Computational Studies of C_6H_2 Isomers

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Received November 22, 1999

Abstract: High-level ab initio methods are used to characterize nine isomers of C_6H_2. These include the thermodynamically favored triacetylene form and hexapentaenylidene, which is known to exist in the interstellar medium. Also included in the survey are three cyclic forms of tetradehydrobenzene and four additional structures that have not been investigated previously. Structures, dipole moments, parameters of rotational Hamiltonians, vibrational frequencies, intensities, and ^{13}C isotopic shifts are documented for all forms to assist efforts aimed at detecting these species in the laboratory. Perhaps the best candidate for detection in space is ethynylbutatriehylidene, which has a substantial dipole moment and a thermodynamic stability comparable to that of hexapentaenylidene. Notably, the symmetric disubstituted vinylidene isomer has a small and perhaps vanishing barrier to rearrangement.

I. Introduction

Although the interstellar medium (ISM) was once thought to be chemically barren, it has become clear that quite the opposite is true. Indeed, more than 100 species have been detected in space, and the list is growing by several molecules each year.[1] While some of the molecules known to be present are prosaic from a terrestrial perspective (e.g., water, hydrogen cyanide, ammonia), the majority of them are rather exotic. Particularly prominent among the more unusual molecules are carbon-rich species such as the cyanopolyynes, acetylenic radicals, cumulene carbenes $:CC_nH_2$ ($n = 2$, 3, and 5), and the three-membered ring compound cyclopropenylidene.[2]

The abundance of molecules in the ISM that would otherwise decompose or react rapidly at appreciable temperatures and pressures suggests that chemical intuition and thermodynamic considerations are of limited value for predicting which species might be present. A telling consequence of this is the famous problem of the diffuse interstellar bands (DIBs), which consist of more than 200 absorptions in the visible region of the spectrum.[3] It appears that not one of these is due to a molecule that is commonly found on earth. Only recently has a nearly definitive assignment been made; Maier and co-workers noted compelling coincidences between four of the DIBs and transitions found in a gas-phase cavity ring down the electronic spectrum of C_7^-.[4] That the first reasonably conclusive assignment of specific diffuse interstellar bands involves an electronic transition in a polycarbon anion serves to underscore the strange chemical composition of the ISM.

The list of molecules known to be present in space is strongly biased toward polar species because the principal means that has been used to identify them is radioastronomy. Since the intensity of microwave transitions is proportional to the square of the electric dipole moment, searches for astronomical species are particularly senisitive to highly polar molecules such as the family of cumulene carbenes. Nevertheless, the confirmed presence of even-numbered members of this family such as $:C{=}C{=}C{=}CH_2$ (butatrienylidene)[5] and $:C{=}C{=}C{=}C{=}C{=}CH_2$ (hexapentaenylidene)[6] is remarkable. In the thermodynamic sense, both of these structures are highly unstable with respect to the corresponding linear polyacetylene isomers (diacetylene and triacetylene). Although the latter species are nonpolar, and their abundance therefore unknown, the presence of detectable amounts of the corresponding cumulene carbenes suggests that the isomeric partitioning of these species is far from that which would be predicted from equilibrium considerations.

A particularly fruitful approach of preliminary laboratory investigation followed by radioastronomical search has been used in recent years to identify ISM molecules. Figuring prominently in this area is the research of Thaddeus and co-workers, who have identified a number of new carbon-rich molecular species by studying Fourier transform microwave spectra of discharges.[7] By varying source conditions and other experimental parameters, it is possible to enhance signals that correspond to specific chemical species selectively and to determine their rotational constants and approximate molecular structures. The resonant microwave frequencies found in the laboratory study then serve to guide searches for the same species in space.

The laboratory identification of molecules mentioned above is certainly not straightforward. The discharge produces a large number of molecular species, and the carriers for over 50% of

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[1] For a relatively up-to-date list of known astronomical molecules, visit the Web page http://cfa-www.harvard.edu/cfa/mmw/mmwlab/ismmolecules-_carbon.html that is maintained by the Thaddeus group at the Center for Astrophysics at Harvard University.

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10.1021/ja9940874 CCC: $19.00

the observed transitions are unknown.[8] In many cases, however, the structure of a molecule can be calculated with sufficient accuracy to assist in the search for and assignment of its laboratory microwave spectrum. In a particularly notable recent example of this useful area of application for quantum chemistry, two high-lying isomers of C_5H_2 that had been characterized theoretically[9] were found in the microwave spectrum of an acetylene discharge by McCarthy et al.[10,11] as was the ring-chain isomer of the isoelectronic HC_4N species.[12] In these cases, observed rotational constants agreed with those estimated from the principal moments of inertia of the calculated equilibrium structure to within 1%. The present paper focuses on isomers of the C_6H_2 molecule and is a logical extension of studies carried out by our group and collaborators for the other carbon-rich systems such as C_3H_2,[13] C_5H,[14] and C_5H_2.[9] While triacetylene and hexapentaenylidene (hereafter referred to as **1** and **2**, respectively) are the only species of C_6H_2 that have been observed, others have been studied computationally. In a significant recent paper, Bettinger et al. studied the para, meta, and ortho isomers of the tetradehydrobenzene form of C_6H_2 (hereafter **3**, **4**, and **5**, respectively), providing predictions of their relative stabilities and infrared spectra.[15] To our knowledge, the only other unstable (i.e., non-triacetylene) isomer of C_6H_2 that has been characterized theoretically is **2**, which was included in the oft-cited cumulene carbene survey of Maluendes and McLean.[16] Although our initial intention was to investigate “all” reasonable structures of C_6H_2, the number of isomers found to represent local minima on the potential energy surface in a preliminary low-level survey was depressingly large. In order to make things manageable, the scope of the study was significantly restricted. In this work, only those isomers of C_6H_2 that have been mentioned above, as well as other forms that can be obtained from the C_5H_2 isomers studied in ref 9 by replacing a lone pair of electrons with :C=, are considered. These are ethynylbutatrienylidene, **6**; the “eiffelene” isomer, **7** (3-(didehydropropadienylidene)cyclopropene); (3-(didehydromethylene)-1-ethynylcyclopropene), **8**; and the disubstituted vinylidene, **9**. For reasons that will be discussed later, another molecule that falls into this category—butadiynyl vinylidene—is not included. The atomic connectivity for all of the isomers is depicted in Figure 1. Other schemes could have been used to select isomers for study, and the present research certainly should not be considered an exhaustive *survey* of C_6H_2 isomers. Rather, we have chosen to perform exhaustive *calculations* on the structure and relative energies of the isomers that were considered.

