THE JOURNAL OF PHYSICAL CHEMISTRY A

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A: Spectroscopy, Molecular Structure, and Quantum Chemistry

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J. Phys. Chem. A, **Just Accepted Manuscript** • DOI: 10.1021/acs.jpca.8b08809 • Publication Date (Web): 26 Oct 2018

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From High-energy C_7H_2 Isomers with A Planar Tetracoordinate Carbon Atom to An Experimentally Known Carbene

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Abstract

In this work, we use high-level ab initio procedures to show that the high-energy isomers of C_7H_2 with a planar tetracoordinate carbon (ptC) atom serve as reactive intermediate leading to the formation of an experimentally known ring-chain carbene, 1-(buta-1,3-diynyl)cyclopropenylidene (**2**). Among the experimentally known isomers of C_7H_2, the latter is the only low-lying ring-chain carbene identified by Fourier-transform microwave spectroscopy. Here we investigate the ring opening pathways of C-C single bonds connected to the ptC atom in three different C_7H_2 isomers using coupled-cluster and density functional theory methods. These three isomers [**ptC1** (C_{2v}; $\widetilde{X}^1A_1$), **ptC2** (C_s; $\widetilde{X}^1A'$), and **ptC3** (C_s; $\widetilde{X}^1A'$)] are found to be local minima on the C_7H_2 potential-energy surface at both CCSD(T)/cc-pVTZ and B3LYP/6-311+G(d,p) levels of theory. The transition states and minimum-energy pathways connecting the reactants (ptC isomers) and the products have been found via intrinsic reaction coordinate calculations at the B3LYP/6-311+G(d,p) level of theory. The high-energy ptC isomers (**ptC2** and **ptC3**) lead to the formation of **2**, whilst the low-energy ptC isomer, **ptC1**, rearranges to a bicyclic carbene, bicyclo[4.1.0]hepta-4,6-diene-2-yne-7-ylidene (**6**). In the latter, we note that both the reactant and the product are yet to be identified in the laboratory. Relative energies, activation energies, reaction energies, and nucleus independent chemical shift values have been calculated to access the thermodynamic and kinetic stabilities and the aromatic nature of these peculiar molecules. Rotational and centrifugal distortion constants have also been estimated for all ptC isomers, which may assist the efforts of microwave spectroscopists.

Introduction

In a given elemental composition, the limelight of hypothetical molecules may always remain poor unless and until they are identified in the laboratory. The energy difference between the low-energy isomers and the hypothetical molecules predicted to be local minima computationally is often an important factor in the acceptance or negligence of the latter. However, it is important to consider potential rearrangements or dissociations involving unidentified high-energy intermediates. To date, the concept of planar tetracoordinate carbon (ptC) has rather been seen as an odd feature as they can be considered as *anti van't Hoff-Le Bel* compounds.[1–3] Nevertheless, it has gained some momentum experimentally[4–8] though it was suggested nearly 50 years ago. First introduced by Monkhorst,[9] the idea of how to stabilize a molecule containing a ptC atom was started by Hoffmann and co-workers.[10] Although only a handful of molecules were identified in the laboratory,[4–8] theoretically many molecules were proposed to date. These include hydrocarbons stabilized by electronic effects[11–17] as well as hydrocarbons stabilized by steric effects such as alkaplanes and hemispiroalkaplanes.[18–22] Doped hydrocarbons or carbon clusters with lithium,[23] beryllium/boron,[24,25] boron,[26–30] nitrogen,[31] silicon,[32] phosphorus,[33,34] and late transition metals[35] with a ptC, ptB, ptN, ptSi, or ptP atom are also reported. It is worth to note here that planar penta,[36–43] hexa,[44–48] and hepta[49,50] coordinated carbon compounds are also actively pursued due to the potential implications of these molecules in making new materials.[51]

In this work, we explored the dissociation pathways of three different isomers of C_7H_2, which contain a ptC atom. **ptC1**, **ptC2**, and **ptC3** (see Fig. 1) can be named as 2,7-(didehydro)-tricyclo[4.1.0.0^{1,3}]hepta-2,4,6-triene, 2,5-(didehydro)-1-ethynylspiro[2.2]penta-1,4-diene, and 2,4-(didehydro)-1-ethynylspiro[2.2]penta-1,4-diene, respectively.[52] The equilibrium geometry of **ptC1** has been reported elsewhere more than a decade before.[15,16] Nevertheless, it remains elusive in the laboratory to date though energetically lying close to 1,1-(diethynyl)propadienylidene (**11**) and the cumulene carbene isomer of C_7H_2, heptahexaenylidene (**9**), which are experimentally known.[53,54] The latter molecule and also 1-(buta-

1,3-diynyl)cyclopropenylidene (**2**) have been identified using Fourier transform microwave (FTMW) spectroscopy by McCarthy and co-workers.[53,55] To the best of our knowledge, the important spectroscopic parameters such as rotational and centrifugal distortion constants have not been reported in other theoretical works to date,[15,16,32] for **ptC1**, which may aid the detection of this peculiar molecule using FTMW spectroscopy in the laboratory.

