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# Energetic and spectroscopic properties of the low-lying $C_7H_2$ isomers: a high-level *ab initio* perspective†

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We use high-level *ab initio* CCSD(T) and CCSDT(Q) methods to investigate the energetic and spectroscopic properties of nine low-lying isomers of  $C_7H_2$ , which lie within 1 eV. Among these, heptatriynylidene (**1**), 1-(buta-1,3-diyne)cyclopropenylidene (**2**) and heptahexaenylidene (**9**) have been detected experimentally. The other six isomers, 1,2-(diethynyl)cyclopropenylidene (**3**), bicyclo[4.1.0]hepta-1,2,4,5-tetraene-7-ylidene (**4**), cyclohepta-1,2,3,4-tetraen-6-yne (**5**), bicyclo[4.1.0]hepta-4,6-diene-2-yne-7-ylidene (**6**), bicyclo[4.1.0]hepta-1,5-diene-3-yne-7-ylidene (**7**) and 1-(buta-1,3-diyne)propadienylidene (**8**), remain hypothetical to date. Except for **1**, all of the isomers are associated with a non-zero dipole moment ( $\mu \neq 0$ ). Although Fourier-transform microwave spectroscopy had detected **2** and **9**, our study reveals that six hypothetical isomers (**3–8**) are thermodynamically sandwiched between the experimentally known and astronomically relevant isomers **2** and **9**. The structural parameters, dipole moments, rotational and centrifugal distortion constants, harmonic vibrational frequencies, and infra-red intensities presented here may be useful for the laboratory detection of these previously unidentified isomers (**3–8**) and also all others (**2–9**) in astronomical sources.

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## 1 Introduction

Identification of molecules in non-terrestrial environments is definitely an open challenge for the scientific community. Paradoxically, in the vast majority of cases, this challenge can only be completely resolved by the synthesis of these new (non-terrestrial) molecules in terrestrial environments.<sup>1–12</sup> Although radioastronomers observe rotational transitions in space, we need a match to confirm the presence of the exact same molecule on earth. Needless to say, quite exotic molecules have been detected in the interstellar medium (ISM) along with simple molecules.<sup>1,12–23</sup> The challenges associated with the synthesis and identification of these new molecules on earth is one of the primary reasons why only 200 molecules have been confirmed so far in space, instead of a greater number.<sup>12</sup> Apart from acetylenic radicals ( $C_nH$ )<sup>24–31</sup> and cyanopolynes ( $HC_nN$ ),<sup>27,32–36</sup> cumulene carbenes ( $C_nH_2$ ),<sup>16–18,27,37–47</sup> which show a significant increase in dipole moment with respect to increase in the carbon

chain length, have also been found in the ISM. Ever since three cumulene carbenes (where,  $n = 3, 4$ , and  $6$ ) were identified in space<sup>16–18</sup> followed by their detection in the laboratory,<sup>27,37–39</sup> both experimentalists and theoreticians have started focusing their attention not only on these compounds but also on their isomers and higher homologous series.<sup>40–43,48–57</sup>

Although more than hundreds of structural isomers are theoretically possible for  $C_7H_2$ ,<sup>58</sup> to date merely six isomers (see Fig. 1 and 2) have been detected experimentally<sup>43,59,60–63</sup> and none have been detected in space. Heptatriynylidene (**1**), whose dipole moment is zero by symmetry, was first detected in a 5 K Ne-matrix<sup>59</sup> and later detected by cavity ringdown spectroscopy<sup>61,62</sup> as well as charge reversal and neutralization re-ionization mass spectra of the corresponding anion.<sup>63</sup> 1-(buta-1,3-diyne)cyclopropenylidene (**2**)<sup>60</sup> and heptahexaenylidene (**9**)<sup>43</sup> were detected with a Fourier-transform microwave (FTM) spectrometer. Bowie and co-workers characterized five isomers (**1**, **9**, **11**, **14**, and **15**) after synthesizing four  $C_7H_2$  radical anion precursors using charge reversal and neutralization reionization spectra.<sup>63</sup> Though laboratory investigations suggested the possibility of other low-lying isomers,<sup>1</sup> it is not clear what the structures of these low-lying isomers are on the  $C_7H_2$  potential-energy surface (PES). On the contrary, earlier theoretical studies either did not mention the bicyclic/seven-membered rings (**4–7**)<sup>63,68</sup> or predicted the wrong relative stability of the isomers (**4**, **5**, and **7**).<sup>58</sup> The motivation behind the current study not only stems from the electronic structures

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† Electronic supplementary information (ESI) available: Cartesian coordinates, total electronic energies, ZPVEs, and dipole moments corresponding to the optimized geometries of **1–9** at different levels of theory are given. The isotopic shifts ( $^{12}C$ -mono-substituted- $^{13}C$ ) in harmonic vibrational frequencies are also given. See DOI: 10.1039/c7cp02848b



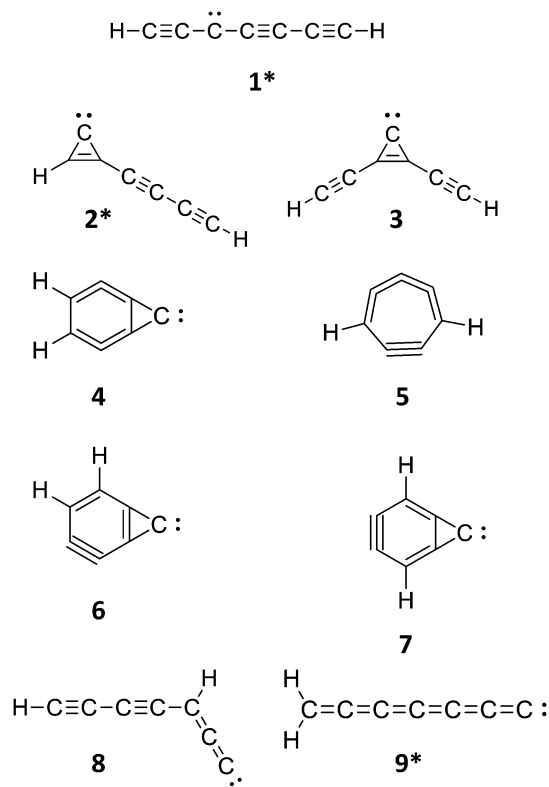


Fig. 1 Energetically low-lying isomers of  $C_7H_2$  considered in the present work. The experimentally detected isomers are marked with an asterisk symbol. Isomer **1** is a triplet and all others are singlets.

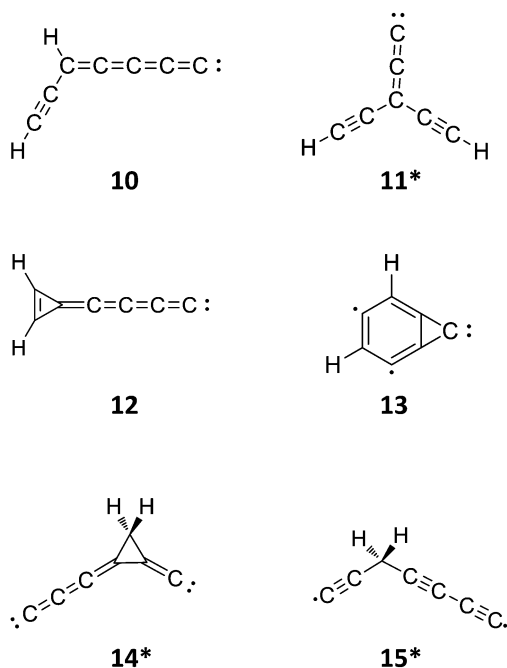


Fig. 2 Energetically high-lying isomers of  $C_7H_2$  considered in the previous work. The experimentally detected isomers are marked with an asterisk symbol. Isomers **13** and **15** are triplets and all others are singlets.

of these isomers but also from the relative stabilities of these isomers on the  $C_7H_2$  PES.

The present work is an elaborate theoretical investigation of nine low-lying isomers of  $C_7H_2$  (1–9; see Fig. 1). Specifically, we obtain the energies of these isomers at the CCSDT(Q)/CBS level by means of the W3lite-F12 composite method.<sup>64</sup> This method approximates the coupled cluster energy with single, double, triple, and quasiperturbative quadruple excitations (CCSDT(Q)) at the complete basis-set (CBS) limit.<sup>65,66</sup> We also calculate the equilibrium geometries and a range of spectroscopic constants for these molecules at the CCSD(T) level. The high energy isomers (10–15; see Fig. 2), which lie above the cumulene carbene isomer (9), are not considered here in detail.<sup>67</sup>

Aoki and Ikuta have carried out geometry optimizations at the MP2/D95\*\* level of theory for eight different isomers of  $C_7H_2$  (1–3, 8–11 and also a bent carbene, whose structure is not given here),<sup>68</sup> but their study did not include any bicyclic or seven-membered ring structures. While seven of the structures reported by them are given in Fig. 1, a bent geometry (4' as per their labelling) reported as a minimum by them was not found to be a minimum in our earlier study at the CCSD(T)/cc-pVTZ level of theory.<sup>69</sup> We found that the bent geometry becomes linear at higher levels of theory.<sup>69</sup> Also, their study predicted that **2** is the most stable isomer.<sup>68</sup> Isomers **3** and **1** were predicted to lie above **2** with a relative energy difference of 1.8 and 4.9 kcal mol<sup>−1</sup>, respectively. Aromatic stability (Hückel's  $(4n + 2)\pi$  electrons rule with  $n = 0$  here) due to the presence of  $2\pi$  electrons inside the three-membered ring was justified as the reason why **2** and **3** were more stable than the triplet ground electronic state of **1**.<sup>68</sup> Nevertheless, density functional theory (DFT) calculations done by two different groups showed that **1** is the most stable isomer.<sup>58,63</sup> Our earlier and present work also confirm this result.<sup>69</sup> Apart from their experimental work, Bowie and co-workers have carried out DFT calculations at the B3LYP/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory for ten different isomers of  $C_7H_2$  (1–3, 8–12, and 14–15).<sup>63,70</sup> Once again, no bicyclic or seven-membered ring structures were included in their study. Unequivocally, the latter are not only structurally intriguing but also energetically low-lying as we found in the present work (see Table 1).