Unlike the smaller odd-numbered C_nH_2 species, where low-lying nonlinear and cyclic forms are thermodynamically competitive with linear (or quasilinear) HC_nH isomers,[9,13] triacetylene is clearly the most stable form of C_6H_2. Nevertheless, the presence of **2** in the ISM suggests the possibility that other isomers of C_6H_2 might also be found in space. The work presented here should facilitate laboratory detection of previously unobserved C_6H_2 isomers under conditions where they are present in reasonable abundance. The most likely scenarios for observation of these structures are in discharges studied by microwave spectroscopy and in rare-gas matrixes probed by infrared spectroscopy. Hence, the properties computed for these isomers have been specifically chosen to be those which are related to observable and determinable quantities associated with these branches of spectroscopy.

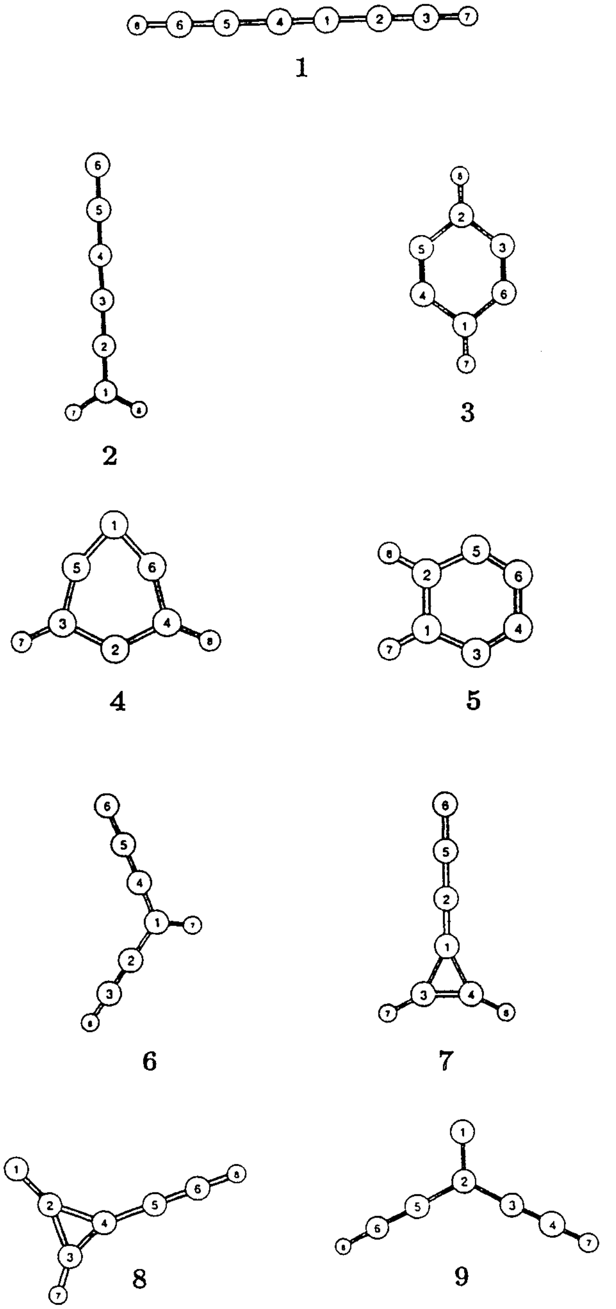

Figure 1. Isomers of C_6H_2 considered in the present study.

II. Computational Methods

Geometries for C_6H_2 isomers were optimized at three different levels of theory. The first is partial fourth-order many-body perturbation theory[17] [SDQ-MBPT(4)] using the triple-zeta plus double polarization

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Table 1. Cartesian Coordinates (in Bohr) for C_6H_2 isomers **1**−**9**[a]