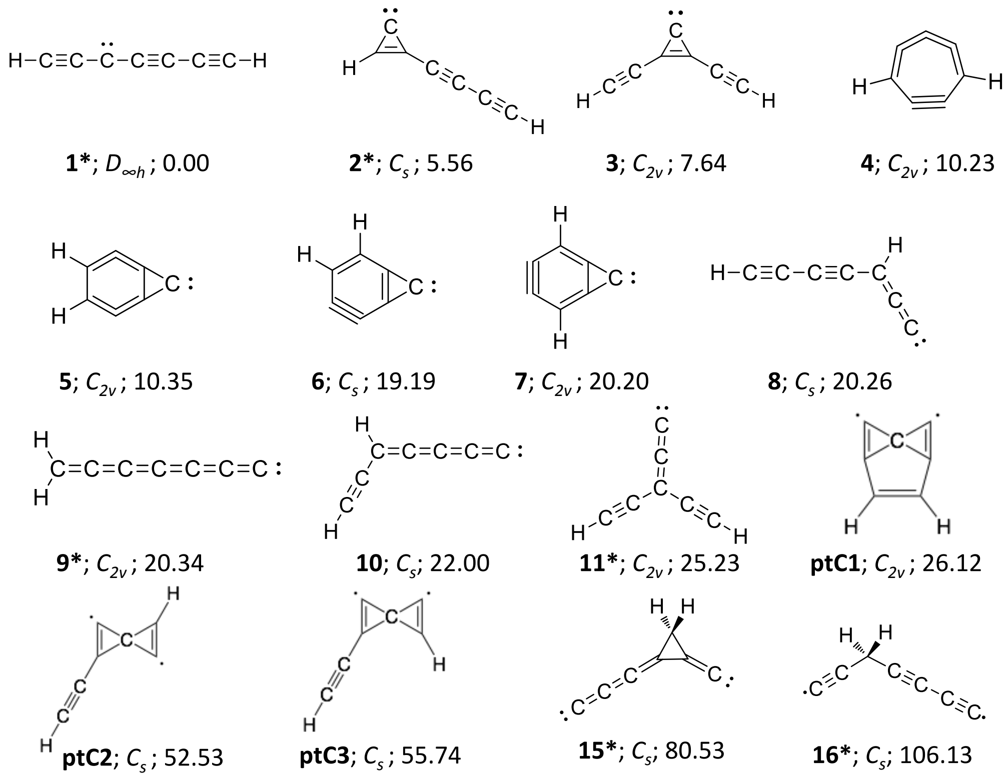

Figure 1: Various isomers of C_7H_2 considered in this and previous theoretical works.[59,60] The relative energy differences were calculated at the W3lite-F12 level of theory.[123] ZPVEs are calculated at the CCSD(T)/cc-pVTZ level and scaled by a factor of 0.9868.[99] The experimentally detected isomers are marked with an asterisk symbol. Isomers **1** and **16** are triplets and all others are singlets.

The high-energy ptC isomers, **ptC2** and **ptC3** have not been considered before theoretically.[15,16,54,56–60] Based on CCSD(T)/cc-pVTZ//UB3LYP/6-311G(d,p) calculations, Sun *et al.* have proposed 113 isomers of C_7H_2,[58] however ptC isomers were not considered in their study. To date, six isomers of C_7H_2 have been detected experimentally.[53–55,61–63] Interest in C_7H_2 isomers largely stems from the fact that four carbene molecules of the lower homologous series [cyclopropenylidene (c-C_3H_2),[64] propadienylidene (C_3H_2),[65] butatrienylidene (C_4H_2),[66] and hexapentaenylidene (C_6H_2)[67]] have been identified in interstellar sources. We also emphasize here that detection of these molecules in the laboratory[64,68–70] is a crucial factor in the confirmation of several identified lines in the astronomical sources. The isotopologue of C_3H_2, the doubly deuterated cyclopropenylidene (c-C_3D_2) has also recently been found in the interstellar sources.[71] Although there is no evidence for the isomers of C_7H_2 in the spectral line surveys of IRC+10216[72] and W51,[73] chemical models of Herbst and Leung[74] suggest that the abundance of C_7H_2 (unspecific to any particular isomer) in TMC-1 is comparable to HC_5N[75,76] and C_3N,[77] which were observed in space. However, based on the available laboratory data of C_7H_2 isomers,[53,55] McCarthy and co-workers had stated that the limits on the abundances of C_7H_2 isomers were not determined in the carbon-chain rich source of TMC-1 as their spectral line surveys have not been published yet. Here, our interest in ptC isomers of C_7H_2 emerge from the fact that their dissociation predominantly leads to low-energy isomers (**2**, 1,2-(diethynyl)cyclopropenylidene (**3**), and bicyclo[4.1.0]hepta-4,6-diene-2-yne-7-ylidene (**6**); see Table 1) depending upon the ptC isomer, and its corresponding C-C single bond connected to the ptC atom being broken. In particular, the major product obtained upon the dissociation (see Figs. 3 and 4) of the high-energy ptC isomers (**ptC2** and **ptC3**) is the experimentally known molecule of C_7H_2, **2**.[55] Therefore, one can unequivocally say that the latter serve as reactive intermediates within equilibrium thermodynamic considerations. It is also worth mentioning here that the production and identification of C_7H_2 isomers using FTMW spectroscopy involved an electrical discharge of 1 % mixture of diacetylene in Ne with the supersonic nozzle of about 1000 Volts.[55,78] The latter quantity certainly does not indicate the amount of energy being imparted on the precursor gases. Nevertheless, understanding the thermochemistry of C_7H_2 isomers on the high-energy regions of the potential energy surface (PES) is important for predicting potential rearrangements. While we do not discard the formation of C_7H_2 isomers by radical recombination of diacetylene sub-units, the scope of our work in this paper is limited to equilibrium thermodynamic considerations.

In continuation of earlier theoretical[15,16,54,56–58] and experimental studies on C_7H_2 isomers,[53–55,61–63] in this work, we explored the possibilities of arriving at new isomers of C_7H_2 with a ptC atom. **ptC1** was initially reported as a local minimum on the C_7H_2 PES elsewhere at the B3LYP/6-311++G(2d,2p) level of theory.[15,16] Nevertheless, our theoretical study differs from the earlier theoretical works as far as high-energy ptC isomers (**ptC2** and **ptC3**) and their dissociation are concerned. Our main motivation in this work is to determine the relative energies (ΔE_0), activation energies ($\Delta E^{\ddagger}$), and also the reaction energies (ΔE_r) by studying their dissociation, which may give an idea of the thermodynamic versus kinetic stabilities of these peculiar molecules. We have also computed nucleus independent chemical shift (NICS) values[79,80] for all the three ptC isomers of C_7H_2 to gauge the aromatic nature of these compounds. Optimal geometries and spectroscopic parameters, which are especially relevant to the FTMW spectroscopy are also collected. We believe that our efforts would assist the efforts of the experimentalists in the identification of these peculiar molecules in the future.

