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# Energetic and Spectroscopic Properties of the Low-lying $C_7H_2$ Isomers: A High-Level Ab Initio Perspective<sup>†</sup>

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We use the high-level ab initio CCSD(T) and CCSDT(Q) methods to investigate the energetic and spectroscopic properties of the nine low-lying isomers of  $C_7H_2$ , which lies within 1 eV. Among these, heptatriynylidene (1), 1-(buta-1,3-diynyl)cyclopropenylidene (2) and heptahexaenylidene (9) were 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-diynyl)propadienylidene (8), remain hypothetical to date. Except 1, all 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, infra-red intensities, and isotopic shifts ( $^{12}C$  – mono-substituted- $^{13}C$ ) in harmonic vibrational frequencies 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.

## 1 Introduction

Identification of molecules in non-terrestrial environments is definitely an open challenge to the scientific community. Paradoxically, in the vast majority of the 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) apart from simple molecules<sup>1,12-23</sup>. The challenges associated in the synthesis and identification of these new molecules on earth is one of the prime 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 greatest increase in

dipole moment with respect to increase in carbon chain length, have also been found in the ISM. Ever since three cumulene carbenes (where,  $n = 3, 4$ , and  $6$ ) have been 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 focussing their attention not only on these compounds but also on their isomers and higher homologous series<sup>40-43,48-57</sup>.

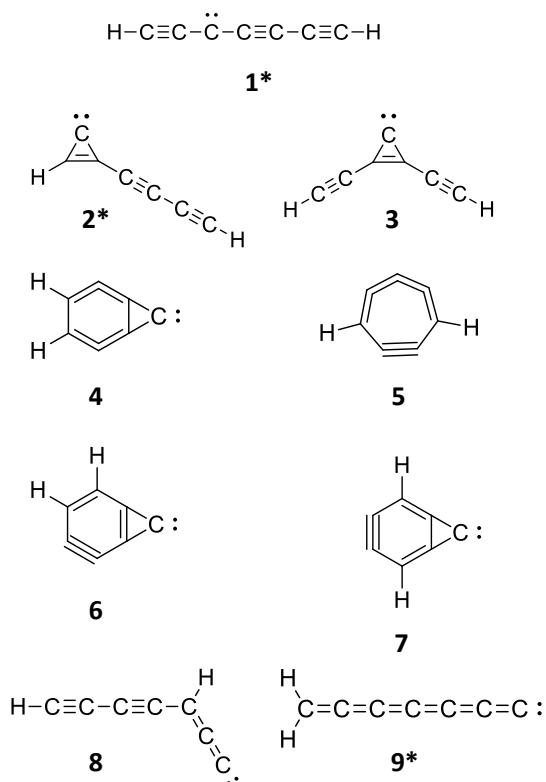
Although more than hundreds of structural isomers are theoretically possible for  $C_7H_2$ <sup>58</sup>, to date merely six isomers (see Figures 1 and 2) have been detected experimentally<sup>43,59-63</sup> and none were detected in space. Heptatriynylidene (1), whose dipole moment is zero by symmetry, 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 reionization mass spectra of the corresponding anion<sup>63</sup>. 1-(buta-1,3-diynyl)cyclopropenylidene (2)<sup>60</sup> and heptahexaenylidene (9)<sup>43</sup> were detected with a Fourier-transform microwave (FTM) spectrometer. Bowie and co-workers had 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 wasn't clear what would be the possibility of the structures of these low-lying isomers on the  $C_7H_2$  potential-energy surface (PES). On the con-**

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<sup>†</sup> 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 are given]. See DOI: 10.1039/b000000x/

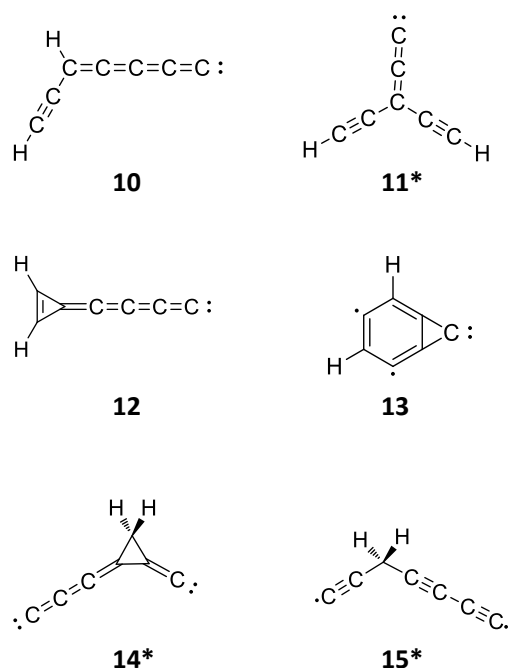
trary, earlier theoretical studies either didn't mention anything about the bicyclic/seven-membered rings (4-7)<sup>63,68</sup> or if they do (4, 5, and 7)<sup>58</sup>, it mislead the relative stability of these isomers. Our motivation behind the current study not only stems from the electronic structures of these isomers but also from the stabilities of these molecules on the low-energy side of the C<sub>7</sub>H<sub>2</sub> PES.



**Fig. 1** Energetically low-lying isomers of C<sub>7</sub>H<sub>2</sub> considered in the present theoretical work. The experimentally found isomers are marked with an asterisk symbol. Isomer 1 is a triplet and all others are singlets.

The present work is an elaborate theoretical investigation of nine low-lying isomers of C<sub>7</sub>H<sub>2</sub> (1-9; see Figure 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 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 Figure 2), which lies above cumulene carbene isomer (9), are not considered here in detail<sup>67</sup>.

Aoki and Ikuta have done geometry optimizations at MP2/D95\*\* level of theory for eight different (1-3, 8-11 and also a bent carbene, whose structure is not given here) isomers of C<sub>7</sub>H<sub>2</sub><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 Figure 1, a bent geometry (4' as per their labelling) reported as minimum by them was not found to be a minimum in our earlier study at CCSD(T)/cc-pVTZ level of



**Fig. 2** Energetically high-lying isomers of C<sub>7</sub>H<sub>2</sub> considered in the previous theoretical work. The experimentally found isomers are marked with an asterisk symbol. Isomers 13 and 15 are triplets and all others are singlets.

theory<sup>69</sup>. We found that the bent geometry becomes linear at higher levels of theories<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)π electrons rule with n = 0 here) due to the presence of 2π 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 had 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 done DFT calculations at the B3LYP/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory for ten different isomers of C<sub>7</sub>H<sub>2</sub> (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 later are not only structurally intriguing but also energetically low-lying as we found in our studies (see Table 1).