Thaddeus and co-workers stated that there may be other isomers of  $C_7H_2$  within 1 eV apart from what Aoki and Ikuta predicted in their theoretical work.<sup>1,68</sup> The present study supports this comment made by experimentalists several years ago. Three bicyclic rings (bicyclo[4.1.0]hepta-1,2,4,5-tetraene-7-ylidene (**4**), bicyclo[4.1.0]hepta-4,6-diene-2-yne-7-ylidene (**6**), and bicyclo[4.1.0]hepta-1,5-diene-3-yne-7-ylidene (**7**)) and one seven-membered ring (cyclohepta-1,2,3,4-tetraen-6-yne (**5**)) are indeed within 1 eV at the CCSDT(Q)/CBS level of theory, and surprisingly all of them (**4–7**) are energetically below the experimentally detected cumulene carbene isomer of  $C_7H_2$  (**9**) (see Table 1). Though this paper is not an exhaustive survey of all isomers, it is quite clear that the experimentalists' remark is true. We believe that our study will inspire experimental investigations for detecting these elusive molecules. Although thermodynamically more stable than **9**, isomers **3–8** are yet to be found in the laboratory. We note, however, that the kinetic stability of these isomers still remains to be investigated. From the structural point of



**Table 1** Relative energies ( $\Delta E_{\text{rel}}$ ; in kcal mol<sup>-1</sup>) of the C<sub>7</sub>H<sub>2</sub> isomers with respect to isomer **1** calculated using the W3lite-F12 thermochemical protocol

Level	Protocol	$\Delta E_{\text{rel}}$							
		2	3	4	5	6	7	8	9
SCF	W2-F12	-17.79	-16.06	15.63	18.75	15.29	19.32	2.86	13.08
CCSD	W2-F12	18.01	18.08	-3.46	-5.45	2.56	-1.35	15.09	11.31
(T)	W2-F12	2.75	3.17	-6.60	-7.29	-3.40	-3.12	0.61	-4.33
Inner-shell	W2-F12	0.61	0.65	1.29	1.04	1.17	1.15	0.87	0.89
Scalar relativistic	W2-F12	-0.06	-0.07	-0.08	-0.05	-0.05	-0.03	-0.12	-0.11
T-(T)	W3.2lite	-0.39	-0.40	0.78	0.66	0.26	0.39	-0.60	-0.63
(Q)	W3.2lite	0.65	0.76	-0.94	-1.32	-0.29	-0.03	0.23	-0.83
$E_{\text{c}}[\text{CCSD(T)}/\text{CBS}]$	W2-F12	3.52	5.77	6.78	7.01	15.57	15.97	19.32	20.85
$E_{\text{c}}[\text{CCSDT(Q)}/\text{CBS}]$	W3.2lite-F12	3.77	6.13	6.62	6.35	15.54	16.33	18.94	19.38
ZPVE	CCSD(T)/cc-pVTZ	1.79	1.51	3.73	3.88	3.65	3.87	1.32	0.96
$E_{\text{0}}[\text{CCSDT(Q)}/\text{CBS}]$	W3.2lite-F12	5.56	7.64	10.35	10.23	19.19	20.20	20.26	20.34

view, **4** and **5** clearly exhibit a biradical character and therefore trapping these two molecules might certainly present some challenges to experimentalists. However, we believe that these can be trapped in low-temperature environments using matrix-isolation techniques.

Sun *et al.* calculated the relative energies of 113 isomers of C<sub>7</sub>H<sub>2</sub> at the CCSD(T)/cc-pVTZ//UB3LYP/6-311G(d,p) level of theory.<sup>58</sup> However, their relative energies are in disagreement with the more accurate energies reported here at the CCSDT(Q)/CBS//CCSD(T)/cc-pVTZ level of theory. These differences are partly attributed to the differences between the B3LYP and CCSD(T) structures and the post-CCSD(T) energetic contributions, which are considered in the present work. Moreover, optimization for some of the isomers (**4**, **5**, **7**, and **9**) reported by them had been done at a lower symmetry. Though the correct point group symmetry is C<sub>2v</sub> for the later isomers, optimizations were done with a C<sub>s</sub> symmetry point group. This could also be one of the contributing factors for the differences in relative energies between our results and theirs. Moreover, we note that isomer **6** was not among the 113 isomers that were part of their study.

In this paper, our focus is largely on six isomers (**2–4** and **6–8**). Our earlier work focused on isomers **1**, **5**, and **9**.<sup>69</sup> Therefore, an elaborate discussion of these isomers is avoided here and interested readers are referred to our earlier work.<sup>69</sup> However, for the purpose of relative energy comparison and completeness, we have taken values from our earlier work and also have done calculations at higher levels of theory to get the thermodynamic stability of the low-lying isomers of C<sub>7</sub>H<sub>2</sub>. While isomers **2** and **9** have already been found in the laboratory by FTM spectroscopy,<sup>43,60</sup> it is worth noting that the dipole moments of **3–8** are also non-zero (see Table 2).<sup>71</sup> Both **2** and **3** can be considered as derivatives of cyclopropenylidene (c-C<sub>3</sub>H<sub>2</sub>). The latter molecule and also its doubly deuterated derivative (c-C<sub>3</sub>D<sub>2</sub>) were not only found in the laboratory but also in space.<sup>15,19</sup> Also, **8** can be considered as a derivative of propadienylidene (the shortest member of cumulene carbene), which has also been found in the laboratory and in space.<sup>16,37</sup> On the contrary, the bicyclic rings (**4**, **6**, and **7**) and the seven-membered ring isomer (**5**) thermodynamically fall between these two important astronomically relevant derivatives, which has not been discussed thus far in the literature. We hope that the rotational constants,

centrifugal distortion constants, optimal geometry parameters, dipole moments and harmonic vibrational frequencies of <sup>12</sup>C and <sup>13</sup>C isotopes, and infrared intensities of these hypothetical isomers of C<sub>7</sub>H<sub>2</sub> (**3–8**) will encourage experimentalists to find some of these isomers in the laboratory. Perhaps without finding these molecules in the laboratory, it would be a herculean task to confirm the presence of these molecules in space.

## 2 *Ab initio* calculations

The geometries of all isomers of C<sub>7</sub>H<sub>2</sub> reported in this study were optimized using both second-order Møller-Plesset perturbation theory<sup>72</sup> and coupled-cluster (CC) methods. The considered CC methods are CC with single and double excitations (CCSD)<sup>73,74</sup> and CCSD with quasiperturbative triple excitations (CCSD(T)).<sup>75–77</sup> These calculations were carried out with the correlation-consistent cc-pVnZ basis sets of Dunning<sup>78</sup> (n = D and T), which consist of 108 and 238 basis functions, respectively, for the C<sub>7</sub>H<sub>2</sub> isomers. The frozen-core approximation is utilized in the geometry optimizations. To speed up the geometry optimization, the force constant matrix obtained at a lower level is used successively at a higher level. For all the stationary points obtained, harmonic vibrational frequencies were determined by analytic calculation of second derivatives.<sup>79</sup> These electronic structure calculations were done with the CFOUR program package.<sup>80</sup>

In order to obtain reliable relative energies for isomers **1–9**, high-level benchmark data have been obtained using the W3lite-F12 theory.<sup>64,66</sup> The W3lite-F12 theory (and its earlier version, the W3.2lite theory)<sup>81–83</sup> represents layered extrapolations to the relativistic, all-electron CCSDT(Q)/CBS limit and can achieve near-benchmark accuracy for atomization reactions (*i.e.*, they are associated with root-mean-square deviations, RMSDs, from accurate atomization energies of about 1 kJ mol<sup>-1</sup> = 0.24 kcal mol<sup>-1</sup>).<sup>64</sup> For example, the related W3-F12 theory is associated with an RMSD of 0.27 kcal mol<sup>-1</sup> for a set of 140 very accurate atomization energies obtained at the full configuration interaction (FCI) infinite basis-set limit.<sup>64,66,81,83</sup> The W3lite-F12 theory combines F12 methods<sup>84</sup> with basis-set extrapolations in order to reproduce the CCSDT(Q)/CBS energy. In W3lite-F12, the CCSD(T)/CBS energy is obtained from the