Computational Methods

The geometries of all C_7H_2 isomers with a ptC atom and their corresponding dissociative products were optimized using second-order Møller-Plesset perturbation theory,[81] density functional theory (DFT), and also with coupled-cluster singles and doubles[82,83] augmented with perturbative treatments of triple excitations (CCSD(T)) to incorporate a high-level treatment of electron correlation effects.[84–86] For the MP2 and CCSD(T) calculations, the correlation-consistent polarized valence n zeta (cc-pVnZ) basis sets of Dunning's (n = D and T) were employed.[87] For ptC isomers alone, we have also done geometry optimizations at the MP2/aug-cc-pVQZ level of theory to check consistencies in bond lengths and bond angles. The frozen-core approximation is utilized in all MP2 and CCSD(T) calculations. These calculations were done with the CFOUR[88] and MOLPRO[89,90] program packages. All DFT calculations were done with the B3LYP hybrid-functional[91,92] using the 6-311+G(d,p) basis set.[93,94] All the transition states corresponding to the dissociation of C-C bonds connected to the ptC atom were obtained at the latter level. IRC calculations[95,96] and NICS values[79,80] were also estimated at the same level. NICS values reported here have been calculated at 1 Å above the plane of the ptC isomers. These calculations were done with the Gaussian 09 program.[97] We note that for all the stationary points obtained, harmonic vibrational frequencies were calculated by analytic calculation of second derivatives.[98] Zero-point vibrational energies (ZPVEs) calculated at the CCSD(T)/cc-pVTZ level of theory are scaled by a scaling factor of 0.9868 as recommended elsewhere.[99]

In order to obtain reliable relative energies and reaction profiles, high-level benchmark data have been obtained using W1-F12 and W3lite-F12 theories.[100–104] These theories represent layered extrapolations to the relativistic, all-electron CCSD(T)/CBS (W1-F12) and CCSDT(Q)/CBS (W3lite-F12) levels. W3lite-F12 theory can achieve benchmark accuracy for atomization reactions (i.e., it is associated with root-mean-square deviations, RMSDs, from accurate atomization energies of about 1 kJ mol^{-1} = 0.24 kcal mol^{-1}). For example, the related W3-F12 theory is associated with an RMSD of 0.27 kcal mol^{-1} for a set of 140 very accurate atomization energies obtained at the full configuration interaction (FCI) infinite basis-set limit.[105] The performance of W1-F12 theory has been recently evaluated against an even larger set of of 200 very accurate atomization energies,[106] for this extended data-set of atomization energies W1-F12 theory achieves an RMSD of 0.72 kcal mol^{-1}. The computational details of W3lite-F12 and W1-F12 theories have been specified and rationalized in great detail in Refs.,[101,103] see also Ref.[104] for a recent review. We note that all the CCSD(T) energy calculations involved in the W3lite-F12 energies were done with the MOLPRO program package,[89,90] whereas the post-CCSD(T) calculations were carried out with the MRCC program.[107,108]

Results and Discussion

The relative energies (ΔE_0), activation energies ($\Delta E^{\ddagger}$), reaction energies (ΔE_r), and NICS (1Å) values calculated at different levels are given in Table 1. Schematic reaction profile diagrams connecting the reactants, **ptC1**, **ptC2**, and **ptC3** and their dissociative products via the relevant transition states are shown in Figs. 2, 3, and 4, respectively. The rotational and centrifugal distortion constants, inertial axis dipole moment components, and absolute dipole moments calculated at the CCSD(T)/cc-pVTZ level of theory for all ptC isomers are collected in Table 2. The optimal geometries of **ptC1**, **ptC2**, and **ptC3** calculated at different levels are documented in Tables 3, 4, and 5, respectively. Energetic and spectroscopic properties of other low-lying isomers (**1**-**9**) are documented in our earlier works.[59,60] For brevity the Cartesian coordinates of the optimized geometries, total electronic energies, ZPVEs, harmonic vibrational frequencies, and infra-red intensities of all ptC isomers calculated at different levels are given in the supporting information.

Activation and reaction energies

For **ptC1**, two different transition states have been identified with respect to breaking of the C-C single bond connected to the ptC atom (see Fig. 2). The activation energy calculated for pathways **A** and **B** are 11.02 and 32.96 kcal mol^{-1}, respectively, at the W1-F12 level of theory. The activation energy for pathway **A** is in good agreement with the value of 9.08 kcal mol^{-1} calculated at the B3LYP/6-311++G(2d,2p) level of theory by an earlier theoretical work.[15] Nevertheless, our theoretical study differs from this earlier theoretical work with respect to dissociation pathway **B**, where it was concluded that it rearranges to **ptC1** itself. However, we find via IRC calculations that both the pathways lead to isomer **6**. For pathway **B**, we have noticed a ring-expansion (five-membered ring to six-membered ring) from the bicarbene like transition state (**ptC1-TS-B**), which once again leads to **6**. The calculated reaction energy of -5.65 kcal mol^{-1} for **ptC1** indicates the exothermic nature