Thaddeus and co-workers had stated that there may be other isomers of C<sub>7</sub>H<sub>2</sub> within 1 eV apart from what Aoki and Ikuta had 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 as per coupled-cluster approximations and surprisingly all of them (4-7) are energetically below the experimentally found 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 would rather encourage the experimentalists to find some of these elusive molecules if not all. Although thermodynamically stable than 9, isomers 3-8 are yet to be found in the laboratory. Nevertheless, how stable they are kinetically is an open question, which we can not answer right away. From the structural point of view, 4 and 5 clearly exhibit biradical character and therefore trapping these two molecules might certainly render some challenges to the experimentalists. However, we believe that these can be trapped in low-temperature environments using matrix-isolation techniques.

Although Sun et al., have optimized 113 isomers of  $C_7H_2$  at UB3LYP/6-311G(d,p) level of theory, we are in disagreement with the relative energies (consequently, the relative stabilities) reported by them<sup>58</sup>. They have done single-point energy calculations at CCSD(T)/cc-pVTZ level of theory based on the optimized geometries obtained at the former level. As we mentioned in our earlier article, optimizing the isomers at one level of theory followed by single point energy calculations at other level might not account the thermodynamic stabilities of isomers in a comparable fashion<sup>69</sup>. 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  $C_{2v}$  for the later isomers, optimizations were done with a  $C_s$  symmetry point group. This could also be one of the contributing factors for the differences in relative energies between us and them. Moreover, we note that isomer 6 was not part of their study among the 113 isomers.

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, 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  $C_7H_2$ . While isomers 2 and 9 have already been found in the laboratory by FTM spectroscopy<sup>43,60</sup>, it is worth to note 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 a derivative of cyclopropenylidene ( $c-C_3H_2$ ). The later molecule and also its doubly deuterated derivative ( $c-C_3D_2$ ) 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 is 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 is not been discussed thus far in the literature. We hope that the rotational constants, centrifugal distortion constants, optimal geometry parameters, dipole moments and harmonic vibra-

tional frequencies of  $^{12}C$  and  $^{13}C$  isotopes, and infrared intensities of these hypothetical isomers of  $C_7H_2$  (3-8) would encourage the 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  $C_7H_2$  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 a 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  $C_7H_2$  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 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 W3lite-F12 theory<sup>64,66</sup>. W3lite-F12 theory (and its earlier version W3.2lite theory)<sup>81-83</sup> represent 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  $1 \text{ kJ mol}^{-1} = 0.24 \text{ kcal mol}^{-1}$ )<sup>64</sup>. For example, the related W3-F12 theory is associated with an RMSD of  $0.27 \text{ kcal mol}^{-1}$  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>. 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 W2-F12 theory<sup>64</sup>, and the post-CCSD(T) contributions are obtained from W3.2lite 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 cal-

culated 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>.

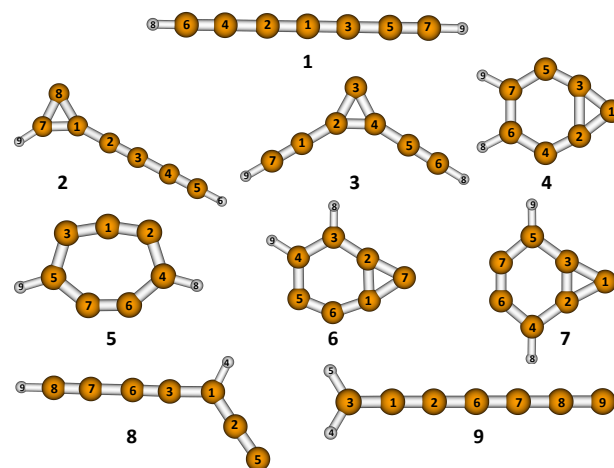
The W3lite-F12 single-point energy calculations were carried out using our CCSD(T)/cc-pVTZ equilibrium geometries. Zero-point vibrational energies (ZPVEs) are calculated at the same level of theory and scaled by a scaling factor of 0.9868 as recommended in Ref.<sup>94</sup>. All the CCSD(T) energy calculations 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<sub>7</sub>H<sub>2</sub> isomers are 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 in harmonic vibrational frequencies (<sup>12</sup>C-<sup>13</sup>C) for isomers 1-3, 4-6, and 7-9 calculated at the same level of theory are documented in the supporting information in Tables S18, S19, and S20, respectively.** The atom numbering scheme we have adopted for isomers 1-9 is given in Figure 3, which is relevant for calculating the isotopic shifts. In the matrix-isolation of C<sub>3</sub>H<sub>2</sub> 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 Supporting Information. We also note that the electronic structure of isomers 1, 5, and 9 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. 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



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

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 being 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 the 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 scalar relativistic corrections, on the other hand, systematically decrease the relative energies of the isomers, but are fairly small. Namely, they range between 0.05 (isomers 5 and 6) to 0.12 (isomer 8) kcal mol<sup>-1</sup>.

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) kcal mol<sup>-1</sup>. 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) kcal mol<sup>-1</sup>. 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 before<sup>60</sup>. It is noteworthy that the parent molecule, cyclopropenylidene (*c*-C<sub>3</sub>H<sub>2</sub>) had also been detected in the same laboratory, which was crucial in the identification of several previously detected lines (for example, 85,338 and 18,343 MHz) in astronomical sources<sup>15</sup>. Few years before, the doubly deuterated cyclopropenylidene (*c*-C<sub>3</sub>D<sub>2</sub>) had also been detected in the ISM<sup>19</sup>. In comparison with the parent molecule, we believe

**Table 1** Relative energies ( $\Delta E_{rel}$ ; 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        | $\Delta E_{rel}$ |        |       |       |       |       |       |       |
|----------------------|-----------------|------------------|--------|-------|-------|-------|-------|-------|-------|
|                      |                 | 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 |
| $E_e$ [CCSD(T)/CBS]  | W2-F12          | 3.52             | 5.77   | 6.78  | 7.01  | 15.57 | 15.97 | 19.32 | 20.85 |
| $E_e$ [CCSDT(Q)/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  |
| $E_0$ [CCSDT(Q)/CBS] | W3.2lite-F12    | 5.56             | 7.64   | 10.35 | 10.23 | 19.19 | 20.20 | 20.26 | 20.34 |