	isomer **1**			isomer **2**			isomer **3**	
0.0000	0.0000	−1.1499	0.0000	0.0000	−5.9044	2.8008	0.0000	0.0000
0.0000	0.0000	−3.7290	0.0000	0.0000	−3.4245	−2.8008	0.0000	0.0000
0.0000	0.0000	−6.0191	0.0000	0.0000	−1.0085	−1.1960	2.1011	0.0000
0.0000	0.0000	1.1499	0.0000	0.0000	1.3935	1.1960	−2.1011	0.0000
0.0000	0.0000	3.7290	0.0000	0.0000	3.8378	−1.1960	−2.1011	0.0000
0.0000	0.0000	6.0191	0.0000	0.0000	6.2712	1.1960	2.1011	0.0000
0.0000	0.0000	−8.0212	−1.7576	0.0000	−6.9368	4.8290	0.0000	0.0000
0.0000	0.0000	8.0212	1.7576	0.0000	−6.9368	−4.8290	0.0000	0.0000
	isomer **4**			isomer **5**			isomer **6**	
0.0000	0.0000	−3.1084	1.3505	0.0000	−2.1361	1.1403	−1.5742	0.0000
0.0000	0.0000	2.5145	−1.3505	0.0000	−2.1361	3.3303	−0.0325	0.0000
−2.3328	0.0000	1.3050	2.5376	0.0000	0.2109	5.2329	1.2304	0.0000
2.3328	0.0000	1.3050	1.2609	0.0000	2.2549	−1.1808	−0.6730	0.0000
−1.6655	0.0000	−1.1864	−2.5376	0.0000	0.2109	−3.4619	0.1553	0.0000
1.6655	0.0000	−1.1864	−1.2609	0.0000	2.2549	−5.7529	0.9988	0.0000
−4.1797	0.0000	2.1242	2.3124	0.0000	−3.9257	1.3569	−3.6067	0.0000
4.1797	0.0000	2.1242	−2.3124	0.0000	−3.9257	6.8848	2.3596	0.0000
	isomer **7**			isomer **8**			isomer **9**	
0.0000	0.0000	−1.4819	−4.0115	−2.1780	0.0000	0.0000	0.0000	−3.3324
0.0000	0.0000	0.9515	−2.4618	−0.2808	0.0000	0.0000	0.0000	−0.8189
−1.2354	0.0000	−3.9392	−1.6321	2.3617	0.0000	0.0000	−2.3816	0.4385
1.2354	0.0000	−3.9392	0.1892	0.7197	0.0000	0.0000	−4.4317	1.4404
0.0000	0.0000	3.3995	2.6954	−0.0514	0.0000	0.0000	2.3816	0.4385
0.0000	0.0000	5.8326	4.8509	−0.8072	0.0000	0.0000	4.4317	1.4404
−3.0154	0.0000	−4.9018	−2.3444	4.2534	0.0000	0.0000	−6.2180	2.3428
3.0154	0.0000	−4.9018	6.7500	−1.4438	0.0000	0.0000	6.2180	2.3428

[a] The coordinates correspond to structures optimized at the CCSD(T) level of theory with the cc-pVTZ basis set, and the ordering of the atoms correspond precisely to the numbering scheme used in Figure 1 for all isomers.

(TZ2P) basis set described in ref 18.[18] The second is coupled-cluster theory[19] with single and double substitutions [CCSD],[20] also using the TZ2P basis. The highest level of theory used here is CCSD augmented by a perturbative treatment of triple excitation effects [CCSD(T)][21] with the correlation-consistent polarized triple zeta (cc-pVTZ) basis set of Dunning.[22] For C_6H_2 isomers, the TZ2P and cc-pVTZ basis sets comprise 162 and 208 basis functions, respectively (spherical harmonic representations of d and f polarization functions were used in all calculations).

Optimizations were performed with analytic energy derivatives[23] and were considered to be converged when the root-mean-square gradient in internal coordinates fell below 10^{-5} au. Components of the dipole moment along the inertial axes were also determined analytically at all levels of theory. At geometries obtained in the SDQ-MBPT(4)/TZ2P optimizations, second derivatives of the energy and first derivatives of the dipole moment with respect to displacements were obtained analytically[24] at the same level of theory. Harmonic vibrational frequencies were determined by diagonalization of the mass-weighted Hessian matrix, and transformation of the dipole moment derivatives to the vibrational normal coordinates yielded the infrared intensities. Rotational constants of the rigid equilibrium structure (A_e, B_e, C_e) were calculated from the inertia tensor corresponding to the optimized structures, and centrifugal distortion parameters corresponding to the A-reduced Hamiltonian in the III^r representation[25] were calculated from the SDQ-MBPT(4)/TZ2P harmonic force constants as detailed in ref 26.[26] A local version of the ACES II program system[27] was used in this work.

Table 2. Total Electronic, Vibrational Zero-Point, and Relative (to Acetylene) Energies of C_6H_2 Isomers[a]

isomer	electronic energy (au)	zero-point energy (kcal/mol)	relative energy (kcal/mol)
1	−229.303033	29.45	0.0
2	−229.221730	28.76	50.3
3	−229.221399	34.43	56.2
4	−229.243071	31.24	39.4
5	−229.230479	31.79	46.3
6	−229.216095	28.96	54.1
7	−229.182121	28.94	75.3
8	−229.179413	28.50	76.6
9	−229.202562	28.31	61.9

[a] The electronic energies are those evaluated at the CCSD(T)/cc-pVTZ level of theory at the corresponding minimum energy geometries, and the zero-point energies are obtained from the SDQ-MBPT(4)/TZ2P harmonic frequencies.

III. Results and Discussion

Cartesian coordinates corresponding to the optimized CCSD(T)/cc-pVTZ geometries of isomers **1**−**9** are documented in Table 1 . Total energies calculated with CCSD(T)/cc-pVTZ at the respective equilibrium geometries are listed in Table 2, along with relative (to triacetylene) values both with and without zero-point vibrational contributions that are estimated from the SDQ-MBPT(4)/TZ2P harmonic force fields. Table 3 gives rotational constants and centrifugal distortion parameters obtained from

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(25) For isomer **2**, the centrifugal distortion constants given in Table 3 are those for the S-reduced Hamiltonian, which is appropriate because this isomer is a near symmetric top. Despite the row label, the parameters given are Δ_J, Δ_{JK}, Δ_K, σ_1, and σ_2, respectively.