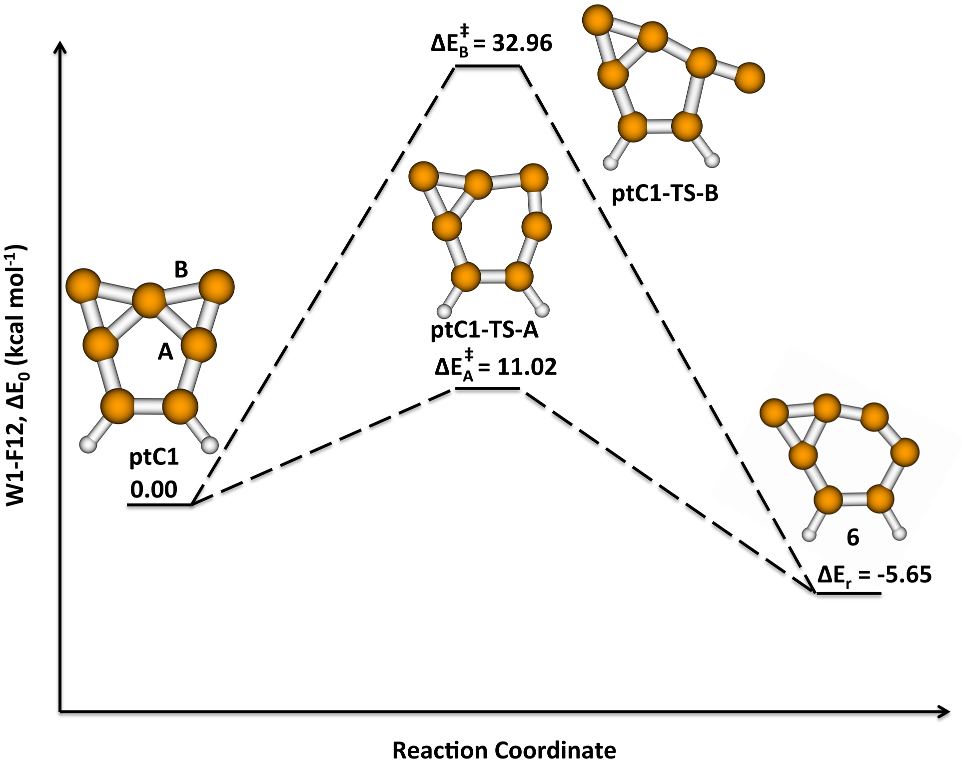

Figure 2: Schematic reaction profile diagram for **ptC1** and its dissociation pathways connected to the ptC atom. The relative energy differences were calculated at the W1-F12 level of theory.

of the minimum-energy pathway in arriving at **6**.

With respect to **ptC2** and **ptC3** dissociation pathways, altogether we have located seven different transition states (see Figs. 3 and 4). Although it appears like four different transition states each, we note that pathway **C** for **ptC2** and pathway **D** for **ptC3** energetically lead to the same transition state. In both **ptC2** and **ptC3**, pathways **A** and **B** lead to isomer **2**. Isomer **3** is obtained via pathway **D** in **ptC2** and pathway **C** in **ptC3**. The lowest activation energy path (pathway **C** in **ptC2** and pathway **D** in **ptC3**) in both cases lead to a bicarbene structure, whose geometry is very similar to **ptC3** except that one of the C-C bonds connected to the ptC atom is broken. One can also arrive at **ptC2** geometry from this bicarbene structure by internal rotation of its C-C bond connected to the three-membered ring. It is worth to note that, in terms of relative energy, **ptC2** is more stable than the bicarbene product (isomer **BC**).[109] Therefore, for pathway **C** alone, the reaction energy is

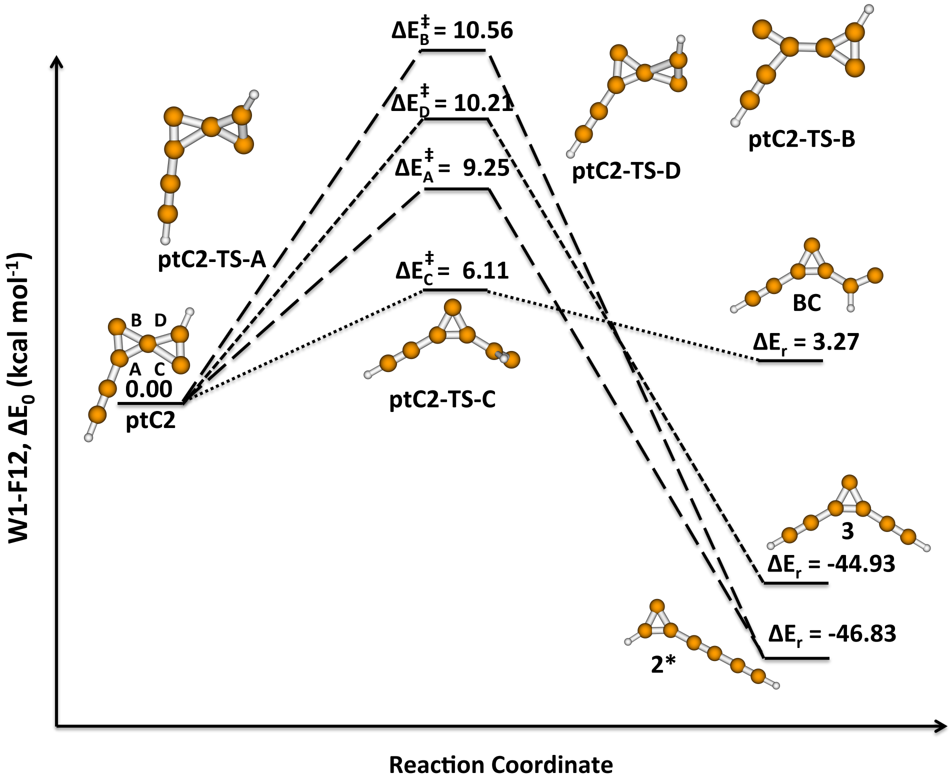

Figure 3: Schematic reaction profile diagram for **ptC2** and its dissociation pathways connected to the ptC atom. The relative energy differences were calculated at the W1-F12 level of theory.

endothermic (3.27 kcal mol^{-1}). Though this pathway has the lowest activation energy (6.11 kcal mol^{-1}) compared to other pathways in **ptC2**, thermodynamically the reactant is more stable than the product. On the contrary, for the lowest activation energy path (pathway **D**) in **ptC3**, the reaction energy is zero at the W1-F12 level of theory. Without ZPVE correction, the reaction energy is still slightly exothermic (-0.22 kcal mol^{-1}; see Table S9 in the supporting information).