**Table 2** Rotational and centrifugal distortion constants (in MHz), and inertial axis dipole moment components (in Debye;  $\perp^r$  representation) of C<sub>7</sub>H<sub>2</sub> isomers calculated at 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>       |
| $\Delta_J$            | $0.8546 \times 10^{-5}$  | $0.1689 \times 10^{-4}$          | $0.3985 \times 10^{-3}$  | $0.3330 \times 10^{-3}$  | $0.2028 \times 10^{-3}$  | $0.2360 \times 10^{-3}$ | $0.3912 \times 10^{-3}$ | $0.1501 \times 10^{-3}$  | $0.8562 \times 10^{-5}$            |
| $\Delta_K$            | $0.8546 \times 10^{-5}$  | 0.127735                         | 0.109249                 | $0.3272 \times 10^{-2}$  | $-0.1822 \times 10^{-3}$ | $0.2216 \times 10^{-2}$ | $0.6910 \times 10^{-3}$ | 2.59533                  | 22.1709                            |
| $\Delta_{JK}$         | $-0.1709 \times 10^{-4}$ | $0.6908 \times 10^{-2}$          | $-0.1116 \times 10^{-1}$ | $-0.2984 \times 10^{-3}$ | $0.2185 \times 10^{-2}$  | $0.3640 \times 10^{-3}$ | $0.1218 \times 10^{-4}$ | $-0.3223 \times 10^{-1}$ | $0.1098 \times 10^{-1}$            |
| $\delta_J$            | -                        | $0.5514 \times 10^{-6}$          | $0.1455 \times 10^{-3}$  | $0.1301 \times 10^{-3}$  | $0.7111 \times 10^{-4}$  | $0.8193 \times 10^{-4}$ | $0.1577 \times 10^{-3}$ | $0.3137 \times 10^{-4}$  | $-0.2595 \times 10^{-7}$           |
| $\delta_K$            | -                        | $0.3622 \times 10^{-2}$          | $0.8015 \times 10^{-3}$  | $0.4231 \times 10^{-3}$  | $0.1345 \times 10^{-2}$  | $0.5942 \times 10^{-3}$ | $0.5253 \times 10^{-3}$ | $0.2501 \times 10^{-2}$  | $-0.6170 \times 10^{-8}$           |
| $\mu_a$               | -                        | 2.306                            | 3.774                    | -3.357                   | -1.878                   | 2.311                   | 3.068                   | 4.659                    | -7.336                             |
| $\mu_b$               | -                        | 2.855                            | -                        | -                        | -1.855                   | 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 a S-reduced Hamiltonian, whereas for all other isomers they are from the A-reduced Hamiltonian.<sup>b</sup> From Ref. <sup>69</sup>. See the discussions therein for detail.<sup>c</sup> From Ref. <sup>60</sup>.<sup>d</sup> From Ref. <sup>43</sup>.

that the derivative (2) is also astronomically relevant as it can be obtained by replacing a H atom with the butadiynyl (C<sub>4</sub>H) group. The dipole moment of 2 is 3.67 Debye estimated at 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 kcal mol<sup>-1</sup> above 1 (see Table 1). Aoki and Ikuta had initially predicted that isomer 2 is the most stable isomer of C<sub>7</sub>H<sub>2</sub> 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 kcal mol<sup>-1</sup> 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 endeavor 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 kcal mol<sup>-1</sup> 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 kcal mol<sup>-1</sup><sup>58</sup>. As we aforementioned, 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 C<sub>2</sub>C<sub>3</sub> and C<sub>4</sub>C<sub>5</sub>, and also the double bond distance of C<sub>1</sub>C<sub>7</sub>, and also the longer bond lengths of C<sub>3</sub>C<sub>4</sub>, C<sub>1</sub>C<sub>2</sub> and C<sub>1</sub>C<sub>8</sub> 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 C<sub>1</sub>C<sub>7</sub> distance estimated by Sun and co-workers<sup>58</sup>. As far as bond angles are concerned, four of them (C<sub>1</sub>C<sub>2</sub>C<sub>3</sub>, C<sub>2</sub>C<sub>3</sub>C<sub>4</sub>, C<sub>3</sub>C<sub>4</sub>C<sub>5</sub>, and C<sub>4</sub>C<sub>5</sub>H<sub>6</sub>) are nearly 180 degree at levels, which rather confirms that the butadiynyl chain is linear. Once again, our values are in disagreement with the Sun and co-workers values for two of the angles (C<sub>1</sub>C<sub>7</sub>H<sub>9</sub> and C<sub>8</sub>C<sub>1</sub>C<sub>2</sub>) but in agreement with the other previous theoretical studies. The strongest vibrational mode turns out to be C-H stretch of  $a'$  symmetry whose frequency is 3456 cm<sup>-1</sup> at CCSD(T)/cc-pVTZ level of theory (see Table 9). The isotopic shifts (<sup>12</sup>C – <sup>13</sup>C) in frequencies (see Table S18) should serve as a guide in identifying other high frequency vibrational modes. We also note that all the carbon atoms are environmen-

tally different for this isomer and that's the reason the isotopic shift in frequencies are calculated for all the carbon atoms.

### 3.3 1,2-(diethynyl)cyclopropenyldiene (**3**)

This isomer can also be considered as a derivative of cyclopropenyldiene 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 is 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 appears 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 tells us that the valence structure given in Figure 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 levels 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 at 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 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 UB3LYP/6-311G(d,p) level of theory<sup>58</sup>, which is once again unconventional. 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  $3400$  to  $3500 \text{ cm}^{-1}$ . There are four different carbon atoms for **3** whose isotopic shifts are given in Table S18. 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 CCSD(T)/cc-pVTZ level of theory with ZPVE correction. As we aforementioned in the introduction, calculations at further higher level of theory has not been done for **13**. It is worth to note here that among the  $\text{C}_6\text{H}_2$  isomers, the meta-form of tetradehydrobenzene 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 Figure 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 biradical character, for the former the ground electronic state is a singlet but for the later 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 tetradehydrobenzenes ( $\text{C}_6\text{H}_2$ ), where the dipole moment of the para-form is zero by symmetry and for the ortho and meta forms they are 1.15 and 1.43 Debye (at CCSD(T)/cc-pVTZ level), respectively, the dipole moments of the bicyclic rings in  $\text{C}_7\text{H}_2$  are quite high and comparable to isomer **2**, which is already detected in the laboratory<sup>60</sup>.