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Table 3. Rotational Constants, Centrifugal Distortion Constants, and Inertial Axis Dipole Moment Components (III^r Representation) for Isomers **2**−**9**[a]

	isomer **2**	isomer **3**	isomer **4**	isomer **5**
A (MHz)	289835.8	8516.8	7766.0	7299.3
B (MHz)	1346.6	5937.8	6549.3	6844.5
C (MHz)	1340.4	3498.6	3553.0	3532.3
Δ_J (kHz)	0.0253	0.662	1.03	1.45
Δ_K (kHz)	22300.	2.40	2.57	2.63
Δ_{JK} (MHz)	0.0208	0.00108	−0.000708	−0.000574
δ_J (kHz)	−0.000124	0.253	0.424	0.642
δ_K (kHz)	−0.0000303	1.40	0.789	1.55
μ_a (D)	−6.098		1.427	−1.151
$\|\mu\|$ (D)	6.098		1.427	1.151

	isomer **6**	isomer **7**	isomer **8**	isomer **9**
A (MHz)	21399.8	32837.5	11336.2	8727.8
B (MHz)	1664.0	1795.8	2509.2	2633.1
C (MHz)	1543.9	1702.8	2054.5	2022.7
Δ_J (kHz)	0.579	0.0575	1.06	1.02
Δ_K (kHz)	2510.	55.2	167	81.2
Δ_{JK} (MHz)	−0.0662	0.0162	−0.0147	−0.00100
δ_J (kHz)	0.144	0.00326	0.377	0.434
δ_K (kHz)	3.53	8.42	5.97	8.16
μ_a (D)	3.718	−7.936	3.571	
μ_b (D)	−1.325		3.322	2.034
$\|\mu\|$ (D)	3.947	7.936	4.877	2.034

[a] Centrifugal distortion constants are based on the A-reduced Hamiltonian representation for all isomers except **2**, where the S-reduced Hamiltonian is used.

the CCSD(T)/cc-pVTZ equilibrium geometries and SDQ-MBPT(4)/TZ2P harmonic force fields, respectively, as well as the principal axis dipole moment components. In Table 4, the SDQ-MBPT(4)/TZ2P harmonic vibrational frequencies and infrared intensities are given for the nine isomers; information about ^{13}C isotopic frequency shifts is given in Table 5.

Supporting Information that accompanies this paper includes energies and full sets of internal coordinates that correspond to optimized structures at the SDQ-MBPT(4)/TZ2P, CCSD/TZ2P, and CCSD(T)/cc-pVTZ levels of theory.

A. Triacetylene (1) and Hexapentaenylidene (2). Triacetylene is energetically below and well-separated from other isomers of C_6H_2, as clearly shown in Table 2. Unlike the odd-numbered linear C_nH_2 species which can be considered to be relatively unstable diradicals with small singlet−triplet splittings, **1** is clearly a closed-shell singlet. However, due to a combination of its lack of a dipole moment and explosive properties, the structure of this isomer has apparently not been determined experimentally. Analysis of infrared bands has shown that the rotational constant is about 1325 MHz,[28] in striking agreement with the 1322 MHz value for B_e that corresponds to the CCSD(T)/cc-pVTZ equilibrium structure. Bond lengths found at this level of theory are 1.059 Å for the CH distance and 1.212, 1.365, and 1.217 Å for the CC distances (outermost−innermost). With respect to those found at the SCF level of theory with a 6-31G** basis set (1.188, 1.385, 1.191, and 1.057 Å, respectively), the latter exhibit less bond alternation, a feature that is characteristically exaggerated at the SCF level of theory. The harmonic vibrational frequencies listed in Table 4 are also in good agreement with the experimental fundamentals [in cm^{-1}: 3313, 2201, 2109, 625 (σ_g); 3329, 2129, 1115 (σ_u); 622, 491, 258 (π_g); and 621, 443, 108 (π_u)].[29] With the exception of the stiffest bending frequencies having even and odd inversion symmetry, the calculated values lie above the observed frequencies, as expected from simple considerations of vibrational anharmonicity.

Hexapentaenylidene (**2**) lies approximately 50 kcal/mol above **1**, a separation that is larger than those estimated for vinylidene and acetylene (43.7 ± 0.6 kcal/mol[30]) and butatrienylidene and diacetylene (46.4 kcal/mol[31]). This suggests that energy differences between polyacetylenes and the corresponding cumulene carbenes may increase with chain length. In this context, it is interesting to note that the fractional abundance of **2** in space is known to be an order of magnitude lower than that of butatrienylidene,[32] while models predict that the total amount of C_6H_2 greatly exceeds that of C_4H_2 when all isomers are considered.[33] Given that the equilibrium constant for isomerization of **l** to **2** is $\sim 10^{-40}$ even at room temperature, however, the presence of detectable amounts of **2** in the ISM suggests that thermodynamic considerations are largely irrelevant. If the models are correct, it seems more likely that other isomers of C_6H_2 are present but have not yet been detected, including some of those studied in this work.

The structure of **2** obtained in the CCSD(T)/cc-pVTZ calculation (1.288, 1.294, 1.271, 1.279, and 1.312 Å for the CC distances [top to bottom in Figure 1]; 1.079 Å for the CH distance; and 120.4° for the CCH bond angle) is quite similar to that obtained at the MBPT(2)/6-31G** level by Maluendes and McLean[16] (1.289, 1.304, 1.275, 1.287, and 1.317 Å; 1.081 Å and 120.6°). *B* and *C* rotational constants corresponding to the calculated equilibrium structure are again in excellent agreement with the observed values of 1348 and 1341 MHz,[34] differing by only 1 MHz in both cases. Centrifugal distortion constants (in the S-reduced representation) are also in satisfactory agreement; calculated (observed) Δ_J and Δ_{JK} values are 0.025 (0.028) kHz and 0.021 (0.016) MHz, respectively. The CCSD(T)/cc-pVTZ dipole moment of 6.1 D is only slightly smaller than that reported by Maluendes and McLean.[16] Harmonic vibrational frequencies calculated for **2** suggest that the infrared spectrum should be completely dominated by three very strong C−C stretching modes between 1700 and 2200 cm^{-1}. Observation of these absorptions combined with isotopic shifts similar to those predicted in Table 5 should provide a straightforward means for confirming the presence of **2** in rare-gas matrixes. It should be noted that **2** has C_{2v} symmetry, but the softest vibrational mode has a predicted harmonic frequency of only 91 cm^{-1}. This is the smallest vibrational frequency yet calculated for a cumulene carbene and corresponds to an in-plane kinking motion of the carbon chain. This may be attributed to a second-order Jahn−Teller interaction[35] that couples the ground state to a low-lying $^1B_2$ excited state. In general, one expects excitation energies of cumulene chains to decrease with size. If the nonadiabatic coupling matrix elements that link the ground and excited states are insensitive to size, it is probable that equilibrium geometries of large cumulene carbenes will have kinked carbon chains. However, no clear evidence of this