**Table 2** Rotational and centrifugal distortion constants (in MHz), and inertial axis dipole moment components (in Debye;  $\perp$  representation) of  $C_7H_2$  isomers calculated at the CCSD(T)/cc-pVTZ level of theory

Constant <sup>a</sup>	1 <sup>b</sup>	2	3	4	5 <sup>b</sup>	6	7	8	9 <sup>b</sup>
$A_e$	—	34343.21 (34722.14) <sup>c</sup>	7716.69	6210.57	6117.11	6941.35	5613.16	18527.26	289548.07 (276259.00) <sup>d</sup>
$B_e$	832.63	1034.45 (1045.21) <sup>c</sup>	1539.34	3851.13	3745.45	3603.21	4194.48	992.86	842.85 (851.91) <sup>d</sup>
$C_e$	—	1004.20 (1014.26) <sup>c</sup>	1283.34	2377.10	2323.06	2371.95	2400.61	942.36	840.40 (849.29) <sup>d</sup>
$A_J$	$0.8546 \times 10^{-5}$	$0.1689 \times 10^{-4}$	$0.3985 \times 10^{-3}$	$0.3330 \times 10^{-3}$	$0.2028 \times 10^{-3}$	$0.2360 \times 10^{-3}$	$0.3912 \times 10^{-3}$	$0.1501 \times 10^{-3}$	$0.8562 \times 10^{-5}$
$A_K$	$0.8546 \times 10^{-5}$	$0.127735$	$0.109249$	$0.3272 \times 10^{-2}$	$-0.1822 \times 10^{-3}$	$0.2216 \times 10^{-3}$	$0.6910 \times 10^{-3}$	$2.59533$	$22.1709$
$A_{JK}$	$-0.1709 \times 10^{-4}$	$0.6908 \times 10^{-2}$	$-0.1116 \times 10^{-1}$	$-0.2984 \times 10^{-3}$	$0.2185 \times 10^{-2}$	$0.3640 \times 10^{-3}$	$0.1218 \times 10^{-4}$	$-0.3223 \times 10^{-1}$	$0.1098 \times 10^{-1}$
$\delta_J$	—	$0.5514 \times 10^{-6}$	$0.1455 \times 10^{-3}$	$0.1301 \times 10^{-3}$	$0.7111 \times 10^{-4}$	$0.8193 \times 10^{-4}$	$0.1577 \times 10^{-3}$	$0.3137 \times 10^{-4}$	$-0.2595 \times 10^{-7}$
$\delta_K$	—	$0.3622 \times 10^{-2}$	$0.8015 \times 10^{-3}$	$0.4231 \times 10^{-3}$	$0.1345 \times 10^{-2}$	$0.5942 \times 10^{-3}$	$0.5253 \times 10^{-3}$	$0.2501 \times 10^{-2}$	$-0.6170 \times 10^{-8}$
$\mu_a$	—	2.306	3.774	-3.357	-1.878	2.311	3.068	4.659	-7.336
$\mu_b$	—	2.855	—	—	—	-1.855	—	2.413	—
$ \mu $	—	3.670	3.774	3.357	1.878	2.964	3.068	5.247	7.336

<sup>a</sup> Centrifugal distortion constants for isomer 9 is from an S-reduced Hamiltonian, whereas for all other isomers they are from the A-reduced Hamiltonian. <sup>b</sup> From ref. 69. See the discussions therein for detail. <sup>c</sup> From ref. 60. <sup>d</sup> From ref. 43.

W2-F12 theory,<sup>64</sup> and the post-CCSD(T) contributions are obtained from the W3.lite theory.<sup>82</sup> In brief, the Hartree–Fock (HF) component is calculated with the cc-pVQZ-F12 basis set of Peterson *et al.*, which was developed for explicitly correlated calculations.<sup>85,86</sup> Note that the complementary auxiliary basis (CABS) singles correction is included in the self-consistent field (SCF) energy.<sup>87–89</sup> The valence CCSD-F12 correlation energy is extrapolated from the cc-VTZ-F12 and cc-VQZ-F12 basis sets, using the  $E(L) = E_\infty + A/L^\alpha$  two-point extrapolation formula, with  $\alpha = 5.94$ . In all of the explicitly-correlated CC calculations, the diagonal, fixed-amplitude 3C(FIX) ansatz<sup>88,90,91</sup> and the CCSD-F12b approximation<sup>89,92</sup> are employed. The quasiperturbative triples, (T), corrections are calculated with the cc-pVTZ-F12 basis set and scaled by the factor  $f = 0.987 \times E_{MP2-F12}/E_{MP2}$ . This approach has been shown to accelerate the basis-set convergence.<sup>64,92</sup> The post-CCSD(T) corrections are obtained from standard CC calculations (*i.e.*, without inclusion of F12 terms). Specifically, the higher-order connected triples (CCSDT–CCSD(T)) valence correlation contribution is calculated using the cc-pVDZ and cc-pVTZ(nof1d) basis sets, where cc-pVTZ(nof1d) indicates the combination of the *sp* part of the cc-pVTZ basis set combined with the *d* function from the cc-pVDZ basis set on heavy atoms and the *s* part of the cc-pVTZ basis set combined with the *p* function from the cc-pVDZ basis set on hydrogen.<sup>82</sup> The parenthetical connected quadruples contribution (CCSDT(Q)–CCSDT) is calculated with the cc-pVDZ basis set. The CCSD inner-shell contribution is calculated with the core-valence weighted correlation-consistent aug-cc-pwCVTZ basis set of Peterson and Dunning,<sup>93</sup> whilst the (T) inner-shell contribution is calculated with the cc-pwCVTZ basis set without the *f* functions.<sup>64</sup>

The W3lite-F12 single-point energy calculations were carried out using our 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 in ref. 94. All the CCSD(T) energy calculations involved in the W3lite-F12 energies were done with the Molpro program package,<sup>95,96</sup> whilst the post-CCSD(T) calculations were carried out with the MRCC program.<sup>97,98</sup>

### 3 Results and discussion

The component breakdown of the W3lite-F12 relative energies for the  $C_7H_2$  isomers is given in Table 1. Rotational and centrifugal distortion constants, and inertial axis dipole moment components calculated from the CCSD(T)/cc-pVTZ equilibrium geometries are given in Table 2. The optimal geometry parameters of isomers 2, 3, 4, 6, 7, and 8 at different levels along with other theoretical work (wherever available) are documented in Tables 3, 4, 5, 6, 7, and 8, respectively. The harmonic vibrational frequencies of isomers 1–3, 4–6, and 7–9 calculated at the CCSD(T)/cc-pVTZ level of theory are documented in Tables 9, 10, and 11, respectively. For brevity, the isotopic shifts obtained from the harmonic vibrational frequencies ( $^{12}C$ – $^{13}C$ ) for isomers 1–3, 4–6, and 7–9 calculated at the same level of theory are documented in the ESI,<sup>†</sup> in Tables S18, S19,

**Table 3** Optimal geometry parameters (Å and degrees) of isomer **2** calculated at different levels of theory

Parameter	cc-pVDZ			cc-pVTZ			Other work		
	MP2	CCSD	CCSD(T)	MP2	CCSD	CCSD(T)	Ref. 68 <sup>a</sup>	Ref. 63 <sup>b</sup>	Ref. 58 <sup>c</sup>
$R(C_1C_2)$	1.4008	1.4133	1.4105	1.3865	1.3988	1.3957	1.4000	1.3780	1.2980
$R(C_2C_3)$	1.2431	1.2291	1.2386	1.2266	1.2107	1.2208	1.2380	1.2240	1.2620
$R(C_3C_4)$	1.3767	1.3924	1.3885	1.3614	1.3769	1.3725	1.3750	1.3590	1.3260
$R(C_4C_5)$	1.2385	1.2264	1.2347	1.2209	1.2073	1.2160	1.2340	1.2150	1.2250
$R(C_5H_6)$	1.0767	1.0781	1.0797	1.0624	1.0622	1.0641	1.0680	1.0670	1.0620
$R(C_1C_7)$	1.3559	1.3465	1.3543	1.3406	1.3300	1.3383	1.3510	1.3420	1.5190
$R(C_1C_8)$	1.4631	1.4570	1.4682	1.4412	1.4332	1.4448	1.4530	1.4580	1.4540
$R(C_7H_9)$	1.0917	1.0917	1.0940	1.0769	1.0758	1.0783	1.0810	1.0830	1.0740
$\theta(C_1C_2C_3)$	178.72	179.01	178.73	179.11	179.37	179.16	178.40	179.90	178.60
$\theta(C_2C_3C_4)$	179.39	179.52	179.34	179.66	179.79	179.67	179.40	179.60	179.60
$\theta(C_3C_4C_5)$	179.87	179.90	179.84	179.81	179.86	179.82	179.90	179.90	179.90
$\theta(C_4C_5H_6)$	179.98	179.99	179.96	179.95	179.99	179.96	180.00	179.60	179.90
$\theta(C_1C_7H_9)$	147.84	147.84	147.43	148.26	148.36	147.99	148.40	146.50	138.10
$\theta(C_7C_1C_2)$	149.96	149.72	149.72	150.75	150.45	150.47	149.90	150.80	146.30
$\theta(C_8C_1C_2)$	148.88	148.71	148.94	148.27	148.17	148.34	148.80	149.00	161.80

<sup>a</sup> At the MP2/D95\*\* level of theory. <sup>b</sup> At the B3LYP/6-31G(d) level of theory. <sup>c</sup> At the UB3LYP/6-311G(d,p) level of theory.