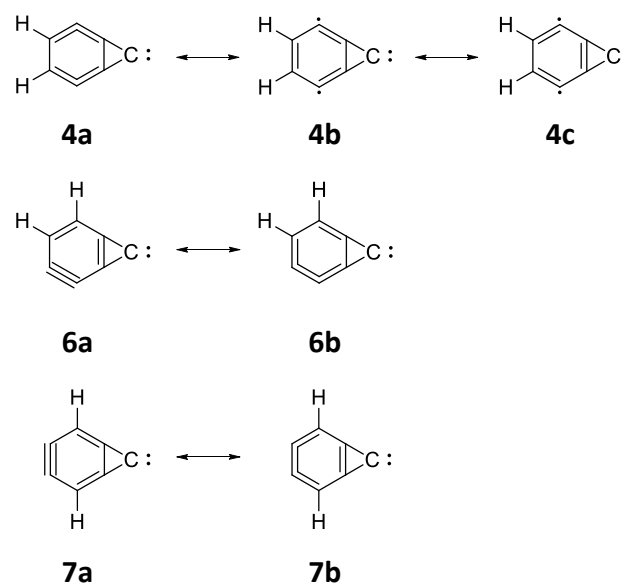


Fig. 4 Possible resonance structures for **4**, **6**, and **7**.

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

| 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 <sub>1</sub> C <sub>2</sub> )                | 1.4008  | 1.4133 | 1.4105  | 1.3865  | 1.3988 | 1.3957  | 1.4000                 | 1.3780                 | 1.2980                 |
| R(C <sub>2</sub> C <sub>3</sub> )                | 1.2431  | 1.2291 | 1.2386  | 1.2266  | 1.2107 | 1.2208  | 1.2380                 | 1.2240                 | 1.2620                 |
| R(C <sub>3</sub> C <sub>4</sub> )                | 1.3767  | 1.3924 | 1.3885  | 1.3614  | 1.3769 | 1.3725  | 1.3750                 | 1.3590                 | 1.3260                 |
| R(C <sub>4</sub> C <sub>5</sub> )                | 1.2385  | 1.2264 | 1.2347  | 1.2209  | 1.2073 | 1.2160  | 1.2340                 | 1.2150                 | 1.2250                 |
| R(C <sub>5</sub> H <sub>6</sub> )                | 1.0767  | 1.0781 | 1.0797  | 1.0624  | 1.0622 | 1.0641  | 1.0680                 | 1.0670                 | 1.0620                 |
| R(C <sub>1</sub> C <sub>7</sub> )                | 1.3559  | 1.3465 | 1.3543  | 1.3406  | 1.3300 | 1.3383  | 1.3510                 | 1.3420                 | 1.5190                 |
| R(C <sub>1</sub> C <sub>8</sub> )                | 1.4631  | 1.4570 | 1.4682  | 1.4412  | 1.4332 | 1.4448  | 1.4530                 | 1.4580                 | 1.4540                 |
| R(C <sub>7</sub> H <sub>9</sub> )                | 1.0917  | 1.0917 | 1.0940  | 1.0769  | 1.0758 | 1.0783  | 1.0810                 | 1.0830                 | 1.0740                 |
| θ(C <sub>1</sub> C <sub>2</sub> C <sub>3</sub> ) | 178.72  | 179.01 | 178.73  | 179.11  | 179.37 | 179.16  | 178.40                 | 179.90                 | 178.60                 |
| θ(C <sub>2</sub> C <sub>3</sub> C <sub>4</sub> ) | 179.39  | 179.52 | 179.34  | 179.66  | 179.79 | 179.67  | 179.40                 | 179.60                 | 179.60                 |
| θ(C <sub>3</sub> C <sub>4</sub> C <sub>5</sub> ) | 179.87  | 179.90 | 179.84  | 179.81  | 179.86 | 179.82  | 179.90                 | 179.90                 | 179.90                 |
| θ(C <sub>4</sub> C <sub>5</sub> H <sub>6</sub> ) | 179.98  | 179.99 | 179.96  | 179.95  | 179.99 | 179.96  | 180.00                 | 179.60                 | 179.90                 |
| θ(C <sub>1</sub> C <sub>7</sub> H <sub>9</sub> ) | 147.84  | 147.84 | 147.43  | 148.26  | 148.36 | 147.99  | 148.40                 | 146.50                 | 138.10                 |
| θ(C <sub>7</sub> C <sub>1</sub> C <sub>2</sub> ) | 149.96  | 149.77 | 149.72  | 150.75  | 150.45 | 150.47  | 149.90                 | 150.80                 | 146.30                 |
| θ(C <sub>8</sub> C <sub>1</sub> C <sub>2</sub> ) | 148.88  | 148.71 | 148.94  | 148.27  | 148.17 | 148.34  | 148.80                 | 149.00                 | 161.80                 |

<sup>a</sup> At MP2/D95\*\* level.<sup>b</sup> At B3LYP/6-31G(d) level.<sup>c</sup> At UB3LYP/6-311G(d,p) level.**Table 4** Optimal geometry parameters (Å and degrees) of isomer **3** calculated at different levels