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Table 4. Harmonic Vibrational Frequencies (in cm^{-1}) and Infrared Intensities (km mol^{-1}, in Parentheses) for Isomers of C_6H_2

mode	isomer **1**		isomer **2**		isomer **3**		isomer **4**		isomer **5**	
1	π_u	108(9)	b_2	91(2)	b_{3u}	350(13)	b_1	469(1)	b_2	369(98)
2	π_g	253(−)	b_1	102(0)	a_u	520(−)	b_1	567(−)	a_2	416(−)
3	π_u	443(4)	b_2	197(7)	b_{3g}	571(−)	a_2	572(−)	a_1	464(67)
4	π_g	495(−)	b_1	223(5)	b_{2g}	591(−)	a_1	606(77)	b_1	469(3)
5	σ_g	612(−)	b_2	363(0)	b_{1u}	633(149)	a_1	616(56)	a_2	549(−)
6	π_g	652(−)	b_1	452(3)	a_g	687(−)	b_2	617(11)	b_2	732(15)
7	π_u	652(172)	b_1	472(0)	b_{3u}	847(34)	b_1	771(58)	b_1	772(51)
8	σ_u	1157(1)	b_2	552(4)	b_{2g}	905(−)	a_2	790(−)	a_2	936(−)
9	σ_g	2102(−)	a_1	650(0)	b_{2u}	959(43)	b_2	972(1)	a_1	1039(15)
10	σ_u	2212(1)	b_1	850(56)	a_g	1097(−)	a_1	997(45)	a_1	1065(1)
11	σ_g	2354(−)	b_2	1013(0)	b_{3g}	1228(−)	a_1	1104(16)	b_2	1152(24)
12	σ_g	3478(−)	a_1	1210(0)	b_{1u}	1297(3)	b_2	1235(0)	a_1	1289(3)
13	σ_u	3478(194)	a_1	1459(1)	b_{2u}	1332(0)	b_2	1269(1)	a_1	1367(4)
14			a_1	1751(203)	b_{3g}	1396(−)	a_1	1277(1)	b_2	1405(1)
15			a_1	2078(304)	b_{2u}	1766(2)	b_2	1607(1)	a_1	1780(12)
16			a_1	2186(1937)	a_g	1963(−)	a_1	1739(137)	b_2	1913(0)
17			a_1	3184(21)	b_{1u}	3269(4)	b_2	3321(4)	b_2	3250(0)
18			b_2	3282(5)	a_g	3273(−)	a_1	3322(1)	a_1	3267(4)

mode	isomer **6**		isomer **7**		isomer **8**		isomer **9**	
1	a'	87(4)	b_2	108(3)	a'	107(7)	a_1	120(2)
2	a'	179(5)	b_1	137(0)	a''	195(7)	b_2	131(4)
3	a''	186(0)	b_2	237(5)	a'	222(6)	b_1	202(2)
4	a''	333(16)	b_1	327(9)	a''	344(0)	a_2	342(−)
5	a'	363(5)	b_1	400(0)	a''	480(0)	b_2	344(9)
6	a''	468(0)	b_2	569(3)	a'	500(6)	a_1	534(12)
7	a'	591(2)	a_1	625(0)	a'	630(0)	b_1	581(0)
8	a''	638(48)	b_1	651(62)	a''	672(27)	a_2	633(−)
9	a'	685(38)	a_2	824(−)	a'	677(38)	b_1	639(94)
10	a''	735(12)	b_2	900(0)	a''	723(40)	b_2	694(14)
11	a'	891(2)	a_1	977(8)	a'	858(6)	a_1	694(53)
12	a'	1051(2)	b_2	1050(20)	a'	942(23)	a_1	740(7)
13	a'	1312(1)	a_1	1210(1)	a'	1027(9)	b_2	1162(12)
14	a'	1713(50)	a_1	1621(20)	a'	1644(143)	a_1	1634(18)
15	a'	2132(742)	a_1	1847(235)	a'	1887(22)	a_1	2191(0)
16	a'	2196(4)	a_1	2123(440)	a'	2213(8)	b_2	2203(0)
17	a'	3201(24)	b_2	3301(21)	a'	3341(25)	b_2	3478(115)
18	a'	3479(81)	a_1	3349(17)	a'	3475(81)	a_1	3479(27)

has been found experimentally for the longer chains H_2C_8, H_2C_9, and D_2C_{10}.[36]

The remarkable agreement between rotational constants calculated at the CCSD(T)/cc-pVTZ level for isomers **1** and **2** and those observed in the laboratory is largely consistent with our previous experience with astronomically relevant carbon-rich hydrocarbons. Of course, any agreement between measured rotational constants (which include contributions from vibration−rotation interaction and centrifugal distortion effects) and A_e, B_e, and C_e values that correspond to rigid rotation is at least partly fortuitous. Nevertheless, the agreement can be rationalized to some extent. At the CCSD(T)/cc-pVTZ level of theory, systematic errors in bond lengths due to basis-set insufficiency are expected to be greater in magnitude than those due to neglect of higher order correlation effects. Since increasing the size of the basis set tends to decrease internuclear separations and correlation tends to increase them,[37] one expects structures at this level of theory to be slightly extended relative to the true equilibrium geometries. Hence, calculated A_e, B_e, and C_e values are generally smaller than the corresponding (and experimentally indeterminable) exact values. However, vibrational effects usually cause the measured rotational constants to be smaller than the equilibrium values, and it appears that the magnitudes of these contributions (residual basis-set effects in the calculations and vibration−rotation interaction in the experiment) are comparable for these molecules. Since the calculated equilibrium rotational constants for all six isomers of C_5H_2[10,11] and C_6H_2[34] that have been observed so far agree with measured values to better than one percent, it is not unrealistic to hope that similarly spectacular agreement will be achieved for the as-yet-unobserved isomers of C_6H_2 discussed in the remainder of this paper. However, it must be emphasized that basis-set effects and vibration−rotation interaction are distinctly different things, and one cannot glibly assume that they will effectively cancel in all cases.

