372
$r(C_6C_7)$	1.3078	1.2856	1.2858
$\theta(H_1C_2C_3)$	178.51	178.84	178.51
$\theta(C_2C_3C_4)$	176.87	178.01	177.94
$\theta(C_3C_4H_5)$	116.53	116.59	116.22
$\theta(C_3C_4C_6)$	123.84	123.74	124.33
$\theta(C_4C_6C_7)$	177.25	178.10	177.53
dipole moment	4.461	4.616	4.787
A	31795	31614	32436
B	2760	2857	2843
C	2539	2620	2613

Harmonic Frequencies and Infrared Intensities

mode	symmetry	frequency	intensity
ω_1	a'	3475.3	58.5
ω_2	a'	3194.0	1.8
ω_3	a'	2169.7	77.7
ω_4	a'	2001.4	611.9
ω_5	a'	1392.5	4.7
ω_6	a'	1162.0	1.4
ω_7	a'	952.5	58.5
ω_8	a'	633.6	49.0
ω_9	a'	560.8	4.3
ω_{10}	a'	277.3	2.1
ω_{11}	a'	121.6	2.3
ω_{12}	a''	859.8	1.5
ω_{13}	a''	669.6	37.4
ω_{14}	a''	296.1	12.3
ω_{15}	a''	214.8	1.0

[a] Bond lengths (Å), bond angles (degrees), dipole moment (Debye), harmonic frequencies (cm⁻¹), infrared intensities (km/mol), and rotational constants calculated from the equilibrium structure (MHz). Atom numbering is shown in Figure 1.

Table 5. Results for 3-(Didehydrovinylidene)cyclopropene (**8**)[a]

Structure, Rotational Constants and Dipole Moment

parameter	CCSD/DZP	CCSD/TZ2P	CCSD(T)/cc-pVTZ
$r(C_1C_2)$	1.2875	1.2646	1.2686
$r(C_2C_3)$	1.3524	1.3363	1.3325
$r(C_3C_4)$	1.4306	1.4114	1.4128
$r(C_4H_6)$	1.0862	1.0738	1.0728
$\theta(C_2C_3C_4)$	151.82	151.85	151.81
$\theta(H_6C_4C_3)$	149.16	149.26	149.39
dipole moment	8.130	8.207	8.156
A	31277	32172	32080
B	3432	3528	3529
C	3092	3180	3179

Harmonic Frequencies and Infrared Intensities

mode	symmetry	frequency	intensity
ω_1	a_1	3329.2	19.0
ω_2	a_1	2045.3	1309.0
ω_3	a_1	1673.9	41.1
ω_4	a_1	1460.0	235.1
ω_5	a_1	979.3	1.6
ω_6	a_1	732.3	1.6
ω_7	a_2	912.3	—
ω_8	b_1	747.5	55.8
ω_9	b_1	451.2	5.8
ω_{10}	b_1	128.8	0.2
ω_{11}	b_2	3291.5	9.0
ω_{12}	b_2	1150.8	9.8
ω_{13}	b_2	950.1	15.2
ω_{14}	b_2	472.4	1.2
ω_{15}	b_2	149.2	0.0

[a] Bond lengths (Å), bond angles (degrees), dipole moment (Debye), harmonic frequencies (cm⁻¹), infrared intensities (km/mol), and rotational constants calculated from the equilibrium structure (MHz). Atom numbering is shown in Figure 1.

structural motifs common to both. However, only **6** contains *both* an ethynyl substituent and a three-membered ring, so perhaps the combined observation of both the C≡C ring stretching mode and the ethynyl CC stretch (these should appear in the intervals 1600−1700 and 2100−2200 cm⁻¹, respectively[46]) can be used to facilitate its identification.