| 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 <sub>1</sub> C <sub>2</sub> , C <sub>4</sub> C <sub>5</sub> )                               | 1.4068  | 1.4191 | 1.4176  | 1.3919  | 1.4037 | 1.4018  | 1.4050                 | 1.3910                 | 1.3410                 |
| R(C <sub>2</sub> C <sub>3</sub> , C <sub>3</sub> C <sub>4</sub> )                               | 1.4525  | 1.4482 | 1.4572  | 1.4299  | 1.4242 | 1.4336  | 1.4450                 | 1.4340                 | 1.3500                 |
| R(C <sub>1</sub> C <sub>7</sub> , C <sub>5</sub> C <sub>6</sub> )                               | 1.2354  | 1.2247 | 1.2322  | 1.2177  | 1.2058 | 1.2138  | 1.2310                 | 1.2120                 | 1.2220                 |
| R(C <sub>7</sub> H <sub>9</sub> , C <sub>6</sub> H <sub>8</sub> )                               | 1.0769  | 1.0784 | 1.0799  | 1.0625  | 1.0626 | 1.0644  | 1.0680                 | 1.0670                 | 1.0630                 |
| R(C <sub>2</sub> C <sub>4</sub> )   | 1.3634  | 1.3506 | 1.3594  | 1.3479  | 1.3339 | 1.3433  | 1.3570                 | 1.3500                 | 1.6390                 |
| θ(C <sub>1</sub> C <sub>2</sub> C <sub>3</sub> , C <sub>5</sub> C <sub>4</sub> C <sub>3</sub> ) | 149.54  | 149.27 | 149.52  | 149.03  | 148.76 | 148.97  | 149.60                 | 149.60                 | 167.50                 |
| θ(C <sub>2</sub> C <sub>3</sub> C <sub>4</sub> )  | 55.98   | 55.59  | 55.61   | 56.23   | 55.85  | 55.87   | -                      | -                      | -                      |
| θ(C <sub>2</sub> C <sub>1</sub> C <sub>7</sub> , C <sub>4</sub> C <sub>5</sub> C <sub>6</sub> ) | 179.84  | 179.65 | 179.55  | 179.91  | 179.95 | 179.93  | 179.90                 | 179.80                 | 178.30                 |
| θ(C <sub>1</sub> C <sub>7</sub> H <sub>9</sub> , C <sub>5</sub> C <sub>6</sub> H <sub>8</sub> ) | 179.78  | 179.90 | 179.97  | 179.48  | 179.61 | 179.57  | 180.00                 | 179.50                 | 179.30                 |
| θ(C <sub>1</sub> C <sub>2</sub> C <sub>4</sub> , C <sub>5</sub> C <sub>4</sub> C <sub>2</sub> ) | 148.45  | 148.53 | 148.29  | 149.08  | 149.17 | 148.96  | 148.40                 | 148.50                 | 139.90                 |

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

### 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  $10.35\text{ kcal mol}^{-1}$  above **1**. The seven-membered ring isomer, **5**, lies just  $0.12\text{ kcal mol}^{-1}$  below **4**. Also, another most remarkable thing about isomer **4** is the  $\text{C}_2\text{C}_3$  bond length (see Table 5). At CCSD(T)/cc-pVTZ level of theory, we got our bond length as  $1.6858\text{ \AA}$ , which is quite longer for a C-C single bond. Perhaps, this is the longest C-C single bond we have seen among the  $\text{C}_7\text{H}_2$  isomers we had 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>. Also, we are in complete disagreement (as far as length is concerned) with the Sun and co-workers<sup>58</sup>, in particular for this bond length alone, although the value is still longer in their calculations as well.

When the basis set is increased within a particular method, normally bond lengths get contracted. That's the trend we had seen throughout for all isomers of  $\text{C}_7\text{H}_2$ , but  $\text{C}_2\text{C}_3$  bond length reported in this paper for isomer **4** is an exception to this. The  $\text{C}_2\text{C}_4$  and  $\text{C}_3\text{C}_5$  bond lengths obtained at all levels are intermediate between a triple bond and a double bond. On the contrary, the  $\text{C}_6\text{C}_7$  bond length rather seems to be an intermediate between a double bond and a single bond. Taking into account of  $\text{C}_1\text{C}_2$ ,  $\text{C}_1\text{C}_3$ ,  $\text{C}_4\text{C}_6$ , and  $\text{C}_5\text{C}_7$  bond lengths (and also other distances obtained at all levels), it is evident that two valence structures (**4a** and **4b**; see Figure 4) are in competition for this isomer and **4c** rather seem to be less dominant.

The harmonic vibrational frequencies are documented in Table 10. The in-plane ring puckering motion of  $b_2$  symmetry should rather be seen between  $700$  to  $800\text{ cm}^{-1}$  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.

### 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 had considered 113 isomers<sup>58</sup>, it is quite surprising that this isomer hasn't been considered. **6** lies  $19.19\text{ kcal mol}^{-1}$  above **1** and just  $1.15\text{ kcal mol}^{-1}$  below **9** (see Table 1). While it is  $8.84\text{ kcal mol}^{-1}$  above the other ortho-form (**4**), it is rather competitively close to the para-form (**7**), which lies  $\sim 1\text{ kcal mol}^{-1}$  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 rather be relatively easier compared to other unidentified ring structures (**3-5**, and **7**). Although a well-balanced Lewis structure is given in Figure 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 Figure 4. The bond lengths of  $\text{C}_5\text{C}_6$  rather seem to be intermediate between a triple bond and a double bond. However, the bond lengths of  $\text{C}_2\text{C}_3$  and  $\text{C}_3\text{C}_4$  appears to be an intermediate between

a double bond and a single bond. The bond lengths of  $\text{C}_1\text{C}_7$ ,  $\text{C}_4\text{C}_5$ ,  $\text{C}_1\text{C}_2$ , and  $\text{C}_2\text{C}_7$  rather looks like a single bond. Nevertheless, only between  $\text{C}_5$  and  $\text{C}_6$ , 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, bond lengths obtained by us suggest that valence structure **6a** is slightly dominant compared to **6b**.

The high-frequency C-C stretching mode (involving the movement of  $\text{C}_5\text{-C}_6$  as per Fig. 3) of  $a'$  symmetry should readily be seen between  $1800$  and  $1900\text{ cm}^{-1}$  in the IR spectra as the intensity for this mode alone is in excess of  $200\text{ km mol}^{-1}$  (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.

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

This isomer lies  $20.20\text{ kcal mol}^{-1}$  above **1**. On the contrary, it is competitively close to three other isomers (**6**, **8**, and **9**) of  $\text{C}_7\text{H}_2$ . This para-form lies  $1.01\text{ kcal mol}^{-1}$  above the unsymmetrical ortho-form (**6**). However, **8** and **9** are just  $0.06$  and  $0.14\text{ kcal mol}^{-1}$ , respectively, above **7**. Sun and co-workers had optimized this molecule with a  $\text{C}_2$  symmetry instead of  $\text{C}_{2v}$  symmetry<sup>58</sup>. The relative energy gap they found relative to **1** is  $62.90\text{ kcal mol}^{-1}$  at UB3LYP/6-311G(d,p) level of theory. The single point energies computed by them at CCSD(T)/cc-pVTZ//UB3LYP/6-311G(d,p) level of theory reduces this gap to  $43.48\text{ kcal mol}^{-1}$ . Nevertheless, these values are  $42.70$  and  $23.28\text{ kcal mol}^{-1}$ , respectively, higher than our best estimate. Once again, we are in disagreement with the relative energies estimated by them.