B. Tetradehydrobenzenes (3−5). Although tetradehydrobenzenes (TDHBs) have been implicated as reactive intermediates in the pyrolysis of pyromellitic (1,2,4,5-) dianhydrides,[38]no conclusive spectroscopic identification of these compounds has emerged apart from some tantalizing evidence for the disubstituted 1,4-bis(trifluoromethyl)-2,3,5,6-tetradehydrobenzene form of the para isomer[39] (**3**). In addition, these systems received little attention from computational chemists until last year when Bettinger et al. carried out geometry optimizations and evaluated harmonic frequencies for all forms.[15] A number of interesting results emerged from their work. First, the meta isomer **4** is evidently the most stable of the TDHBs, despite the fact that it is the one least well described by a traditional Lewis structure.

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Table 5. Predictions of $^{12}C/^{13}C$ Isotopic Shifts (in cm^{-1}) in Harmonic Vibrational Frequencies for Isomers of C_6H_2 Computed at the SDQ-MBPT(4)/TZ2P Level of Theory

	normal mode																	
C	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Isomer **1**																		
1	1	2	3	6	0	0	0	15	11	2	33	0	0					
2	0	2	6	3	5	0	0	1	22	23	7	1	0					
3	1	1	1	0	7	4	0	7	13	10	2	17	0					
Isomer **2**																		
1	1	1	0	0	0	0	1	0	8	8	8	8	6	11	4	1	6	13
2	0	0	1	1	7	4	7	0	3	0	7	1	2	19	23	10	0	0
3	1	1	2	2	2	0	7	6	0	0	0	12	0	6	9	31	0	0
4	1	1	0	1	1	9	1	12	1	0	0	10	2	10	11	25	0	0
5	0	0	4	3	1	6	0	3	4	0	0	0	0	14	33	6	0	0
6	1	1	1	1	0	0	0	0	8	0	0	11	2	11	8	1	0	0
Isomer **3**																		
1	2	0	1	3	2	6	6	2	8	10	1	10	9	12	0	1	9	2
3	1	5	6	4	5	3	0	0	3	5	4	7	1	3	18	17	0	0
Isomer **4**																		
1	0	2	0	14	2	1	0	0	0	2	4	14	5	3	17	0	0	0
2	7	1	0	4	1	0	0	0	18	9	10	3	0	0	4	13	0	0
3	0	5	2	2	2	0	2	2	9	8	11	1	15	2	7	4	11	1
5	5	2	5	10	10	1	0	0	0	1	1	5	2	0	14	20	0	0
Isomer **5**																		
1	0	0	1	1	6	9	3	4	7	12	5	8	6	9	2	1	6	4
3	2	1	6	6	3	5	0	0	7	1	5	0	8	2	16	19	0	0
4	6	7	2	2	0	0	0	0	6	1	3	2	14	1	21	13	0	0
Isomer **6**																		
1	0	1	1	0	0	0	0	0	0	11	18	15	9	20	4	1	10	0
2	0	1	0	8	7	0	5	1	1	2	2	2	1	0	2	50	0	1
3	1	1	0	2	1	0	3	5	5	0	2	6	1	1	0	25	0	17
4	0	0	1	0	3	10	10	0	0	1	4	2	6	18	31	0	0	0
5	0	4	2	0	2	7	2	0	0	0	2	0	0	15	38	0	0	0
6	1	1	2	0	0	0	3	0	0	0	7	5	4	15	6	0	0	0
Isomer **7**																		
1	0	0	2	9	1	2	0	1	0	16	1	0	17	1	24	9	0	0
2	1	2	0	1	6	13	1	0	0	1	0	0	10	7	5	35	0	0
3	0	0	1	0	0	2	5	2	5	7	1	8	5	23	4	1	6	7
5	1	0	5	2	7	2	4	0	0	0	0	0	0	1	23	28	0	0
6	2	2	1	0	1	0	7	0	0	0	1	0	11	3	13	4	0	0
Isomer **8**																		
1	2	0	1	2	0	1	0	0	0	0	11	0	1	18	7	0	0	0
2	0	0	2	8	2	6	4	0	0	0	5	1	1	26	16	0	0	0
3	0	1	1	0	0	1	5	0	0	7	9	10	11	6	15	1	13	0
4	0	2	1	0	8	1	5	0	0	3	6	15	1	16	25	5	0	0
5	0	2	2	2	6	9	4	1	0	0	0	2	0	0	2	50	0	1
6	1	1	1	0	0	1	5	5	5	0	0	5	1	1	3	22	0	17
Isomer **9**																		
1	0	0	2	0	0	1	13	0	1	0	0	3	33	38	1	3	0	0
2	0	3	1	0	0	1	1	0	0	0	0	9	0	25	0	0	0	0
3	0	0	1	5	5	8	4	0	0	0	0	3	1	0	46	5	1	0
4	1	0	1	1	1	2	1	3	1	5	0	5	5	0	21	4	17	0

While two isolated triple bonds can be assigned to both **3** and the ortho form, **5**, the situation with **4** is more complicated. Computationally, Bettinger et al. found that the structure adopts an effectively bicyclic geometry, which can be seen in Figure 1, a finding that was reproduced in our study. Second, the singlet−triplet gaps of all TDHBs were found to be quite large at high levels of theory [CCSD(T) with a TZ2P basis set that differs slightly from that used in this work], a somewhat surprising result for **3** since the most logical Lewis structure for this species is a biradical.