A.4. Ethynylpropadienylidene (7). While the isomers of C_5H_2 discussed in previous subsections have all been observed in the laboratory, ethynylpropadienylidene remains a hypothetical molecule. Nevertheless, both the known isomer **6** and this species (**7**) are related to the established stable C_3H_2 species cyclopropenylidene and propadienylidene, respectively, via substitution of ethynyl for one of two equivalent hydrogens in the parent molecules. The polarity of **7** is expected to be somewhat greater than **2** because π electrons of the ethynyl group can be delocalized into the fragment that corresponds to the cumulene carbons of **2**. This confers stability to the resonance structure in which the carbene carbon (C_7 in Figure 1) bears a formal negative charge while the carbon β to the tricoordinate carbon (C_2 in Figure 1) is positively charged. Indeed, calculations at the CCSD(T)/cc-pVTZ level predict a dipole moment of 4.6 D for **7** (see Table 4), a value that may be compared to 4.1 D found at the same level of theory for **2**.[45]

The qualitative rationalization for the greater polarity of **7** also provides a basis for understanding aspects of the equilibrium structure of the former isomer. The two internuclear distances in the cumulene fragment at the CCSD(T)/cc-pVTZ level are 1.286 and 1.337 Å for $r(C_6-C_7)$ and $r(C_4-C_6)$, shorter and longer respectively than the corresponding bond distances in

propadienylidene (1.289 and 1.327 Å) calculated at the same level of theory.[2d] Thus, increased participation of the aforementioned polar resonance structure results in more triple-bond character in the outer CC interaction and a correspondingly shorter internuclear distance. Similar arguments explain why the bond between C_4 and C_6 is lengthened in **7** relative to **2**.

Infrared spectra of matrix-isolated C_5H_2 isomers should provide an unambiguous means of identifying isomer **7**. It is the only structure investigated here that should display the characteristic intense stretching feature associated with the cumulene carbenes while simultaneously lacking any other strong absorptions in the region 1000−2000 cm⁻¹. Thus, while cumulene stretching modes are likely to be seen for **5**, **7**, and **8**, only ethynylpropadienylidene (**7**) will have an otherwise unremarkable spectrum in this wavelength range.

A.5. 3-(Didehydrovinylidene)cyclopropene (8). Like ethynylcyclopropenylidene, isomer **8** is structurally related to the most stable form of C_3H_2 (**3**), but differs in that it is obtained from the parent species by addition of C_2 to the carbene carbon rather than replacement of hydrogen by an ethynyl radical. Thus, **8** contains structural features found in both cumulene carbenes and in cyclopropenylidene. Properties of this species are thus expected to exhibit some degree of similarity with both **2** and **3**. The nominal double- and single-bond distances in the three-membered ring of **8** (see Table 5) (1.335 and 1.413 Å at the CCSD(T)/cc-pVTZ level) are longer and shorter than those in **3**,[2d] consistent with the expected increase in conjugation. Similarly, the terminal CC bond in **8** is shorter than that calculated at the same level of theory for **2** (1.269 vs 1.289 Å) while the adjacent bond is longer (1.335 vs 1.327 Å). Altogether, this suggests that resonance structures bearing a formal negative charge on the carbene carbon and a positive charge on one of the carbons in the ring are important in a qualitative

Table 6. Predicted $^{12}C/^{13}C$ Isotopic Shifts of Harmonic Vibrational Frequencies for C_5H_2 Isomers That Contain One Labeled Carbon Atom[a]