**Table 4** Optimal geometry parameters (Å and degrees) of isomer **3** calculated at different levels of theory

Parameter	cc-pVDZ			cc-pVTZ			Other work		
	MP2	CCSD	CCSD(T)	MP2	CCSD	CCSD(T)	Ref. 68 <sup>a</sup>	Ref. 63 <sup>b</sup>	Ref. 58 <sup>c</sup>
$R(C_1C_2, C_4C_5)$	1.4068	1.4191	1.4176	1.3919	1.4037	1.4018	1.4050	1.3910	1.3410
$R(C_2C_3, C_3C_4)$	1.4525	1.4482	1.4572	1.4299	1.4242	1.4336	1.4450	1.4340	1.3500
$R(C_1C_7, C_5C_6)$	1.2354	1.2247	1.2322	1.2177	1.2058	1.2138	1.2310	1.2120	1.2220
$R(C_7H_9, C_6H_8)$	1.0769	1.0784	1.0799	1.0625	1.0626	1.0644	1.0680	1.0670	1.0630
$R(C_2C_4)$	1.3634	1.3506	1.3594	1.3479	1.3339	1.3433	1.3570	1.3500	1.6390
$\theta(C_1C_2C_3, C_5C_4C_3)$	149.54	149.27	149.52	149.03	148.76	148.97	149.60	149.60	167.50
$\theta(C_2C_3C_4)$	55.98	55.59	55.61	56.23	55.85	55.87	—	—	—
$\theta(C_2C_1C_7, C_4C_5C_6)$	179.84	179.65	179.55	179.91	179.95	179.93	179.90	179.80	178.30
$\theta(C_1C_7H_9, C_5C_6H_8)$	179.78	179.90	179.97	179.48	179.61	179.57	180.00	179.50	179.30
$\theta(C_1C_2C_4, C_5C_4C_2)$	148.45	148.53	148.29	149.08	149.17	148.96	148.40	148.50	139.90

<sup>a</sup> At the MP2/D95\*\* level of theory. <sup>b</sup> At the B3LYP/6-31G(d) level of theory. <sup>c</sup> At the UB3LYP/6-311G(d,p) level of theory.

**Table 5** Optimal geometry parameters (Å and degrees) of isomer **4** calculated at different levels of theory

Parameter	cc-pVDZ			cc-pVTZ			Other work
	MP2	CCSD	CCSD(T)	MP2	CCSD	CCSD(T)	Ref. 58 <sup>a</sup>
$R(C_1C_2, C_1C_3)$	1.4209	1.3997	1.4082	1.3996	1.3797	1.3870	1.4100
$R(C_2C_4, C_3C_5)$	1.3444	1.2931	1.3166	1.3258	1.2737	1.2951	1.3620
$R(C_4C_6, C_5C_7)$	1.3827	1.4018	1.3980	1.3686	1.3879	1.3848	1.3840
$R(C_6H_8, C_7H_9)$	1.0976	1.0981	1.1001	1.0836	1.0829	1.0852	1.0850
$R(C_2C_3)$	1.5012	1.7624	1.6697	1.5013	1.7630	1.6858	1.4350
$R(C_6C_7)$	1.4802	1.4401	1.4600	1.4680	1.4258	1.4448	1.4200
$\theta(C_1C_2C_4, C_1C_3C_5)$	178.74	166.39	171.21	177.75	165.22	169.36	—
$\theta(C_2C_4C_6, C_3C_5C_7)$	119.19	123.88	121.71	119.87	124.51	122.66	121.00
$\theta(C_4C_6H_8, C_5C_7H_9)$	123.82	122.27	122.53	123.95	122.34	122.60	121.30
$\theta(C_1C_2C_3, C_1C_3C_2)$	58.12	50.98	53.64	57.57	50.29	52.58	59.40
$\theta(C_2C_1C_3)$	63.77	78.04	72.72	64.87	79.42	74.84	61.20

<sup>a</sup> At the UB3LYP/6-311G(d,p) level of theory.

and S20, respectively. The atom numbering scheme we have adopted for isomers **1–9** is given in Fig. 3, which is relevant for calculating the isotopic shifts. In the matrix-isolation of  $C_3H_2$  isomers,<sup>40,47</sup> such values were proven to be very useful in assigning the infrared spectra rather than the absolute

harmonic vibrational frequencies. Cartesian coordinates, total electronic energies, ZPVEs, ZPVE corrected total electronic energies, and dipole moments corresponding to the optimized geometries of **1–9** at different levels are also given in the ESI.† We also note that the electronic structure of isomers **1**, **5**, and **9**





**Table 6** Optimal geometry parameters (Å and degrees) of isomer **6** calculated at different levels of theory

Parameter	cc-pVDZ			cc-pVTZ		
	MP2	CCSD	CCSD(T)	MP2	CCSD	CCSD(T)
$R(C_1C_2)$	1.4246	1.4281	1.4322	1.4185	1.4157	1.4243
$R(C_2C_3)$	1.4018	1.4229	1.4218	1.3863	1.4090	1.4070
$R(C_3C_4)$	1.4343	1.4047	1.4172	1.4242	1.3902	1.4036
$R(C_4C_5)$	1.4126	1.4596	1.4512	1.4005	1.4484	1.4410
$R(C_5C_6)$	1.2855	1.2825	1.2892	1.2666	1.2662	1.2736
$R(C_2C_7)$	1.4825	1.4273	1.4484	1.4568	1.4038	1.4223
$R(C_1C_7)$	1.4344	1.4681	1.4664	1.4154	1.4464	1.4459
$R(C_1C_6)$	1.3844	1.3525	1.3650	1.3615	1.3327	1.3421
$R(C_3H_8)$	1.0948	1.0939	1.0961	1.0807	1.0790	1.0814
$R(C_4H_9)$	1.0956	1.0975	1.0992	1.0816	1.0821	1.0842
$\theta(C_1C_2C_3)$	122.95	125.15	124.36	122.95	125.20	124.42
$\theta(C_2C_3C_4)$	118.82	118.22	118.49	118.92	118.09	118.45
$\theta(C_3C_4C_5)$	115.15	119.27	118.42	115.36	119.31	118.65
$\theta(C_4C_5C_6)$	124.19	110.56	114.00	122.72	110.08	112.69
$\theta(C_3C_2C_7)$	177.96	172.97	174.44	178.09	173.07	174.53
$\theta(C_2C_3H_8)$	123.78	121.58	121.95	123.65	121.59	121.85
$\theta(C_3C_4H_9)$	119.16	118.85	118.79	119.00	118.96	118.80

had been discussed in detail in an earlier work by us and therefore these details are not repeated here.<sup>69</sup>

### 3.1 Benchmark CCSDT(Q)/CBS energies

Table 1 gathers the component breakdown of the W3lite-F12 relative energies for the isomers **1–9**. An inspection of Table 1 reveals that the correlation effects are very important for describing the relative energies of these isomers. At the HF/CBS level of theory, isomers **2** and **3** are energetically more stable than isomer **1** by as much as 17.79 and 16.06 kcal mol<sup>−1</sup>, respectively. It is also worth noting that for these two isomers the SCF and CCSD components nearly cancel each other out (see Table 1). At the CCSD/CBS level of theory, isomers **1** and **2** are nearly isoenergetic and the energy gap between them is merely 0.22 kcal mol<sup>−1</sup>. The valence (T) correlation contributions can be quite large, reaching up to 7.29 kcal mol<sup>−1</sup> for isomer **5**. The higher-order triple excitations, T–(T), are still chemically significant, reaching up to 0.78 kcal mol<sup>−1</sup> (in absolute value) for isomer **4**. The quasiperturbative quadruple excitations, (Q), tend to have an opposite sign to the T–(T) component, and can reach up to 0.94 kcal mol<sup>−1</sup> (in absolute value) for isomer **4**. The core–valence correlation contributions systematically increase the relative energies of the isomers by chemically significant amounts. In particular, they range between 0.61 (isomer **2**) and 1.29 (isomer **4**) kcal mol<sup>−1</sup>. The

**Table 7** Optimal geometry parameters (Å and degrees) of isomer **7** calculated at different levels of theory

Parameter	cc-pVDZ			cc-pVTZ			Other work
	MP2	CCSD	CCSD(T)	MP2	CCSD	CCSD(T)	Ref. 58 <sup>a</sup>
$R(C_1C_2, C_1C_3)$	1.4790	1.4712	1.4817	1.4587	1.4490	1.4600	1.3760
$R(C_2C_3)$	1.3750	1.3617	1.3691	1.3596	1.3447	1.3527	1.4940
$R(C_2C_4, C_3C_5)$	1.4431	1.4570	1.4581	1.4315	1.4453	1.4463	1.3930
$R(C_4C_6, C_5C_7)$	1.3899	1.3777	1.3867	1.3756	1.3615	1.3708	1.4040
$R(C_4H_8, C_5H_9)$	1.0934	1.0927	1.0949	1.0791	1.0773	1.0797	1.0810
$R(C_6C_7)$	1.2958	1.2937	1.3045	1.2782	1.2747	1.2853	1.2820
$\theta(C_2C_1C_3)$	55.40	55.13	55.03	55.56	55.29	55.20	65.70
$\theta(C_3C_2C_4, C_2C_3C_5)$	125.95	125.64	125.66	125.99	125.69	125.73	123.80
$\theta(C_2C_4C_6, C_3C_5C_7)$	104.41	104.50	104.83	104.14	104.14	104.43	106.50
$\theta(C_2C_4H_8, C_3C_5H_9)$	126.65	126.48	126.47	126.70	126.53	126.53	124.50

<sup>a</sup> At the UB3LYP/6-311G(d,p) level of theory.