Considering the proximity of these three isomers (**ptC2**, **BC**, and **ptC3**), potential interconversion of **BC** to **ptC2** and **BC** to **ptC3** are quite likely. Moreover, whether it is **ptC2** or **ptC3**, the reaction energies for isomer **2** and **3** are highly exothermic though they are not arrived from the lowest activation energy pathways. Nevertheless, among these two products (**2** and **3**), the pathway leading to the experimentally known ring-chain isomer of C_7H_2 (**2**) is ~ 1.90 kcal mol^{-1} more exothermic than the pathway leading to **3** at the W1-

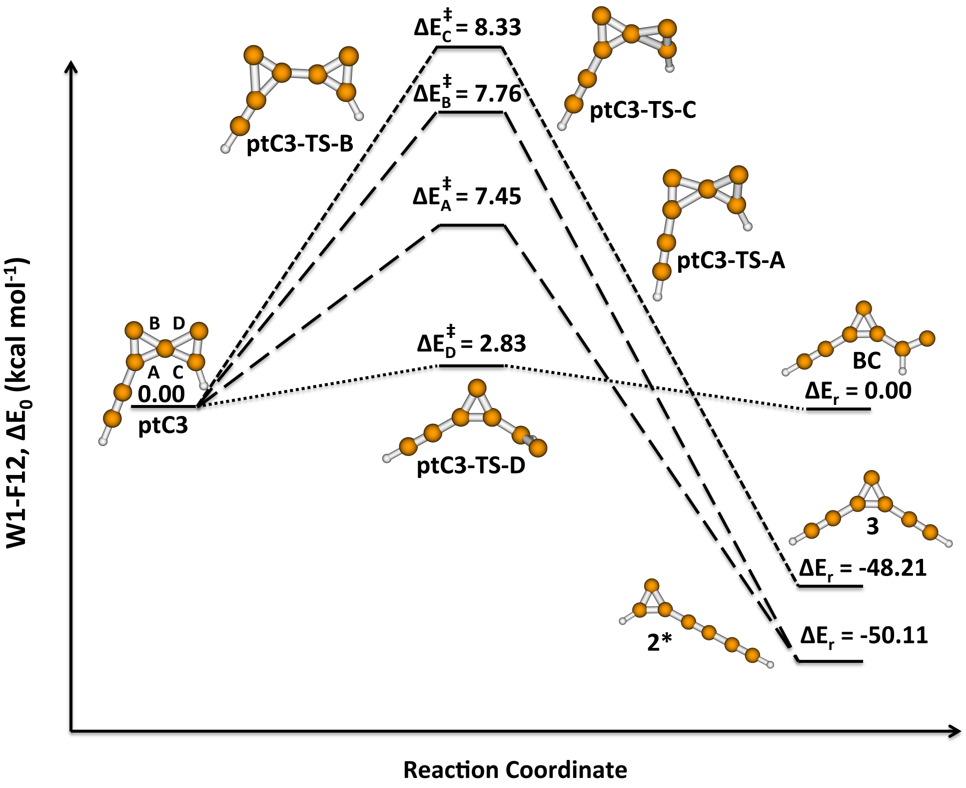

Figure 4: Schematic reaction profile diagram for **ptC3** and its dissociation pathways connected to the ptC atom. The relative energy differences were calculated at the W1-F12 level of theory.

F12 level of theory. At the W3lite-F12 level of theory, these two isomers are energetically apart by 2.08 kcal mol^{-1}. We note that both kinetic and thermodynamic considerations govern the formation of a molecule in electrical discharges.[78] Although **2** alone was detected by FTMW spectroscopy[55] and **3** is yet to observed,[110] we hope that with a different choice of a precursor molecule and considering other kinetic factors such as collision time in the nozzle, the latter isomer could also be detected. In addition, it is worth mentioning here that **2** has an inertial axis dipole moment component in two directions (see Table 2), whereas for **3** it is in one direction.[55,110,111] Therefore, both *a*- and *b*-type rotational transitions are possible for **2** and only *b*-type rotational transition is possible for **3**. However, the latter type of transitions depend on the moment of inertia of both A and C. Therefore, a much more accurate theoretical prediction of its bond lengths and bond angles are required, which would done in the future.

Table 1: Dissociation Pathways of C_7H_2 Isomers with a ptC Atom and Their Corresponding Activation Energies ($\Delta E^{\ddagger}$) and Reaction Energies (ΔE_r) of C_7H_2 Computed at the W1-F12 Level of Theory.

isomer	dissociation pathway	$\Delta E^{\ddagger}$ kcal mol^{-1}	ΔE_r kcal mol^{-1}	NICS (1Å) ppm	ΔE_0^c kcal mol^{-1}
ptC1	A	11.02	-5.65 (**6**)[a]	-11.45	26.12
	B	32.96	(**6**)[a]		
ptC2	A	9.25	-46.83 (**2**)[a]	-7.72	52.53
	B	10.56	(**2**)[a]		
	C	6.11	3.27 (**BC**)[b]		
	D	10.21	-44.93 (**3**)[a]		
ptC3	A	7.45	-50.11 (**2**)[a]	-9.02	55.74
	B	7.76	(**2**)[a]		
	C	8.33	-48.21 (**3**)[a]		
	D	2.83	0.00 (**BC**)[b]		

[a] The dissociation pathway leading to the corresponding product is given in parenthesis. The reaction path is confirmed by IRC calculations. [b] This particular reaction path is not confirmed by IRC calculations. However, reoptimization from the last point of IRC calculation leads to this product. [c] W3lite-F12 relative energies with respect to isomer **1** at 0 K.