carbon	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
						normal mode									
					Isomer **4**										
2	0	23	5	0	13	7	1	4	0	3	0				
3	3	10	9	12	15	1	0	2	0	2	0				
4	0	0	0	0	1	47	0	0	1	1	1				
					Isomer **5**										
1	6	2	6	14	5	10	8	0	1	1	14	8	0	0	1
4	0	23	25	0	6	3	0	7	3	0	0	4	0	4	1
5	0	37	0	6	15	0	0	11	1	1	0	0	7	2	1
6	0	15	35	1	1	4	0	2	4	1	0	0	8	1	0
7	0	2	12	4	10	11	0	0	0	2	0	0	1	1	2
					Isomer **6**										
2	0	13	0	19	13	16	4	4	0	1	1	8	0	0	0
3	0	0	0	3	26	6	4	7	0	3	1	0	0	1	1
4	0	0	4	38	9	18	3	0	0	3	1	3	0	10	2
5	1	0	51	1	0	1	0	5	0	9	1	0	0	6	3
6	17	0	23	4	0	2	1	8	3	1	2	0	5	0	2
					Isomer **7**										
2	17	0	25	0	1	2	6	4	3	1	1	0	5	2	0
3	1	0	51	0	0	1	4	0	8	4	0	2	1	7	0
4	0	10	2	11	21	11	20	0	1	0	1	12	0	0	0
6	0	0	0	51	1	1	1	0	7	4	0	1	0	0	5
7	0	0	0	15	6	10	4	0	3	1	2	0	0	0	2
					Isomer **8**										
1	0	16	7	5	3	10	0	0	0	2	0	0	0	0	2
2	0	48	3	0	0	4	0	1	3	2	0	0	0	8	2
3	0	12	17	22	1	0	0	6	9	0	0	7	11	4	1
4	7	1	16	15	3	5	6	3	0	0	6	14	3	2	0

[a] The mode numbering is consistent with that in Tables 1−5; carbon atoms are numbered as in Figure 1. Values are in cm^{-1} and correspond to $\omega(^{12}C)-\omega(^{13}C)$.

Table 7. Total Electronic[a] and Zero-Point Vibrational Energies for Isomers **4**−**8** at Various Levels of Theory, along with Values Relative to **4**

	electronic energy (au)	zero-point energy[b] (kcal/mol)	relative energy (kcal/mol)
		CCSD/DZP	
4	−191.007027	22.43	0.00
5	−190.987898	25.50	15.07
6	−191.012811	26.18	0.12
7	−190.990022	25.70	13.94
8	−190.981188	26.41	20.19
		CCSD/TZ2P	
4	−191.127547	22.43	0.00
5	−191.104109	25.50	17.78
6	−191.128965	26.18	2.86
7	−191.106269	25.70	16.62
8	−191.096256	26.41	23.62
		CCSD(T)/cc-pVTZ	
4	−191.215187	22.43	0.00
5	−191.198048	25.50	13.82
6	−191.217967	26.18	2.01
7	−191.193656	25.70	16.78
8	−191.187827	26.41	21.14

[a] Includes nuclear repulsion energy. [b] Calculated from CCSD/DZP harmonic frequencies.

description of the electronic structure of **8**. The large charge separation implied by these resonance structures indicates that the molecule should have a substantial dipole moment, an expectation that is confirmed by calculation. The dipole moment at all levels of theory is roughly the same, with the best calculation giving a value of 8.16 D. In passing, we note that the magnitude of the dipole moment is consistent with unlike point charges separated by a distance of about 1.7 Å. This is about half the distance between the carbene carbon and the middle of the three-membered ring, serving to underscore the importance of the polar resonance structures. Hence, it is likely that nucleophilic attack may occur readily at any of the three positions on the ring.

Harmonic frequencies calculated for **8** at the CCSD/DZP level exhibit the anticipated similarities with C_3H_2 isomers **2** and **3**. As in **2**, the in-plane and out-of-plane bending motions of the cumulene fragment have relatively small force constants. The corresponding harmonic frequencies in **8** are somewhat smaller than in **2**, which may again be attributed to the greater participation of polar resonance structures in the former. Similarly, stretching vibrations of the ring carbons in **8** (1673 cm^{-1} for the C=C stretch, 1460 cm^{-1} for the symmetric C−C stretch, and 1151 cm^{-1} for the asymmetric C−C stretch) are similar in magnitude to the corresponding normal mode frequencies in cyclopropenylidene (1634, 1316, and 1089 cm^{-1}, respectively) with conjugation arguments serving to rationalize the increases in stretching frequencies associated with nominal single bonds.