**Table 8** Optimal geometry parameters (Å and degrees) of isomer **8** calculated at different levels of theory

Parameter	cc-pVDZ			cc-pVTZ			Other work		
	MP2	CCSD	CCSD(T)	MP2	CCSD	CCSD(T)	Ref. 68 <sup>a</sup>	Ref. 63 <sup>b</sup>	Ref. 58 <sup>c</sup>
$R(C_1C_2)$	1.3630	1.3508	1.3622	1.3492	1.3350	1.3466	1.3620	1.3460	1.3890
$R(C_1C_3)$	1.4160	1.4328	1.4293	1.4015	1.4181	1.4144	1.4150	1.4010	1.3750
$R(C_1H_4)$	1.1027	1.1011	1.1034	1.0889	1.0861	1.0887	1.0920	1.0950	1.0870
$R(C_2C_5)$	1.3020	1.3074	1.3121	1.2831	1.2869	1.2920	1.2980	1.2850	1.2260
$R(C_3C_6)$	1.2466	1.2301	1.2403	1.2298	1.2115	1.2222	1.2410	1.2240	1.2270
$R(C_6C_7)$	1.3738	1.3923	1.3875	1.3583	1.3762	1.3714	1.3720	1.3580	1.3500
$R(C_7C_8)$	1.2393	1.2264	1.2348	1.2216	1.2072	1.2161	1.2350	1.2150	1.2130
$R(C_8H_9)$	1.0773	1.0784	1.0800	1.0629	1.0625	1.0645	1.0680	1.0670	1.0620
$\theta(C_3C_1C_2)$	123.23	123.69	123.45	123.36	123.89	123.64	122.90	124.30	122.80
$\theta(H_4C_1C_2)$	119.87	119.83	119.96	119.72	119.67	119.80	120.40	119.70	118.20
$\theta(C_1C_2C_5)$	178.15	178.31	178.23	177.85	177.98	177.93	177.00	179.50	171.90
$\theta(C_1C_3C_6)$	178.57	177.76	177.72	179.00	178.24	178.39	179.00	178.70	178.90
$\theta(C_3C_6C_7)$	179.20	178.98	178.78	179.46	179.37	179.31	179.20	179.60	179.90
$\theta(C_6C_7C_8)$	179.87	179.76	179.67	179.95	179.86	179.85	179.90	180.00	180.00
$\theta(C_7C_8H_9)$	179.76	179.72	179.62	179.75	179.74	179.70	179.90	179.90	180.00

<sup>a</sup> At the MP2/D95\*\* level of theory. <sup>b</sup> At the B3LYP/6-31G(d) level of theory. <sup>c</sup> At the UB3LYP/6-311G(d,p) level of theory.



**Table 9** Harmonic vibrational frequencies ( $\text{cm}^{-1}$ ) and IR intensities ( $\text{km mol}^{-1}$ ) of isomers **1**, **2**, and **3** calculated at the CCSD(T)/cc-pVTZ level of theory

Mode	Isomer 1 <sup>a</sup>			Isomer 2			Isomer 3		
	Symmetry	Frequency	Intensity	Symmetry	Frequency	Intensity	Symmetry	Frequency	Intensity
1	$\pi_u$	71	3	$a'$	94	4	$a_1$	96	2
2	$\pi_g$	170	—	$a''$	97	0	$b_1$	179	1
3	$\pi_u$	367	0	$a'$	234	5	$b_2$	227	0
4	$\pi_u$	398	3	$a''$	261	3	$a_2$	230	—
5	$\pi_g$	417	—	$a'$	459	1	$a_1$	418	3
6	$\pi_g$	517	—	$a''$	495	0	$b_1$	461	18
7	$\pi_u$	518	84	$a'$	502	1	$b_2$	540	2
8	$\sigma_g^+$	543	—	$a'$	519	2	$a_1$	606	66
9	$\sigma_u^-$	1041	7	$a''$	540	1	$b_2$	607	24
10	$\sigma_g^+$	1644	—	$a'$	613	43	$a_2$	633	—
11	$\sigma_u^-$	1870	0	$a''$	659	36	$a_1$	678	7
12	$\sigma_g^+$	2008	—	$a''$	887	15	$a_2$	703	—
13	$\sigma_u^-$	2343	17	$a'$	910	2	$b_1$	704	60
14	$\sigma_u^-$	3441	251	$a'$	1006	3	$b_2$	777	5
15	$\sigma_g^+$	3447	—	$a'$	1175	4	$b_2$	1224	36
16				$a'$	1263	49	$a_1$	1237	33
17				$a'$	1715	8	$a_1$	1768	0
18				$a'$	2112	3	$b_2$	2159	26
19				$a'$	2267	27	$a_1$	2169	4
20				$a'$	3260	1	$b_2$	3450	122
21				$a'$	3456	101	$a_1$	3455	32

<sup>a</sup> At the ROCCSD(T)/cc-pVTZ level of theory since the ground electronic state is a triplet.**Table 10** Harmonic vibrational frequencies ( $\text{cm}^{-1}$ ) and IR intensities ( $\text{km mol}^{-1}$ ) of isomers **4**, **5**, and **6** calculated at the CCSD(T)/cc-pVTZ level of theory

Mode	Isomer 4			Isomer 5			Isomer 6		
	Symmetry	Frequency	Intensity	Symmetry	Frequency	Intensity	Symmetry	Frequency	Intensity
1	$b_1$	274	1	$b_1$	254	0	$a''$	184	17
2	$a_1$	379	3	$a_2$	330	—	$a'$	325	135
3	$a_2$	396	—	$b_2$	349	48	$a''$	405	6
4	$b_2$	477	81	$b_2$	507	171	$a''$	465	0
5	$a_1$	499	53	$a_2$	545	—	$a'$	465	27
6	$b_1$	505	11	$b_1$	557	10	$a''$	616	1
7	$a_2$	599	—	$a_1$	561	10	$a'$	636	13
8	$b_2$	731	117	$a_1$	641	9	$a'$	763	8
9	$b_1$	872	15	$a_2$	893	—	$a''$	817	35
10	$b_2$	873	14	$b_1$	896	8	$a'$	925	15
11	$a_1$	959	2	$a_1$	916	72	$a''$	977	0
12	$a_2$	988	—	$a_1$	965	3	$a'$	1022	28
13	$a_1$	1067	2	$b_2$	1148	0	$a'$	1082	15
14	$b_2$	1258	18	$b_2$	1288	13	$a'$	1159	8
15	$a_1$	1321	2	$a_1$	1312	3	$a'$	1340	18
16	$a_2$	1346	33	$b_2$	1344	7	$a'$	1391	10
17	$b_2$	1447	3	$a_1$	1398	8	$a'$	1422	8
18	$b_2$	1768	42	$b_2$	1780	292	$a'$	1611	15
19	$a_1$	1790	54	$a_1$	1902	31	$a'$	1831	231
20	$b_2$	3166	2	$b_2$	3206	11	$a'$	3184	13
21	$a_1$	3183	21	$a_1$	3207	1	$a'$	3221	2

scalar relativistic corrections, on the other hand, systematically decrease the relative energies of the isomers, but are fairly small; that is, they range between 0.05 (isomers **5** and **6**) to 0.12 (isomer **8**)  $\text{kcal mol}^{-1}$ .

Overall, we obtain the following relative energies at the relativistic, all-electron CCSDT(Q)/CBS level of theory: 3.77 (**2**), 6.13 (**3**), 6.62 (**4**), 6.35 (**5**), 15.54 (**6**), 16.33 (**7**), 18.94 (**8**), and 19.38 (**9**)  $\text{kcal mol}^{-1}$ . Inclusion of the ZPVE component, calculated at the CCSD(T)/cc-pVTZ level of theory, results in the following relative energies at 0 K: 5.56 (**2**), 7.64 (**3**), 10.35 (**4**), 10.23 (**5**), 19.19 (**6**), 20.20 (**7**), 20.26 (**8**), and 20.34 (**9**)  $\text{kcal mol}^{-1}$ .