Table 2: Rotational and Centrifugal Distortion Constants (in MHz), and Inertial Axis Dipole Moment Components (in Debye; $\perp^r$ Representation) of ptC Isomers of C_7H_2 Calculated at the CCSD(T)/cc-pVTZ Level of Theory.[a]

constant	**ptC1**	**ptC2**	**ptC3**
A_e	5247.30	7319.09	8109.33
B_e	4710.27	2071.46	1957.82
C_e	2482.15	1614.52	1577.07
Δ_J	0.3423×10^{-3}	0.7399×10^{-3}	0.9046×10^{-3}
Δ_K	0.4666×10^{-3}	0.4814×10^{-1}	0.6579×10^{-1}
Δ_{JK}	0.4593×10^{-3}	-0.6880×10^{-2}	-0.1134×10^{-1}
δ_J	0.1292×10^{-3}	-0.2815×10^{-3}	-0.3153×10^{-3}
δ_K	0.4928×10^{-3}	-0.2258×10^{-4}	-0.2047×10^{-4}
μ_a	-5.84	0.12	-3.65
μ_b	-	-0.92	-4.20
$\|\mu\|$	5.84	0.93	5.56

[a] Centrifugal distortion constants are from A-reduced Hamiltonian for **ptC1** whereas they are estimated using the S-reduced Hamiltonian for **ptC2** and **ptC3** considering the fact that they are approaching close to the prolate limit.

General remarks of ptC isomers in C_7H_2

The NICS (1Å) values calculated at the B3LYP/6-311+G(d,p) level of theory for **ptC1**, **ptC2**, and **ptC3** are -11.45, -7.72, and -9.02 ppm, respectively. The negative values indicate their aromatic nature although they are not synthetically viable to date. We note that the reported NICS (1Å) value for benzene molecule calculated at the same level of theory is -10.20 ppm.[112] Though the aromatic index of **ptC1** is slightly higher than benzene, it remains elusive to date. Nonetheless, we leave this discussion with a caveat that NICS is a response property whereas energetic stability is a ground-state property.[113] The rotational constants (A_e, B_e, and C_e) obtained from the equilibrium geometry at the CCSD(T)/cc-pVTZ level of theory (see Table 2) reveal that all the ptC isomers studied here are asymmetric tops. The centrifugal distortion constants (Δ_J, Δ_K, Δ_{JK}, etc.,) are also computed for these hypothetical molecules with a hope that they will assist the efforts of microwave spectroscopists. We note that the experimentally measured values are vibrationally averaged rotational constants (A_0, B_0, and C_0), whereas the values reported by us lacks the effects of corrections from the zero-point vibrational motion. Also, our calculations on these molecules lack the effect of core-valence correlation in their optimal geometries at the CCSD(T)/cc-pVTZ level of theory.[114] Although these two effects may significantly improve the rotational constants, which would be helpful for the accurate simulation to search for the rotational transitions of any of the ptC isomers, such an endeavor is beyond the scope of our present work and would be undertaken in a forthcoming study. While the inertial axis dipole moment components are in two directions (μ_a and μ_b) for isomers **ptC2** and **ptC3**, it is in only one direction for **ptC1**. Therefore, for the latter only one type of rotational transition is possible whereas for the former both *a*- and *b*-type rotational transitions are possible. Based on the absolute dipole moment values, one can say that **ptC1** and **ptC3** are more polar than **ptC2**. The total dipole moments of **ptC1**, **ptC2**, and **ptC3** are 5.84, 0.92, and 5.69 Debye, respectively, at the CCSD(T)/cc-pVTZ level of theory. The reason why **ptC2** is less polar could be attributed to the fact that the H-atom and ethynyl ($-C{\equiv}C{-}H$) group are in opposite directions (unlike **ptC3**) and this geometrical arrangement affects the electron density distribution. Consequently, it cancels out the net dipole moment for **ptC2** to a large extent.

The optimal geometry parameters of **ptC1**, **ptC2**, and **ptC3** calculated at different levels are collected in Tables 3, 4, and 5, respectively. The atom numbering scheme we have adopted for the ptC isomers of C_7H_2 is given in Fig. 5. At all levels of theory for all ptC isomers, the longer bond lengths of C_1C_2, C_1C_3, C_1C_4, and C_1C_5, and the double bond distance of C_2C_4 and C_3C_5 reflect their diradical valence structures given in Fig. 1. The C_6C_7 bond length for **ptC1** at all levels is once again close to a double bond distance whereas the C_7C_8 bond length for **ptC2** and **ptC3** is that of a triple bond distance at all levels. While nothing surprising one could notice for the C-H bond distance in **ptC1**, the C-H bonds connected to the ethynyl group in **ptC2** and **ptC3** are found to be somewhat shorter as they are connected to a *sp* hybridized carbon in both the cases. Overall, with respect to cc-pVDZ basis set, the bond lengths are found to be systematically overestimated at the MP2 and CCSD(T) levels. These results are consistent with earlier observations and is largely due to the lack of higher angular momentum polarization functions.[115–120] The near 180 degree bond angles of $C_3C_7C_8$ and $C_7C_8H_9$ at all levels in **ptC2** and **ptC3** confirm that the ethynyl chain is linear.