The results of our calculations for the TDHBs are consistent with those of Bettinger et al. The CCSD(T)/cc-pVTZ geometries differ somewhat predictably from those obtained in that work with CCSD and their TZ2P basis (for **3**) and CCSD with a smaller double-zeta plus polarization (DZP) basis (for **4** and **5**). As one would expect, the larger basis used in the present series of calculations gives more compact structures for **3**, while differences between the CCSD/DZP structures and those of the present work also tend in the same direction, indicating that basis-set effects are more important than the triples contribution to the correlation energy. The only exception in which the CCSD(T)/cc-pVTZ bond length is shorter than the best values given in ref 15 is the transannular C−C distance in **4**, where the present value of 1.763 Å is slightly longer than the 1.756 Å found at the CCSD(T)/DZP level, hardly a significant difference. One interesting feature was noted in the present study that went unmentioned in ref 15. Specifically, at the self-consistent field level of theory, the ortho structure **5** distorts from C_{2v} symmetry and adopts a bicyclic structure (vaguely reminiscent of that found for **4**) that is more than 10 kcal/mol lower than the C_{2v} stationary point. While correlation effects remove this feature from the potential energy surface, high-level single-point calculations carried out at the optimized C_{2v} geometry and the distorted geometry found in the SCF calculations show that the energetic separation is rather small. Hence, it seems likely that **5** exhibits rather large amplitude nuclear motions, a feature that might have implications for its study by rotational spectroscopy.[10]

Relative energies calculated for the TDHBs mirror those found by Bettinger et al.; the zero-point corrected energies of **3** and **5** relative to **4** (16.8 and 6.8 kcal/mol, respectively) are similar to the values of 11.0 and 6.2 kcal/mol based on their CCSD(T)/TZ2P calculations and zero-point energies estimated by density functional theory (DFT) calculations. Vibrational frequencies for the TDHBs documented in Table 4 are largely consistent with the DFT results of ref 15 and the CCSD(T)/TZ2P results they report for **4**. For the two less stable TDHBs, the strongest infrared absorption is likely to be found at relatively low frequencies (below 700 cm^{-1}). In particular, the highly symmetric (D_{2h}) isomer **3** is predicted to have no absorptions with appreciable intensity above 1000 cm^{-1}, a finding that is again consistent with the earlier results of ref 15. For the most stable meta isomer **4**, however, a strong absorption is expected near 1700 cm^{-1}, a region where the cumulene carbene **2** is also expected to exhibit a prominent feature. However, a number of other relatively strong absorptions predicted below 1000 cm^{-1} could easily distinguish **4** from **2**, especially when confirmed by measuring isotopic shifts. While the least stable isomer of TDHB has a relative thermodynamic stability comparable to that of the cumulene carbene (**2**), the meta and ortho isomers **4** and **5** are more stable than **2**. Given the presence of **2** in space, it seems plausible that the TDHBs might also be present, although it is not at all clear how they might be made from molecules currently known to reside in the ISM. In any event, however, **3** is clearly not a candidate for astronomical detection. Also, dipole moments for the other two forms are relatively small (about 0.5−0.75 that of water), so they will be very difficult to detect unless present in great abundance. Nevertheless, the data given in Tables 3 and 4 should offer assistance in efforts to identify them in the laboratory.

C. Other Isomers. To our knowledge, none of the remaining isomers covered in this survey have been considered before. Of these, we believe that the most likely candidate for astronomical detection is the monosubstituted butatrienylidene **6**. Both the parent $H_2C{=}C{=}C{=}C{:}$ molecule and ethynyl-substituted versions of other compounds are known to exist in the ISM, so it is plausible to assume that **6** might be found as well. This compound has an appreciable dipole moment (3.9 D at the CCSD(T)/cc-pVTZ level), and there are no obvious low-energy pathways for isomerization to the considerably more stable isomer **1**. Harmonic vibrational frequencies calculated for this isomer exhibit the usual features of a cumulene carbene,[13,9] specifically a strong C—C absorption near 2000 cm^{-1} and low-frequency modes (three below 200 cm^{-1} in this case) for bending. In a low- temperature matrix, however, the infrared spectrum of this compound should be easily discernable from that of unsubstituted cumulene carbenes because of the presence of the very high-frequency CH stretch mode of the ethynyl group that is predicted to carry a relatively large infrared intensity.

Isomer **7** lies a good deal higher in energy than **1**−**6**, but is structurally related to the C_5H_2 eiffelene, 3-(didehydrovinylidene)cyclopropene, which has been detected in an acetylene discharge by Gottlieb et al.[10] Moreover, like for **6**, there appears to be no facile pathway for isomerization to a more stable form of C_6H_2, suggesting that it will exhibit some degree of kinetic stability. The structure predicted for **7** differs in interesting ways from that of the analogous C_5H_2 isomer at the same level of theory.[9] Within the three-membered ring, the formal double bond is somewhat shorter and the formal single bond longer in C_6H_2 (1.308 and 1.455 Å for C_6H_2 vs 1.334 and 1.413 Å in C_5H_2). In addition, the C_5H_2 eiffelene has a very short bond between the outermost carbons (1.269 Å), while C—C distances in **7** are longer than 1.285 Å. All of these features can be attributed to the fact that the C_5H_2 eiffelene possesses relatively favorable resonance structures in which a negative formal charge is placed on the carbene carbon and the balancing positive charge is shared between the two off-axis carbons in the three-membered ring. In these resonance forms, the outermost CC bond is a triple bond, and the double and single bonds in the three-membered rings acquire partial-single- and partial-double-bond character, respectively. There are no corresponding resonance structures for **7**, which helps to explain the rather different geometrical parameters of the two species. Instead, the polarity of **7** can be attributed to a resonance structure in which the positive formal charge is located two atoms away from the carbene carbon, which corresponds to another resonance form of C_5H_2. However, since it lacks the first type of resonance structure (in which the charges are separated by a greater distance), one expects the dipole moment of **7** to be smaller than that of 3-(didehydrovinylidene)cyclopropane, while similar qualitative arguments suggest that the dipole moment of the corresponding C_7H_2 eiffelene should be considerably larger than the value of 8.2 D calculated at the CCSD(T)/cc-pVTZ level for the C_5H_2 form.[9] Indeed, this hand-waving rationalization of the structural features of **7** is supported by the calculated dipole moment, which is 0.2 D smaller than that of the corresponding C_5H_2 structure, despite the greater potential for charge separation. Nevertheless, it is still quite large, and this molecule is a promising candidate for laboratory detection.