The very small energy separations between many of the isomers (e.g., between isomers **4** and **5**, and between isomers **6–9**) demonstrates that one has to use highly accurate theoretical methods in order to capture these energy separations accurately.

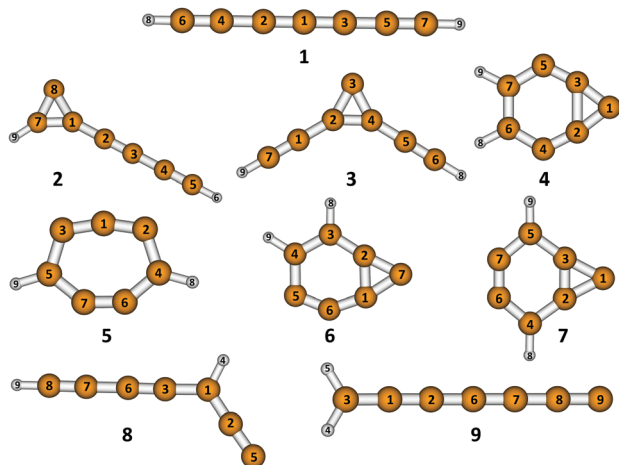
### 3.2 1-(buta-1,3-diynyl)cyclopropenylidene (**2**)

McCarthy and co-workers had detected **2** by FTM spectroscopy nearly two decades ago.<sup>60</sup> It is noteworthy that the parent molecule, cyclopropenylidene ( $\text{c-C}_3\text{H}_2$ ), had also been detected in the same laboratory, which was crucial in the identification of several previously detected lines (for example, 85338 and



**Table 11** Harmonic vibrational frequencies ( $\text{cm}^{-1}$ ) and IR intensities ( $\text{km mol}^{-1}$ ) of isomers **7**, **8**, and **9** calculated at the CCSD(T)/cc-pVTZ level of theory

Mode	Isomer 7			Isomer 8			Isomer 9		
	Symmetry	Frequency	Intensity	Symmetry	Frequency	Intensity	Symmetry	Frequency	Intensity
1	$b_1$	148	17	$a'$	73	4	$b_1$	73	1
2	$b_1$	328	6	$a''$	138	10	$b_2$	76	0
3	$b_2$	402	6	$a'$	177	4	$b_1$	170	11
4	$b_2$	490	44	$a''$	197	3	$b_2$	189	8
5	$a_2$	517	—	$a'$	290	1	$b_2$	268	1
6	$a_1$	607	1	$a''$	318	0	$b_1$	285	0
7	$a_2$	677	—	$a'$	467	0	$b_2$	403	1
8	$b_1$	809	32	$a'$	505	2	$b_2$	455	1
9	$a_1$	845	0	$a''$	506	2	$b_1$	518	1
10	$a_2$	892	—	$a'$	631	41	$a_1$	554	0
11	$b_2$	895	29	$a''$	659	37	$b_1$	556	2
12	$a_1$	1054	37	$a'$	752	49	$b_1$	909	36
13	$b_2$	1186	7	$a''$	870	5	$b_2$	1020	0
14	$a_1$	1211	82	$a'$	1068	15	$a_1$	1048	2
15	$b_2$	1295	44	$a'$	1217	23	$a_1$	1424	12
16	$a_1$	1322	21	$a'$	1396	20	$a_1$	1537	21
17	$b_2$	1419	1	$a'$	1982	891	$a_1$	1891	316
18	$a_1$	1598	3	$a'$	2103	21	$a_1$	2093	304
19	$a_1$	1833	3	$a'$	2253	212	$a_1$	2118	1358
20	$b_2$	3234	4	$a'$	3129	1	$a_1$	3130	0
21	$a_1$	3235	0	$a'$	3453	99	$b_2$	3219	0

**Fig. 3** Atom numbering scheme we have adopted for isomers **1** to **9**.

18 343 MHz) in astronomical sources.<sup>15</sup> A few years before, the doubly deuterated cyclopropenylidene ( $\text{c-C}_3\text{D}_2$ ) was also detected in the ISM.<sup>19</sup> In comparison with the parent molecule, we believe that the derivative (**2**) is also astronomically relevant as it can be obtained by replacing a H atom with the butadiynyl ( $\text{C}_4\text{H}$ ) group. The dipole moment of **2** is 3.67 Debye estimated at the CCSD(T)/cc-pVTZ level of theory (see Table 2), which is comparable to the parent molecule, whose dipole moment is 3.43 Debye.<sup>99</sup> Energetically, **2** lies  $5.56 \text{ kcal mol}^{-1}$  above **1** (see Table 1). Aoki and Ikuta had initially predicted that isomer **2** is the most stable isomer of  $\text{C}_7\text{H}_2$  based on geometry optimizations at the MP2/D95\*\* level of theory.<sup>68</sup> Bowie and co-workers had estimated this energy gap to be  $13.65 \text{ kcal mol}^{-1}$  at the B3LYP/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory.<sup>63</sup> They also stated that both isomers **2** and **3** are low-lying due to aromatic stability because of the presence of  $2\pi$  electrons inside the three-membered ring (Hückel's  $(4n + 2)\pi$  electrons rule

with  $n = 0$ ). The relative energies obtained by us rather support this result much better than the relative energies estimated by them.<sup>70</sup> On the contrary, Sun and co-workers thermodynamically place **2** above **1** at  $49.45 \text{ kcal mol}^{-1}$  estimated at the UB3LYP/6-311G(d,p) level of theory.<sup>58</sup> The CCSD(T)/cc-pVTZ single point energy computed by them using the optimized geometry at the same level decreases this gap to be  $46.26 \text{ kcal mol}^{-1}$ .<sup>58</sup> As we mentioned earlier, we are in disagreement with relative energies estimated by them to a large extent.

The rotational and centrifugal distortion constants estimated by us at the CCSD(T)/cc-pVTZ level of theory are in good agreement with the measured values (see Table 2). We also infer from the values of rotational constants that all isomers except **1** are asymmetric tops. However, considering the small difference between  $B_e$  and  $C_e$ , experimentalists do address isomers **2** and **9** as nearly prolate symmetric tops.<sup>43,60</sup> As far as bond lengths are concerned (see Table 3), they are systematically overestimated at the MP2, CCSD, and CCSD(T) levels in conjunction with the cc-pVDZ basis set. These results are consistent with previous observations, which are largely due to the lack of higher angular momentum polarization functions.<sup>100–105</sup> Considering the shorter bond lengths of  $\text{C}_2\text{C}_3$  and  $\text{C}_4\text{C}_5$ , and also the double bond distance of  $\text{C}_1\text{C}_7$ , and also the longer bond lengths of  $\text{C}_3\text{C}_4$ ,  $\text{C}_1\text{C}_2$  and  $\text{C}_1\text{C}_8$  at all levels estimated by us, the scope for multiple valence structures for **2** rather seem to be slim. Our bond lengths are largely in agreement with the previous theoretical studies except with the  $\text{C}_1\text{C}_7$  distance estimated by Sun and co-workers.<sup>58</sup> As far as bond angles are concerned, four of them ( $\text{C}_1\text{C}_2\text{C}_3$ ,  $\text{C}_2\text{C}_3\text{C}_4$ ,  $\text{C}_3\text{C}_4\text{C}_5$ , and  $\text{C}_4\text{C}_5\text{H}_6$ ) are nearly 180 degrees, which rather confirms that the butadiynyl chain is linear. Once again, our values are in disagreement with Sun and co-workers' values for two of the angles ( $\text{C}_1\text{C}_7\text{H}_9$  and  $\text{C}_8\text{C}_1\text{C}_2$ ) but in agreement with the other previous theoretical studies. The strongest vibrational mode turns out to be the C–H stretch of  $a'$  symmetry





whose frequency is  $3456\text{ cm}^{-1}$  at the CCSD(T)/cc-pVTZ level of theory (see Table 9). The isotopic shifts ( $^{12}\text{C}$ – $^{13}\text{C}$ ) in frequencies (see Table S18, ESI†) should serve as a guide in identifying other high frequency vibrational modes. We also note that all the carbon atoms are environmentally different for this isomer and that's the reason the isotopic shifts in the frequencies are calculated for all the carbon atoms.

### 3.3 1,2-(diethynyl)cyclopropenylidene (3)

This isomer can also be considered as a derivative of cyclopropenylidene by replacing both the H atoms with the ethynyl ( $\text{C}_2\text{H}$ ) group. The dipole moment of this molecule is 3.77 Debye, which is comparable to **2** (see Table 2). Energetically, it lies  $7.64\text{ kcal mol}^{-1}$  above **1** and just  $2.08\text{ kcal mol}^{-1}$  above **2** at our best estimate. Nevertheless, it is yet to be identified in the laboratory to date. For **2**, the inertial axis dipole moment components are in two directions whereas for **3** it is in only one direction (see Table 2). This means that there is only one type of rotational transition possible for **3**, which in part explains why it would be somewhat difficult to identify this molecule in comparison with **2**, where both *a*-type and *b*-type rotational transitions are possible.<sup>60</sup> In fact, while analyzing the isoelectronic  $\text{HC}_6\text{N}$  species,<sup>35</sup> McCarthy and co-workers had pointed out that only *b*-type rotational transitions are possible for **3**. On the contrary, the *a*-type transitions appear to be less sensitive to the angle of the chains with respect to the ring and therefore they can be predicted with greater accuracy than the *b*-type transitions.<sup>35</sup> Moreover, we also speculate that **3** can undergo Bergman cyclization<sup>106</sup> and would become **4**.