Since W1-F12 theory approximates the CCSD(T) basis-set-limit energy, it is of interest to estimate whether the contributions from post-CCSD(T) excitations are likely to be significant for the molecules considered in this work. The percentage of the total atomization energy (TAE) accounted for by the quasiperturbative triple excitations, %TAE[(T)],[100,104,105,121,122] has been shown to be a reliable energy-based diagnostic for the importance of post-CCSD(T) contributions to the TAEs. It has been found that %TAE[(T)] values smaller than ~ 5 % indicate that post-CCSD(T) contributions should normally not exceed 0.5 kcal mol^{-1}.[104] The %TAE[(T)] values for the C_7H_2 isomers considered in this work range between 2.8 - 3.7 % (see Table S16 of the Supporting Information). These values suggest that the considered species are dominated by dynamical correlation effects and that post-CCSD(T) contributions to the

Table 3: Optimal Geometry Parameters (Å and Degrees) of Isomer ptC1 of C_7H_2 Calculated at Different Levels.

	cc-pVDZ		cc-pVTZ		6-311+G(d,p)	aug-cc-pVQZ
parameter	MP2	CCSD(T)	MP2	CCSD(T)	B3LYP	MP2
$R(C_2C_4;C_3C_5)$	1.3836	1.3788	1.3652	1.3593	1.3490	1.3607
$R(C_1C_2;C_1C_3)$	1.4869	1.4858	1.4750	1.4727	1.4694	1.4728
$R(C_1C_4;C_1C_5)$	1.5175	1.5383	1.4965	1.5151	1.5077	1.4905
$R(C_2C_6;C_3C_7)$	1.4289	1.4438	1.4162	1.4303	1.4247	1.4142
$R(C_6C_7)$	1.3949	1.3907	1.3826	1.3772	1.3736	1.3802
$R(C_6H_8;C_7H_9)$	1.0941	1.0956	1.0804	1.0809	1.0821	1.0801
$\theta(C_2C_1C_3)$	94.94	95.71	94.62	95.32	95.61	94.64
$\theta(C_2C_1C_4;C_3C_1C_5)$	54.83	54.22	54.69	54.10	53.87	54.67
$\theta(C_1C_2C_6;C_1C_3C_7)$	116.35	115.80	116.58	116.10	115.81	116.56
$\theta(C_2C_6H_8;C_3C_7H_9)$	126.10	125.76	126.19	125.86	125.87	126.23

Table 4: Optimal Geometry Parameters (Å and Degrees) of Isomer ptC2 of C_7H_2 Calculated at Different Levels.

	cc-pVDZ		cc-pVTZ		6-311+G(d,p)	aug-cc-pVQZ
parameter	MP2	CCSD(T)	MP2	CCSD(T)	B3LYP	MP2
$R(C_2C_4)$	1.3521	1.3402	1.3325	1.3231	1.3123	1.3284
$R(C_3C_5)$	1.3685	1.3921	1.3490	1.3609	1.3532	1.3449
$R(C_1C_2)$	1.6112	1.7859	1.5903	1.6928	1.6950	1.5850
$R(C_1C_3)$	1.4211	1.3972	1.4086	1.3917	1.3928	1.4064
$R(C_1C_4)$	1.4210	1.4426	1.4081	1.4249	1.4219	1.4058
$R(C_1C_5)$	1.5742	1.5282	1.5519	1.5271	1.5165	1.5456
$R(C_3C_7)$	1.4084	1.4205	1.3937	1.4053	1.3937	1.3916
$R(C_7C_8)$	1.2341	1.2306	1.2164	1.2120	1.2034	1.2142
$R(C_4H_6)$	1.0892	1.0912	1.0748	1.0762	1.0779	1.0745
$R(C_8H_9)$	1.0768	1.0799	1.0624	1.0642	1.0635	1.0624
$\theta(C_4C_1C_2)$	52.51	42.60	52.34	49.31	48.84	52.32
$\theta(C_1C_4C_2)$	70.99	79.75	70.88	75.95	76.51	70.79
$\theta(C_1C_4H_6)$	132.11	128.57	132.35	129.82	130.13	132.35
$\theta(C_4C_1C_5)$	128.99	139.81	129.49	135.64	134.99	129.83
$\theta(C_1C_3C_7)$	134.99	140.16	135.06	138.30	139.28	135.00
$\theta(C_2C_1C_5)$	178.50	172.59	178.17	175.06	176.18	177.85
$\theta(C_4C_1C_3)$	176.93	163.57	176.56	169.02	169.77	176.21
$\theta(C_3C_7C_8)$	179.66	179.48	179.51	179.82	179.67	179.00
$\theta(C_7C_8H_9)$	179.82	179.73	179.93	179.84	179.87	179.66

Table 5: Optimal Geometry Parameters (Å and Degrees) of Isomer ptC3 of C_7H_2 Calculated at Different Levels.

	cc-pVDZ		cc-pVTZ		6-311+G(d,p)	aug-cc-pVQZ
parameter	MP2	CCSD(T)	MP2	CCSD(T)	B3LYP	MP2
$R(C_2C_4)$	1.3527	1.3471	1.3327	1.3274	1.3153	1.3284
$R(C_3C_5)$	1.3689	1.3770	1.3486	1.3531	1.3473	1.3442
$R(C_1C_2)$	1.4341	1.4403	1.4237	1.4286	1.4260	1.4227
$R(C_1C_3)$	1.4390	1.4183	1.4295	1.4102	1.4093	1.4282
$R(C_1C_4)$	1.5913	1.6738	1.5644	1.6286	1.6447	1.5561
$R(C_1C_5)$	1.5571	1.5714	1.5314	1.5491	1.5311	1.5245
$R(C_3C_7)$	1.4067	1.4211	1.3917	1.4053	1.3931	1.3897
$R(C_7C_8)$	1.2353	1.2312	1.2177	1.2127	1.2044	1.2157
$R(C_2H_6)$	1.0904	1.0922	1.0760	1.0769	1.0784	1.0759
$R(C_8H_9)$	1.0771	1.0800	1.0626	1.0643	1.0636	1.0627
$\theta(C_5C_3C_1)$	67.30	68.39	66.83	68.16	67.44	66.64
$\theta(C_5C_3C_7)$	158.18	155.10	158.67	155.72	155.09	158.94
$\theta(C_3C_1C_2)$	127.21	134.59	125.78	132.44	133.12	125.05
$\theta(C_1C_2H_6)$	133.25	131.70	133.46	132.07	132.24	133.42
$\theta(C_4C_1C_2)$	52.81	50.58	52.72	50.96	50.11	52.74
$\theta(C_5C_1C_4)$	125.78	120.27	127.45	122.43	122.42	128.17
$\theta(C_2C_1C_5)$	178.59	170.85	179.84	173.38	172.53	179.09
$\theta(C_4C_1C_3)$	179.98	174.83	178.49	176.60	176.77	177.79
$\theta(C_3C_7C_8)$	178.52	179.36	178.57	179.37	179.44	177.93
$\theta(C_7C_8H_9)$	178.68	179.14	178.88	179.28	179.20	178.61