The  $\text{C}_6\text{C}_7$  bond length obtained at levels (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  $\text{C}_1\text{C}_2$  and  $\text{C}_1\text{C}_3$  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  $\text{C}_4\text{C}_6$  and  $\text{C}_5\text{C}_7$  in comparison to  $\text{C}_2\text{C}_4$  and  $\text{C}_3\text{C}_5$ , 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 ( $\text{C}_6\text{H}_2$ ) where the dipole moment is zero by symmetry<sup>42</sup>, the dipole moment of **7** is  $3.07$  Debye, which is quite comparable to the detected isomer of  $\text{C}_7\text{H}_2$  such as, **2**. The harmonic vibrational frequencies are listed in Table 11. The highest intensity mode of  $a_1$  symmetry, which represents the three-membered ring elongation via carbene carbon atom ( $\text{C}_1$ ), should rather be seen in the IR spectra around  $1150\text{-}1250\text{ cm}^{-1}$ . The second highest intensity mode of  $b_2$  symmetry, which is close-by ( $1295\text{ cm}^{-1}$ ) 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.

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

| Parameter   | cc-pVDZ |        |         | cc-pVTZ |        |         | Other work             |
|---|---------|--------|---------|---------|--------|---------|------------------------|
|   | MP2     | CCSD   | CCSD(T) | MP2     | CCSD   | CCSD(T) | Ref. [58] <sup>a</sup> |
| R(C <sub>1</sub> C <sub>2</sub> , C <sub>1</sub> C <sub>3</sub> )                               | 1.4209  | 1.3997 | 1.4082  | 1.3996  | 1.3797 | 1.3870  | 1.4100                 |
| R(C <sub>2</sub> C <sub>4</sub> , C <sub>3</sub> C <sub>5</sub> )                               | 1.3444  | 1.2931 | 1.3166  | 1.3258  | 1.2737 | 1.2951  | 1.3620                 |
| R(C <sub>4</sub> C <sub>6</sub> , C <sub>5</sub> C <sub>7</sub> )                               | 1.3827  | 1.4018 | 1.3980  | 1.3686  | 1.3879 | 1.3848  | 1.3840                 |
| R(C <sub>6</sub> H <sub>8</sub> , C <sub>7</sub> H <sub>9</sub> )                               | 1.0976  | 1.0981 | 1.1001  | 1.0836  | 1.0829 | 1.0852  | 1.0850                 |
| R(C <sub>2</sub> C <sub>3</sub> )   | 1.5012  | 1.7624 | 1.6697  | 1.5013  | 1.7630 | 1.6858  | 1.4350                 |
| R(C <sub>6</sub> C <sub>7</sub> )   | 1.4802  | 1.4401 | 1.4600  | 1.4680  | 1.4258 | 1.4448  | 1.4200                 |
| θ(C <sub>1</sub> C <sub>2</sub> C <sub>4</sub> , C <sub>1</sub> C <sub>3</sub> C <sub>5</sub> ) | 178.74  | 166.39 | 171.21  | 177.75  | 165.22 | 169.36  | -                      |
| θ(C <sub>2</sub> C <sub>4</sub> C <sub>6</sub> , C <sub>3</sub> C <sub>5</sub> C <sub>7</sub> ) | 119.19  | 123.88 | 121.71  | 119.87  | 124.51 | 122.66  | 121.00                 |
| θ(C <sub>4</sub> C <sub>6</sub> H <sub>8</sub> , C <sub>5</sub> C <sub>7</sub> H <sub>9</sub> ) | 123.82  | 122.27 | 122.53  | 123.95  | 122.34 | 122.60  | 121.30                 |
| θ(C <sub>1</sub> C <sub>2</sub> C <sub>3</sub> , C <sub>1</sub> C <sub>3</sub> C <sub>2</sub> ) | 58.12   | 50.98  | 53.64   | 57.57   | 50.29  | 52.58   | 59.40                  |
| θ(C <sub>2</sub> C <sub>1</sub> C <sub>3</sub> )  | 63.77   | 78.04  | 72.72   | 64.87   | 79.42  | 74.84   | 61.20                  |

<sup>a</sup> At UB3LYP/6-311G(d,p) level.**Table 6** Optimal geometry parameters (Å and degrees) of isomer 6 calculated at different levels