Confirmation of the presence of **8** in the laboratory can probably be based on its two most intense infrared absorptions: the cumulene stretching vibration (ω_2) and the ring stretch mode (ω_4). Strong absorptions near 2000 cm^{-1} are a charac-

teristic feature of cumulene carbenes, and the presence of such a spectral feature in a study of C_5H_2 isomers would clearly implicate either **5**, **7**, or **8**. Of these, however, only **8** also contains a cyclopropenylidene fragment. Hence, the simultaneous presence of strong transitions near 2000 and 1400 cm^{-1} could be used to identify **8**, provided their relative intensities are strongly correlated under experimental conditions. In addition, the predicted isotopic shifts in Table 6 can be used to provide additional support for the assignments.

Clearly, **8** is an ideal candidate for detection by radioastronomy. It has a dipole moment more than twice that of the abundantly distributed cyclopropenylidene (**3**). Provided it exists in appreciable concentrations in molecular clouds, its microwave signals should be conspicuous. It is hoped that the rotational constants calculated from the equilibrium structure (see Table 5) will assist laboratory gas-phase experiments in detecting this species, a necessary prerequisite for efficient search by radioastronomy.

B. Energetics. Absolute and relative energies for the five isomers of C_5H_2 studied here are given in Table 7. At all levels of theory considered in this work, a picture vaguely reminiscent of C_3H_2 emerges.[48] The two most stable forms of both are a quasi-linear triplet and a singlet featuring a three-membered ring with the carbene carbon in the apical position. While the cyclic isomer **3** seems to be the global minimum for C_3H_2,[2d] the order may be reversed in C_5H_2, where the linear isomer **4** is found to lie somewhat below the cyclic form **6** at all levels of theory used here. However, the present results are not adequate to

(48) General trends found for relative stabilities in this work are largely similar to those found at the QCISD/6-31G* level in ref 33, but it is perhaps worthy of mention that density functional calculations using the BLYP parametrization provide a somewhat different picture. Using the 6-31G* level, relative energies of the isomers (in kcal/mol, from ref 33) are as follows: 0.0 (**4**), 8.7 (**5**), 10.0 (**6**), 19.1 (**7**), 23.1 (**8**). Thus, isomers **6** and **7** are predicted to be considerably less stable than at the CCSD(T)/cc-pVTZ level. It is possible that this behavior is related to the documented inadequacy of DFT methods in accounting for the relative energies of allene and propyne. Several different functionals and basis sets predict that allene is the more stable,[16a] but propyne is known from experiment to be thermodynamically the favored isomer, see: Benson, S. W.; Garland, L. J. *J. Phys. Chem.* **1991**, *95*, 4915. These results are consistent with those documented here, as it is the isomers of C_5H_2 that contain an ethynyl substituent that seem to be systematically disfavored in DFT calculations. Hence, some caution may be warranted when DFT methods are applied to problems involving unsaturated carbenes.