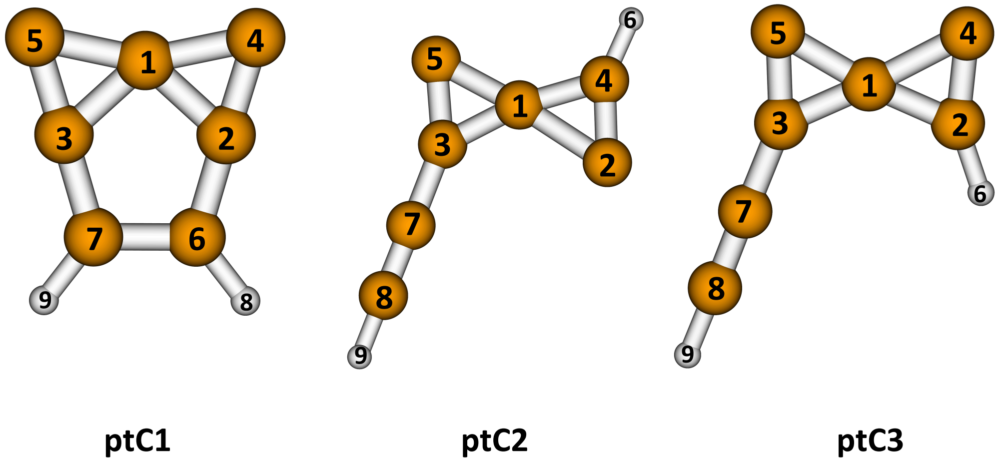

Figure 5: Atom numbering scheme we have adopted for ptC isomers.

TAEs should not exceed the 0.5 kcal mol^{-1} mark. Thus, the predicted reaction energies and barrier heights obtained in the present work are expected to be little affected by post-CCSD(T) contributions.

Conclusions

Three isomers of C_7H_2 with a ptC atom and their dissociation pathways of C-C single bonds connected to the ptC atom have been theoretically studied. Energetically, isomer **ptC1** was found to lie $\sim$ 5.78 kcal mol^{-1} above the experimentally well-known and astronomically relevant cumulene carbene isomer of C_7H_2 (**9**) at the W3lite-F12 level of theory. Therefore, the dissociation of this molecule was studied in detail including IRC calculations to be aware of its kinetic stability. Key spectroscopic parameters relevant to microwave spectroscopists are also documented. We conclude that both the dissociation pathways for **ptC1** lead to

6. However, the latter also remains elusive to date though thermodynamically more stable than **9**.

Though **ptC2** and **ptC3** can be considered as high-energy isomers from the thermodynamic perspective, their dissociation (except the lowest activation energy path) leads to low-energy isomers **2** and **3**, depending upon which C-C bond connected to the ptC atom is being broken. Among these two products, **2** is already identified by FTMW spectroscopy and **3** lies just 2.08 kcal mol^{-1} above **2** at the W3lite-F12 level of theory. In all the cases (except pathway **C** in **ptC2**), the reaction appears to be exothermic. In conclusion, the dissociation pathways of ptC isomers lead us to three low-energy isomers (**2**, **3**, and **6**) of C_7H_2. However, the only low-lying ring-chain carbene identified to date is **2** and the other two isomers (**3** and **6**) remain elusive though both of them are energetically more stable than **9**.

In this work, by studying the dissociation pathways of ptC isomers, we have shown that the high-energy ptC isomers (**ptC2** and **ptC3**) serve as reactive intermediate to an experimentally known carbene molecule (**2**). Nevertheless, the most obvious question in front of us is, is it possible to identify the ptC isomers itself within C_7H_2 elemental composition? Based on the activation energies and the reaction energies calculated in this work, we are hopeful that the identification of **ptC1** isomer is viable. If not, at least their dissociative products, isomers **3** and **6**, are the potential candidates for detection. We believe that our theoretical studies on these compounds would motivate the experimentalists in the synthesis and identification of these molecules in the near future.

Acknowledgement

Initial part of this work is supported by a research grant (Project No: YSS/2015/000099) from the Science and Engineering Research Board, Department of Science and Technology (DST), New Delhi, Government of India (to VST). One of the authors (AK) thank Australian

Research Council (ARC) Future Fellowship (Project No. FT170100373) for support received in part. We gratefully acknowledge the generous allocation of computing time from the National Computational Infrastructure (NCI) National Facility, and system administration support provided by the Faculty of Science at the University of Western Australia (UWA) to the Linux cluster of the Karton group. Additional computational facility provided (for KT) at the VIT University to carry out part of this work is also gratefully acknowledged.

Supporting Information Available

The Cartesian coordinates of the optimized geometries, total electronic energies, ZPVEs, harmonic vibrational frequencies, and infra-red intensities of all ptC isomers calculated at different levels are given in the supporting information. This material is available free of charge via the Internet at `http://pubs.acs.org/`.

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Graphical TOC Entry