Isomer **8** is the ethynyl-substituted analogue of the C_4H_2 isomer previously studied by Collins et al. as a candidate for astronomical observation.[40] Although efforts were made to detect the unsubstituted compound in the laboratory, they proved unsuccessful. The structure of **8** is strikingly similar to that calculated for the C_4H_2 analogue at the CCSD/TZ2P level. The exocyclic and three-membered ring CC double-bond distances of 1.297 and 1.294 Å, respectively, are similar to the 1.294 and 1.291 Å distances of ref 40, and the average of the two CC single bond distances in the ring (1.495 and 1.472 Å) is close to the 1.488 Å found for C_4H_2. Another similarity between **8** and the corresponding C_4H_2 species is its energy relative to the corresponding polyacetylene. Collins et al. found a separation of about 80 kcal/mol, just slightly greater than that predicted for **8** at the CCSD(T)/cc-pVTZ level of theory.

The final isomer investigated in this work is diethynylvinylidene **9**. While it is clear that a 1,2 migration of an ethynyl group leads directly to the considerably more stable triacetylene isomer of C_6H_2, it was initially thought that the barrier for this process was sufficiently large that the molecule might have some degree of kinetic stability. While little is apparently known about 1,2 migrations in vinylidenes for substituents other than hydrogen, computational investigation of 1,2 fluorine migrations shows an appreciable barrier of >20 kcal/mol.[41] However, during the course of this investigation, the transition state for the ethynyl migration in **9** was located at the SCF level and the barrier found to be about 10 kcal/mol. Subsequent work being carried out in our laboratory[42] has shown that barriers for ethynyl and cyano migrations in substituted vinylidenes are very small (certainly less than 10 kcal/mol in all cases), and the results of this ongoing independent investigation suggest the possibility that **9** is not a minimum on the potential surface, but rather rearranges spontaneously to **1**. While the structure is a bona fide minimum at the SDQ-MBPT(4)/TZ2P level, the lowest vibrational frequency (which is best described as a rotation of the C═C: double bond that leads to its insertion in the carbon chain) is just 120 cm^{-1}, and the barrier height is 5.7 kcal/mol. Single-point CCSD(T)/cc-pVTZ calculations at the SDQ-MBPT(4)/TZ2P equilibrium and transition state geometries indicate that the height of the barrier is less than 11 kcal/mol at this level of theory. Hence, it seems certain that **9** has a very short lifetime and may not even be a metastable isomer of C_6H_2. Efforts to detect it will be difficult in the former and futile in the latter case. Calculations were also performed for butatriynylvinylidene, and it was found that this structure spontaneously rearranges to **1** at the SDQ-MBPT(4)/TZ2P level; no further effort was made to characterize it with CCSD(T)/cc-pVTZ. However, our work on 1,2 rearrangements has demonstrated that the smaller ethynylvinylidene is a stable minimum at the SDQ-MBPT(4) 14 level but ceases to exist at the CCSD(T)/cc-pVTZ level,[42] thereby confirming an expectation previously expressed in the literature.[43] It therefore seems most unlikely that the butatriynylvinylidene structure would "reappear" as a minimum at the higher level of theory.

In this context, it should be noted that isomer **8** is also a substituted vinylidene, but a 1,2 shift in this case would lead to a presumably highly disfavored substituted 1,2-didehydrocyclobutadiene species. Indeed, inspection of the lowest frequency SDQ-MBPT(4)/TZ2P normal mode for this structure suggests that isomerization to the para isomer of TDHB (**3**) is considerably more likely.

IV. Summary

This work has focused on the quantum chemical characterization of several isomers of the C_6H_2 molecular system. While it is clear that triacetylene lies far below all other forms on the potential energy surface, kinetic barriers might render some of the other isomers sufficiently metastable to be studied spectroscopically under ambient conditions. At very low temperatures, such as those characteristically found in the interstellar medium and in rare-gas matrix isolation studies, these species might be

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stable for long periods of time. The confirmed presence of the cumulene carbene hexapentaenylidene **2** in space suggests the possibility that other "unstable" forms of C_6H_2 might be present as well. Among these, the TDHB isomers **4** and **5** are particularly intriguing (despite their relatively small dipole moments) subjects for astronomical searches, as no six-membered rings have yet been found in the ISM. However, of those studied here, we believe that the most likely structure to be found in space is **6**, which should have a relatively high degree of kinetic stability and is structurally related to other systems that have already been observed. It is our hope that the results presented in this paper will prove useful in laboratory searches for these unusual forms of C_6H_2.

Acknowledgment. This work was supported by the Robert A. Welch and National Science Foundations. We are indebted to M.C. McCarthy and C.A. Gottlieb (Harvard) for suggesting this study and for many helpful discussions. Aspects of this work were also enhanced by dialogue with R. J. McMahon (Madison) and C. H. DePuy (Boulder).

Supporting Information Available: Energies and full sets of internal coordinates that correspond to optimized structures at the SDQ-MBPT(4)/TZ2P, CCSD/TZ2P, and CCSD(T)/cc-pVTZ levels of theory (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA9940874