provide a definitive answer to the question of which is actually the more stable form. While all calculations find a lower electronic energy for the singlet **6**, the very soft bending vibrations of the linear CCCCC framework in **4** result in a zero-point energy that is substantially lower than that of ethynylcyclopropenylidene. Nevertheless, the reader is reminded that the vibrational corrections are based on the assumption of a quadratic potential energy function, which is probably not a good approximation for **4**. Thus, a fair degree of uncertainty surrounds the magnitude of the vibrational contribution to the thermodynamic energy difference. This consideration, coupled with the very small differences found between electronic energies of **4** and **6** and the apparently opposite effects associated with basis set expansion (which seemingly favors **4**) and higher-level correlation contributions (that stabilize **6**), means that the present results can only be used to argue that these two forms are thermodynamically competitive and that they are both more stable than the other singlet isomers studied in this work.[49] The CCSD(T)/cc-pVTZ calculations predict that the open chain carbenes **5** and **7** lie ca. 15 kcal/mol above the two most stable forms of C_5H_2. Consistency of results obtained at the three levels of theory strongly suggests that **5** and **7** (like **4** and **6**) are essentially equienergetic. Triple excitation effects preferentially stabilize isomer **5**, and it appears that this is the favored form. Looking at the structures of **5** and **7**, it seems plausible that a 1,3-hydrogen shift provides a facile means for isomerization. The question of isomerization will be dealt with in future work on this system that focuses on both automerization and isomerization mechanisms on the C_5H_2 surface. Finally, isomer **8** is predicted to lie a few kcal/mol above **5** and **7**, thereby placing it about 20 kcal/mol relative to **4** and **6**. It is

(49) An intriguing bipyramidal structure of C_5H_2 has also been investigated previously.[50] At the HF/6-31G* level singlet pentacyclo[2.1.0.0.^{1,3} 0.^{2,4} 0.^{2,5}]pentane (**9**) lies about 100 kcal/mol higher than **4**. Remarkably, this difference drops to about 30 kcal/mol when the MBPT(2) treatment of correlation is used with the same basis set.[50a]

9

However, higher level calculations using both density functional theory and correlation treatments based on the coupled-cluster approximation predict substantially higher energies for **9**, in the range 50−70 kcal/mol. Therefore, the MBPT(2) result appears to be anomalous, and the bipyramidal structure is apparently considerably less stable than the isomers studied in the body of the text.

(50) (a) Balaji, V.; Michl, J. *Pure Appl. Chem.* **1988**, *60*, 189. (b) Ekholm, M.; Nevalainen, V.; Pyykkö, P. *Finn. Chem. Lett.* **1989**, *16*, 107. (c) Gund, P.; Gund, T. M. *J. Am. Chem. Soc.* **1981**, *103*, 4458.

possible that most, if not all, of the forms of this intriguing molecule pictured in Scheme 2 may be present in the interstellar medium. In that environment, where rates of thermal reactions are extremely sluggish, the relative proportions of the isomers are determined largely by completely unknown formation mechanisms. Laboratory identification of the as-yet-unobserved species **7** and **8** may be facilitated by the results presented in this paper. The corresponding rotational constants given in Tables 1−5 should help to confirm microwave assignments for these isomers. Isomers **5**−**8** possess significant dipole moments and therefore represent ideal candidates for observation in the laboratory and in interstellar clouds.

Summary

The equilibrium structure and thermodynamic stabilities of five isomers of C_5H_2 have been computed at three levels of theory: CCSD/DZP, CCSD/TZ2P, and CCSD(T)/cc-pVTZ. The calculations suggest that triplet pentadiynylidene (**4**) is the global minimum, although the energy separation between this isomer and singlet ethynylcyclopropenylidene (**6**) is so small that a definitive conclusion regarding the most stable form of C_5H_2 cannot be formed. The relative stabilities of the five isomers cluster into three groups, with the lowest comprising **4** and **6**. About 15 kcal/mol above these species lie pentatetraenylidene (**5**) and ethynylpropadienylidene (**7**), two isomers that appear to be associated with effectively degenerate minima on the potential energy surface. Somewhat above these lies 3-(didehydrovinylidene)cyclopropene (**8**), a species that is expected to have an extremely large dipole moment.

Detailed studies of isomerization, automerization, and mechanistic photochemistry in the C_3H_2 system have elucidated many processes that may be transferable to C_5H_2. Accordingly, we maintain a keen interest in the latter, and hope soon to study isomers of this system in low-temperature matrices. To this end, the harmonic vibrational frequencies and the associated $^{12}C-^{13}C$ isotopic shifts listed in the matrix given in Table 6 should be invaluable in the unambiguous identification of C_5H_2 isomers.