| Parameter  | cc-pVDZ |        |         | cc-pVTZ |        |         |
|--|---------|--------|---------|---------|--------|---------|
|  | MP2     | CCSD   | CCSD(T) | MP2     | CCSD   | CCSD(T) |
| R(C <sub>1</sub> C <sub>2</sub> )                | 1.4246  | 1.4281 | 1.4322  | 1.4185  | 1.4157 | 1.4243  |
| R(C <sub>2</sub> C <sub>3</sub> )                | 1.4018  | 1.4229 | 1.4218  | 1.3863  | 1.4090 | 1.4070  |
| R(C <sub>3</sub> C <sub>4</sub> )                | 1.4343  | 1.4047 | 1.4172  | 1.4242  | 1.3902 | 1.4036  |
| R(C <sub>4</sub> C <sub>5</sub> )                | 1.4126  | 1.4596 | 1.4512  | 1.4005  | 1.4484 | 1.4410  |
| R(C <sub>5</sub> C <sub>6</sub> )                | 1.2855  | 1.2825 | 1.2892  | 1.2666  | 1.2662 | 1.2736  |
| R(C <sub>2</sub> C <sub>7</sub> )                | 1.4825  | 1.4273 | 1.4484  | 1.4568  | 1.4038 | 1.4223  |
| R(C <sub>1</sub> C <sub>7</sub> )                | 1.4344  | 1.4681 | 1.4664  | 1.4154  | 1.4464 | 1.4459  |
| R(C <sub>1</sub> C <sub>6</sub> )                | 1.3844  | 1.3525 | 1.3650  | 1.3615  | 1.3327 | 1.3421  |
| R(C <sub>3</sub> H <sub>8</sub> )                | 1.0948  | 1.0939 | 1.0961  | 1.0807  | 1.0790 | 1.0814  |
| R(C <sub>4</sub> H <sub>9</sub> )                | 1.0956  | 1.0975 | 1.0992  | 1.0816  | 1.0821 | 1.0842  |
| θ(C <sub>1</sub> C <sub>2</sub> C <sub>3</sub> ) | 122.95  | 125.15 | 124.36  | 122.95  | 125.20 | 124.42  |
| θ(C <sub>2</sub> C <sub>3</sub> C <sub>4</sub> ) | 118.82  | 118.22 | 118.49  | 118.92  | 118.09 | 118.45  |
| θ(C <sub>3</sub> C <sub>4</sub> C <sub>5</sub> ) | 115.15  | 119.27 | 118.42  | 115.36  | 119.31 | 118.65  |
| θ(C <sub>4</sub> C <sub>5</sub> C <sub>6</sub> ) | 124.19  | 110.56 | 114.00  | 122.72  | 110.08 | 112.69  |
| θ(C <sub>3</sub> C <sub>2</sub> C <sub>7</sub> ) | 177.96  | 172.97 | 174.44  | 178.09  | 173.07 | 174.53  |
| θ(C <sub>2</sub> C <sub>3</sub> H <sub>8</sub> ) | 123.78  | 121.58 | 121.95  | 123.65  | 121.59 | 121.85  |
| θ(C <sub>3</sub> C <sub>4</sub> H <sub>9</sub> ) | 119.16  | 118.85 | 118.79  | 119.00  | 118.96 | 118.80  |

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

| Parameter   | cc-pVDZ |        |         | cc-pVTZ |        |         | Other work             |
|---|---------|--------|---------|---------|--------|---------|------------------------|
|   | MP2     | CCSD   | CCSD(T) | MP2     | CCSD   | CCSD(T) | Ref. [58] <sup>a</sup> |
| R(C <sub>1</sub> C <sub>2</sub> , C <sub>1</sub> C <sub>3</sub> )                               | 1.4790  | 1.4712 | 1.4817  | 1.4587  | 1.4490 | 1.4600  | 1.3760                 |
| R(C <sub>2</sub> C <sub>3</sub> )   | 1.3750  | 1.3617 | 1.3691  | 1.3596  | 1.3447 | 1.3527  | 1.4940                 |
| R(C <sub>2</sub> C <sub>4</sub> , C <sub>3</sub> C <sub>5</sub> )                               | 1.4431  | 1.4570 | 1.4581  | 1.4315  | 1.4453 | 1.4463  | 1.3930                 |
| R(C <sub>4</sub> C <sub>6</sub> , C <sub>5</sub> C <sub>7</sub> )                               | 1.3899  | 1.3777 | 1.3867  | 1.3756  | 1.3615 | 1.3708  | 1.4040                 |
| R(C <sub>4</sub> H <sub>8</sub> , C <sub>5</sub> H <sub>9</sub> )                               | 1.0934  | 1.0927 | 1.0949  | 1.0791  | 1.0773 | 1.0797  | 1.0810                 |
| R(C <sub>6</sub> C <sub>7</sub> )   | 1.2958  | 1.2937 | 1.3045  | 1.2782  | 1.2747 | 1.2853  | 1.2820                 |
| θ(C <sub>2</sub> C <sub>1</sub> C <sub>3</sub> )  | 55.40   | 55.13  | 55.03   | 55.56   | 55.29  | 55.20   | 65.70                  |
| θ(C <sub>3</sub> C <sub>2</sub> C <sub>4</sub> , C <sub>2</sub> C <sub>3</sub> C <sub>5</sub> ) | 125.95  | 125.64 | 125.66  | 125.99  | 125.69 | 125.73  | 123.80                 |
| θ(C <sub>2</sub> C <sub>4</sub> C <sub>6</sub> , C <sub>3</sub> C <sub>5</sub> C <sub>7</sub> ) | 104.41  | 104.50 | 104.83  | 104.14  | 104.14 | 104.43  | 106.50                 |
| θ(C <sub>2</sub> C <sub>4</sub> H <sub>8</sub> , C <sub>3</sub> C <sub>5</sub> H <sub>9</sub> ) | 126.65  | 126.48 | 126.47  | 126.70  | 126.53 | 126.53  | 124.50                 |

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

### 3.8 1-(buta-1,3-diynyl)propadienylidene (8)

This molecule is a butadiynyl derivative of the smallest cumulene carbene (:CCCH<sub>2</sub>). The later is not only found in the laboratories but also in ISM<sup>16,37</sup>. The dipole moment of **8** at 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. We believe that synthesizing this isomer would rather be easier among the rest of 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. Bond lengths of C<sub>3</sub>C<sub>6</sub> and C<sub>7</sub>C<sub>8</sub> obtained at all levels (see Table 8) certainly show the triple bond character. The C<sub>2</sub>C<sub>5</sub> bond length is rather intermediate between a triple bond and a double bond. The presence of a lone pair of electrons on the C<sub>5</sub> carbon is evidently seen on the bond distances as the C<sub>2</sub>C<sub>5</sub> length is somewhat shorter than the C<sub>1</sub>C<sub>2</sub> distance at all levels. Taking into account the other bond lengths, it is quite clear that the valence structure given in Figure 1 for **8** is dominant. Four of the bond angles are nearly 180 degree at levels (C<sub>1</sub>C<sub>3</sub>C<sub>6</sub>, C<sub>3</sub>C<sub>6</sub>C<sub>7</sub>, C<sub>6</sub>C<sub>7</sub>C<sub>8</sub>, and C<sub>7</sub>C<sub>8</sub>H<sub>9</sub>) 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 1950-2300 cm<sup>-1</sup> as the intensities of these two modes are quite high. Modes 17 and 19 show predominant stretching of C<sub>2</sub>-C<sub>5</sub> and C<sub>3</sub>-C<sub>6</sub> bonds, respectively. Also, mode 17 shows an isotopic shift of 50 cm<sup>-1</sup> when C(2) is isotopically substituted (see Table S20), which is the second largest difference we had observed in the isotopic shifts.