The shorter bond lengths of  $\text{C}_1\text{C}_7$  and  $\text{C}_5\text{C}_6$  (see Table 4), and longer bond lengths of  $\text{C}_1\text{C}_2$ ,  $\text{C}_4\text{C}_5$ ,  $\text{C}_2\text{C}_3$ , and  $\text{C}_3\text{C}_4$ , and the double bond distance of  $\text{C}_2\text{C}_4$  at all levels rather tell us that the valence structure given in Fig. 1 for **3** rather seems to be dominant. Theoretical studies on the optimal geometry of **3** were done by others<sup>58,63,68</sup> and our geometrical parameters reported along with previous studies are in good agreement. Four nearly 180 degree bond angles ( $\text{C}_2\text{C}_1\text{C}_7$ ,  $\text{C}_1\text{C}_7\text{H}_9$ ,  $\text{C}_4\text{C}_5\text{C}_6$ , and  $\text{C}_5\text{C}_6\text{H}_8$ ) obtained at all levels of theory indicate that the ethynyl chain is linear. Aoki and Ikuta had predicted that **3** is the second most stable isomer of  $\text{C}_7\text{H}_2$  based on geometry optimizations obtained at the MP2/D95\*\* level of theory.<sup>68</sup> Bowie and co-workers had estimated the energy gap between **1** and **3** to be  $17.51\text{ kcal mol}^{-1}$  at the B3LYP/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory,<sup>63</sup> which is  $\sim 10\text{ kcal mol}^{-1}$  higher than the value we have estimated. Sun and co-workers estimate this energy gap to be  $54.12\text{ kcal mol}^{-1}$  at the UB3LYP/6-311G(d,p) level of theory,<sup>58</sup> which is again inconsistent with our high-level *ab initio* results. The C–H asymmetric stretching vibrational mode of  $b_2$  symmetry with  $122\text{ km mol}^{-1}$  intensity should rather be easily seen in the IR spectra (see Table 9) between  $3400$  and  $3500\text{ cm}^{-1}$ . There are four different carbon atoms for **3** whose isotopic shifts are given in Table S18, ESI†. We believe that this data would be helpful in identifying this hypothetical molecule both in the laboratory and also in space.

### 3.4 Bicyclic rings (4, 6 and 7)

The bicyclic rings definitely seem to reserve a special place on the  $\text{C}_7\text{H}_2$  PES. In comparison with the other bicyclic rings (**6** and **7**) reported in this study, **4** lies  $8.84$  and  $9.85\text{ kcal mol}^{-1}$ , respectively, below the other *ortho*-form (**6**) and the *para*-form (**7**). We note that the *meta*-form (**13**) is  $32.69\text{ kcal mol}^{-1}$  above **4** at the CCSD(T)/cc-pVTZ level of theory with ZPVE correction. As we mentioned in the introduction, calculations at a further higher level of theory have not been done for **13**. It is worth noting here that among the  $\text{C}_6\text{H}_2$  isomers, the *meta*-form of tetrahydrobenzene is the second most stable isomer<sup>42,57</sup> and the presence of an additional carbon atom here had reversed the story as far as energetics are concerned. The resonance structures for **4**, **6**, and **7** are given in Fig. 4. One of the reasons why **4** is more stable than the other two forms could be due to the fact that three reasonable resonance structures can be drawn for this form whereas for **6** and **7** (and also for **13**), we can possibly draw two resonance structures. Although both **4** and **13** exhibit a biradical character, for the former the ground electronic state is a singlet but for the latter the ground electronic state is a triplet. For **6** and **7**, valence structures can be drawn with a clear triple bond for each, whereas the same is not true for **4** and **13**. The dipole moments of **4**, **6**, and **7** are 3.36, 2.96, and 3.07 Debye, respectively.<sup>71</sup> Unlike tetrahydrobenzenes ( $\text{C}_6\text{H}_2$ ), where the dipole moment of the *para*-form is zero by symmetry and for the *ortho* and *meta* forms it is 1.15 and 1.43 Debye (at the CCSD(T)/cc-pVTZ level of theory), respectively, the dipole moments of the bicyclic rings in  $\text{C}_7\text{H}_2$  are quite high and comparable to isomer **2**, which has already been detected in the laboratory.<sup>60</sup>

### 3.5 Bicyclo[4.1.0]hepta-1,2,4,5-tetraene-7-ylidene (4)

While **4** is clearly more stable than the experimentally known cumulene carbene isomer (**9**) by  $9.99\text{ kcal mol}^{-1}$ , it lies

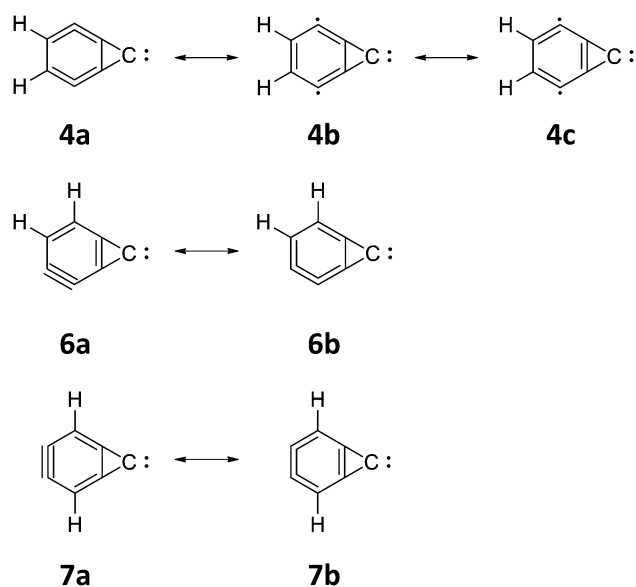


Fig. 4 Possible resonance structures for **4**, **6**, and **7**.



10.35 kcal mol<sup>-1</sup> above **1**. The seven-membered ring isomer, **5**, lies just 0.12 kcal mol<sup>-1</sup> below **4**. Also, another most remarkable thing about isomer **4** is the C<sub>2</sub>C<sub>3</sub> bond length (see Table 5). At the CCSD(T)/cc-pVTZ level of theory, we obtained a bond length of 1.6858 Å, which is quite long for a C–C single bond. Perhaps, this is the longest C–C single bond we have seen among the C<sub>7</sub>H<sub>2</sub> isomers we have studied thus far. Nevertheless, we note that such ultralong C–C single bonds were studied in detail in the past in 11,11-dimethyl-1,6-methano[10]annulene.<sup>107</sup> It is worth pointing out that at the UB3LYP/6-311G(d,p) level of theory Sun *et al.*<sup>58</sup> obtained a much shorter bond length of 1.4350 Å, indicating that this level of theory is inappropriate for this system.

When the basis set is increased within a particular method, normally bond lengths get contracted. That is the trend we had seen throughout for all isomers of C<sub>7</sub>H<sub>2</sub>, but the C<sub>2</sub>C<sub>3</sub> bond length reported in this paper for isomer **4** is an exception to this. The C<sub>2</sub>C<sub>4</sub> and C<sub>3</sub>C<sub>5</sub> bond lengths obtained at all levels are intermediate between a triple bond and a double bond. On the contrary, the C<sub>6</sub>C<sub>7</sub> bond length rather seems to be an intermediate between a double bond and a single bond. Taking into account the C<sub>1</sub>C<sub>2</sub>, C<sub>1</sub>C<sub>3</sub>, C<sub>4</sub>C<sub>6</sub>, and C<sub>5</sub>C<sub>7</sub> bond lengths (and also other distances obtained at all levels), it is evident that two valence structures (**4a** and **4b**; see Fig. 4) are in competition for this isomer and **4c** rather seems to be less dominant.

The harmonic vibrational frequencies are documented in Table 10. The in-plane ring puckering motion of *b*<sub>2</sub> symmetry should rather be seen between 700 and 800 cm<sup>-1</sup> as the intensity of this mode alone is high compared to other vibrational modes. The isotopic shifts of four different carbon atoms are given in Table S19 (ESI†).