## 4 Summary

Nine low-lying isomers of C<sub>7</sub>H<sub>2</sub> (**1-9**) whose relative energies are within 1 eV had been 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 completely in detail or the energy gaps are rather overestimated, which makes us to think that these important molecules lie above isomer **9**. On the contrary, our studies find that the reverse is true. Potential rearrangement of **3** becoming **4** via Bergman cyclization is something need to be explored in detail further, which we would take in a forthcoming study. The transition states connecting other hypothetical isomers (**5-8**) of C<sub>7</sub>H<sub>2</sub> 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 would 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<sup>-1</sup>. Nevertheless, the detection of **9** alone makes us to think that the cumulene carbene isomer of C<sub>7</sub>H<sub>2</sub> is kinetically stable too apart from the higher polarity factor. On the contrary, should new precursors would be of any help in detecting these hypothetical molecules (**3-8**) remain an open question and can only be answered by experimentalists. Perhaps, the kinetic stability of the unidentified isomers can only be answered provided the complete PES of C<sub>7</sub>H<sub>2</sub> can be explored. From our studies we arrive at a conclusion that though thermodynamically not so stable, the cumulene carbene isomer of C<sub>7</sub>H<sub>2</sub> (**9**) appears to be a kinetically stable molecule as it was found in two different experiments. Without exploring the complete PES of C<sub>7</sub>H<sub>2</sub>, it is impossible to comment on the stability of other isomers.

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

| Parameter  | cc-pVDZ |        |         | cc-pVTZ |        |         | Other work                          |                                     |                                     |
|--|---------|--------|---------|---------|--------|---------|-------------------------------------|-------------------------------------|-------------------------------------|
|  | MP2     | CCSD   | CCSD(T) | MP2     | CCSD   | CCSD(T) | Ref. [ <sup>68</sup> ] <sup>a</sup> | Ref. [ <sup>63</sup> ] <sup>b</sup> | Ref. [ <sup>58</sup> ] <sup>c</sup> |
| R(C <sub>1</sub> C <sub>2</sub> )                | 1.3630  | 1.3508 | 1.3622  | 1.3492  | 1.3350 | 1.3466  | 1.3620                              | 1.3460                              | 1.3890                              |
| R(C <sub>1</sub> C <sub>3</sub> )                | 1.4160  | 1.4328 | 1.4293  | 1.4015  | 1.4181 | 1.4144  | 1.4150                              | 1.4010                              | 1.3750                              |
| R(C <sub>1</sub> H <sub>4</sub> )                | 1.1027  | 1.1011 | 1.1034  | 1.0889  | 1.0861 | 1.0887  | 1.0920                              | 1.0950                              | 1.0870                              |
| R(C <sub>2</sub> C <sub>5</sub> )                | 1.3020  | 1.3074 | 1.3121  | 1.2831  | 1.2869 | 1.2920  | 1.2980                              | 1.2850                              | 1.2260                              |
| R(C <sub>3</sub> C <sub>6</sub> )                | 1.2466  | 1.2301 | 1.2403  | 1.2298  | 1.2115 | 1.2222  | 1.2410                              | 1.2240                              | 1.2270                              |
| R(C <sub>6</sub> C <sub>7</sub> )                | 1.3738  | 1.3923 | 1.3875  | 1.3583  | 1.3762 | 1.3714  | 1.3720                              | 1.3580                              | 1.3500                              |
| R(C <sub>7</sub> C <sub>8</sub> )                | 1.2393  | 1.2264 | 1.2348  | 1.2216  | 1.2072 | 1.2161  | 1.2350                              | 1.2150                              | 1.2130                              |
| R(C <sub>8</sub> H <sub>9</sub> )                | 1.0773  | 1.0784 | 1.0800  | 1.0629  | 1.0625 | 1.0645  | 1.0680                              | 1.0670                              | 1.0620                              |
| θ(C <sub>3</sub> C <sub>1</sub> C <sub>2</sub> ) | 123.23  | 123.69 | 123.45  | 123.36  | 123.89 | 123.64  | 122.90                              | 124.30                              | 122.80                              |
| θ(H <sub>4</sub> C <sub>1</sub> C <sub>2</sub> ) | 119.87  | 119.83 | 119.96  | 119.72  | 119.67 | 119.80  | 120.40                              | 119.70                              | 118.20                              |
| θ(C <sub>1</sub> C <sub>3</sub> C <sub>5</sub> ) | 178.15  | 178.31 | 178.23  | 177.85  | 177.98 | 177.93  | 177.00                              | 179.50                              | 171.90                              |
| θ(C <sub>1</sub> C <sub>3</sub> C <sub>6</sub> ) | 178.57  | 177.76 | 177.72  | 179.00  | 178.24 | 178.39  | 179.00                              | 178.70                              | 178.90                              |
| θ(C <sub>3</sub> C <sub>6</sub> C <sub>7</sub> ) | 179.20  | 178.98 | 178.78  | 179.46  | 179.37 | 179.31  | 179.20                              | 179.60                              | 179.90                              |
| θ(C <sub>6</sub> C <sub>7</sub> C <sub>8</sub> ) | 179.87  | 179.76 | 179.67  | 179.95  | 179.86 | 179.85  | 179.90                              | 180.00                              | 180.00                              |
| θ(C <sub>7</sub> C <sub>8</sub> H <sub>9</sub> ) | 179.76  | 179.72 | 179.62  | 179.75  | 179.74 | 179.70  | 179.90                              | 179.90                              | 180.00                              |

<sup>a</sup> At MP2/D95\*\* level.<sup>b</sup> At B3LYP/6-31G(d) level.<sup>c</sup> At UB3LYP/6-311G(d,p) level.**Table 9** Harmonic vibrational frequencies (cm<sup>-1</sup>) and IR intensities (km mol<sup>-1</sup>) of Isomers **1**, **2**, and **3** calculated at CCSD(T)/cc-pVTZ level

| Mode | isomer 1     |           |           | 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        |

**Table 10** Harmonic vibrational frequencies ( $\text{cm}^{-1}$ ) and IR intensities ( $\text{km mol}^{-1}$ ) of isomers 4, 5, and 6 calculated at CCSD(T)/cc-pVTZ level

| 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   | $a_1$    | 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         |

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

| 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         |

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