### 3.6 Bicyclo[4.1.0]hepta-4,6-diene-2-yne-7-ylidene (**6**)

To our knowledge, previous theoretical studies haven't been reported for this isomer. Though Sun and co-workers considered 113 isomers,<sup>58</sup> this isomer hasn't been considered. **6** lies 19.19 kcal mol<sup>-1</sup> above **1** and just 1.15 kcal mol<sup>-1</sup> below **9** (see Table 1). While it is 8.84 kcal mol<sup>-1</sup> above the other *ortho*-form (**4**), it is rather competitively close to the *para*-form (**7**), which lies ~1 kcal mol<sup>-1</sup> above **6**. Notably, for this isomer, the inertial axis dipole moment components are in two directions (see Table 2). This means that both *a*-type and *b*-type rotational transitions are possible for this isomer like **2** and **8**. Therefore, identification of this isomer should be easier compared to other unidentified ring structures (**3–5**, and **7**). Although a well-balanced Lewis structure is given in Fig. 1, another dominant valence structure is certainly possible for this isomer. The optimal geometry obtained by us is collected in Table 6, which rather suggests such an endeavor.

Two possible valence structures (**6a** and **6b**) are given in Fig. 4. The bond lengths of C<sub>5</sub>C<sub>6</sub> rather seem to be intermediate between a triple bond and a double bond. However, the bond lengths of C<sub>2</sub>C<sub>3</sub> and C<sub>3</sub>C<sub>4</sub> appear to be an intermediate between a double bond and a single bond. The bond lengths of C<sub>1</sub>C<sub>7</sub>, C<sub>4</sub>C<sub>5</sub>, C<sub>1</sub>C<sub>2</sub>, and C<sub>2</sub>C<sub>7</sub> rather look like a single bond. Nevertheless, only between C<sub>5</sub> and C<sub>6</sub>, a triple bond can be drawn and anywhere else in the ring, the structure would be unreasonable.

It is clear that both the valence structures are competing with each other. However, our bond lengths suggest that valence structure **6a** is slightly dominant compared to **6b**.

The high-frequency C–C stretching mode (involving the movement of C<sub>5</sub>–C<sub>6</sub> as per Fig. 3) of *a'* symmetry should readily be seen between 1800 and 1900 cm<sup>-1</sup> in the IR spectra as the intensity for this mode alone is in excess of 200 km mol<sup>-1</sup> (see Table 10). We also note that compared to the other *ortho* and *para*-form (**4** and **7**), for **6**, all seven carbon atoms are environmentally different and therefore seven different isotopic shifts were being calculated in Table S19 (ESI†).

### 3.7 Bicyclo[4.1.0]hepta-1,5-diene-3-yne-7-ylidene (**7**)

This isomer lies 20.20 kcal mol<sup>-1</sup> above **1**. On the contrary, it is competitively close to three other isomers (**6**, **8**, and **9**) of C<sub>7</sub>H<sub>2</sub>. This *para*-form lies 1.01 kcal mol<sup>-1</sup> above the unsymmetrical *ortho*-form (**6**). However, **8** and **9** are just 0.06 and 0.14 kcal mol<sup>-1</sup>, respectively, above **7**. Sun and co-workers had optimized this molecule with a C<sub>2</sub> symmetry instead of C<sub>2v</sub> symmetry.<sup>58</sup> The relative energy gap they found relative to **1** is 62.90 kcal mol<sup>-1</sup> at the UB3LYP/6-311G(d,p) level of theory. The single point energy computed by them at the CCSD(T)/cc-pVTZ//UB3LYP/6-311G(d,p) level of theory reduces this gap to 43.48 kcal mol<sup>-1</sup>. Nevertheless, these values are 42.70 and 23.28 kcal mol<sup>-1</sup>, respectively, higher than our best estimate.

The C<sub>6</sub>C<sub>7</sub> bond length obtained at the considered levels of theory (see Table 7) indicates that the distance is intermediate between a triple bond and a double bond. This bond length alone tells us that both the valence structures (**7a** and **7b**) are competing with each other. The longer bond lengths of C<sub>1</sub>C<sub>2</sub> and C<sub>1</sub>C<sub>3</sub> could be attributed to the fact that in both the valence structures, they remain as a single bond. By considering the intermediate distance of a double bond and a single bond of C<sub>4</sub>C<sub>6</sub> and C<sub>5</sub>C<sub>7</sub> in comparison to C<sub>2</sub>C<sub>4</sub> and C<sub>3</sub>C<sub>5</sub>, which are close to single bond lengths, it is clear that the valence structure **7b** is slightly dominant in comparison to **7a**.

Unlike the *para*-form of the tetrahydrobenzene (C<sub>6</sub>H<sub>2</sub>) where the dipole moment is zero by symmetry,<sup>42</sup> the dipole moment of **7** is 3.07 Debye, which is comparable to the detected isomers of C<sub>7</sub>H<sub>2</sub> such as, **2**. The harmonic vibrational frequencies are listed in Table 11. The highest intensity mode of *a*<sub>1</sub> symmetry, which represents the three-membered ring elongation *via* the carbene carbon atom (C<sub>1</sub>), should rather be seen in the IR spectra around 1150–1250 cm<sup>-1</sup>. The second highest intensity mode of *b*<sub>2</sub> symmetry, which is close-by (1295 cm<sup>-1</sup>), represents in-plane ring distortion of the six-membered ring. For this molecule, none of the high frequency vibrational modes have shown appreciable intensity in the IR spectra. The isotopic shifts of four different carbon atoms are given in Table S20 (ESI†).

### 3.8 1-(buta-1,3-diynyl)propadienylydene (**8**)

This molecule is a butadiynyl derivative of the smallest cumulene carbene (:CCCH<sub>2</sub>). The latter is not only found in the laboratory but also in ISM.<sup>16,37</sup> The dipole moment of **8** at the CCSD(T)/cc-pVTZ level of theory is 5.25 Debye, which is less than the cumulene carbene isomer (**9**) but higher than isomers **2–7**. Also, it lies just 0.08 kcal mol<sup>-1</sup> below **9** at the highest level



of theory estimated here. In addition, we note that synthesizing this isomer may be easier compared to the other isomers discussed in this paper.

Like **2** and **9**, the values of  $B_e$  and  $C_e$  for **8** have a small difference and therefore can be considered as a nearly prolate symmetric top. Moreover, the inertial axis dipole moment components are in two directions and therefore both  $a$ -type and  $b$ -type rotational transitions are possible. The bond lengths of  $C_3C_6$  and  $C_7C_8$  obtained at all levels (see Table 8) certainly show the triple bond character. The  $C_2C_5$  bond length is rather intermediate between a triple bond and a double bond. The presence of a lone pair of electrons on the  $C_5$  carbon is evidently seen in the bond distances as the  $C_2C_5$  length is somewhat shorter than the  $C_1C_2$  distance at all levels. Taking into account the other bond lengths, it is quite clear that the valence structure given in Fig. 1 for **8** is dominant. Four of the bond angles are nearly 180 degrees at all levels ( $C_1C_3C_6$ ,  $C_3C_6C_7$ ,  $C_6C_7C_8$ , and  $C_7C_8H_9$ ) like in isomer **2**, which confirms that the butadiynyl chain is linear. Two high frequency modes of C–C stretching type could readily be seen between 1950 and 2300  $cm^{-1}$  as the intensities of these two modes are quite high. Modes 17 and 19 show predominant stretching of  $C_2-C_5$  and  $C_3-C_6$  bonds, respectively. Also, mode 17 shows an isotopic shift of 50  $cm^{-1}$  when C(2) is isotopically substituted (see Table S20, ESI†), which is the second largest difference we had observed in the isotopic shifts.

## 4 Summary

Nine low-lying isomers of  $C_7H_2$  (**1–9**) whose relative energies are within 1 eV were theoretically investigated. Except **1**, all other isomers are potential candidates for detection in the FTM spectrometer as their dipole moments are non-zero. Nevertheless, isomers **2** and **9** have already been detected and we found that the rest of the isomers (**3–8**) thermodynamically lie between these two detected molecules. In earlier theoretical studies, the relative stability of the bicyclic isomers (**4**, **6**, and **7**) and the seven-membered ring isomer (**5**) either has not been discussed in detail or the energy gaps are overestimated. However, we show here that these molecules are energetically positioned well within 1 eV from the lowest-lying isomer (**1**). Potential rearrangement of **3** to **4** via Bergman cyclization is something that needs to be explored in detail further, which we will undertake in a forthcoming study. The transition states connecting other hypothetical isomers (**5–8**) of  $C_7H_2$  especially on the low-energy side of the PES (within 1 eV) also need to be investigated further, which would suggest whether the undetected isomers could easily be detected or interconvert to already detected isomers. The biradical nature of **4** and **5** might certainly render some challenges in the detection of these two isomers. The thermodynamic competitiveness among isomers **6–9** is quite remarkable as we found that these four isomers lie within 1.15 kcal mol $^{-1}$ . Nevertheless, the detection of **9** indicates that the cumulene carbene isomer of  $C_7H_2$  may also be kinetically stable. Whether new precursors would be of any help in

detecting these hypothetical molecules (**3–8**) remains an open question that may be answered experimentally. In addition, the kinetic stability of the undetected isomers can be answered provided the complete PES of  $C_7H_2$  can be explored at sufficiently high levels of theory. Finally we note that though thermodynamically not so stable, the cumulene carbene isomer of  $C_7H_2$  (**9**) appears to be a kinetically stable molecule as it was found in two different experiments. Without exploring the complete PES of  $C_7H_2$ , it is impossible to comment on the stability of other isomers.

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