ORIGINAL RESEARCH
published: 22 June 2022
doi: 10.3389/fphy.2022.907466

Theoretical Investigation on $C_{11}H_8$ Bicyclic Carbene and Allene Isomers

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Recent studies postulate that the presence of polycyclic aromatic hydrocarbons (PAHs) in the interstellar medium (ISM) could have been formed through resonance-stabilized arylcarbene intermediates. However, identifying most of these reactive intermediates is very challenging experimentally due to their metastability and other experimental constrains. Thus, computational studies that cover the thermodynamic versus kinetic stability of various possible structures would be beneficial for successfully identifying new molecules either in the laboratory and/or in the ISM. In this paper, more than four hundred $C_{11}H_8$ carbene isomers have been theoretically investigated employing density functional theory (DFT). Hybrid density functionals B3LYP and ωB97XD with 6-311 + G (d,p) basis set have been used for singlet electronic states, whereas, triplet spin states were optimized at the same level using an unrestricted Hartree-Fock wavefunction. Although the skeletal structures of $C_{11}H_8$ can be categorized into monocyclic, bicyclic, tricyclic, tetracyclic and acyclic isomers, bicyclic carbenes have shown better stability due to the presence of resonance stabilized azulenyl/naphthyl rings. In this category, some isomers (1-, 2-, 5- and 6-azulenylcarbenes and 1- and 2-naphthylcarbenes) have also been detected recently in the laboratory and simple aromatic carbenes such as cyclopropenylidene and its homologues are detected in the ISM. Thus, we have systematically investigated the energetic and spectroscopic properties of resonance stabilized 5-, 6-, 7- and 8-membered ring containing bicyclic isomers of $C_{11}H_8$ and the fingerprint regions of the infrared spectrum for each class of these bicyclic compounds.

Keywords: $C_{11}H_8$, carbene, PAHs, PyAR, DFT

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Specialty section:
This article was submitted to Atomic and Molecular Physics, a section of the journal Frontiers in Physics

Received: *29 March 2022*
Accepted: *26 May 2022*
Published: *22 June 2022*

Citation:
Roy T, Satpati S, Thimmakondu VS and Ghosal S (2022) Theoretical Investigation on $C_{11}H_8$ Bicyclic Carbene and Allene Isomers. Front. Phys. 10:907466. doi: 10.3389/fphy.2022.907466

INTRODUCTION

Carbonaceous organic molecules especially polycyclic aromatic hydrocarbons (PAHs) are ubiquitously the key components in the astrochemical evolution of the interstellar medium (ISM) [1–4]. Understanding the chemical evolution of the Universe through the formation of the PAHs and their abundance in the astrochemical environment are one of the important aspects of astrochemistry [5, 6]. The detection and isolation of the building blocks of PAHs in the laboratory by creating "space-like" environment is experimentally a daunting task. However, the knowledge of the thermodynamic and spectroscopic properties of possible reactive intermediates and building blocks through accurate quantum mechanical calculations will be very helpful to understand the formation of PAHs and their identification in ISM [7–13].

Laboratory experiments with small organic molecules with neutral/radical reactive intermediates [14–16] have been studied by several research groups using advanced techniques including selected ion flow tubes (SIFT) and Ion Cyclotron Resonance (ICR) mass spectrometry, ion trapping using

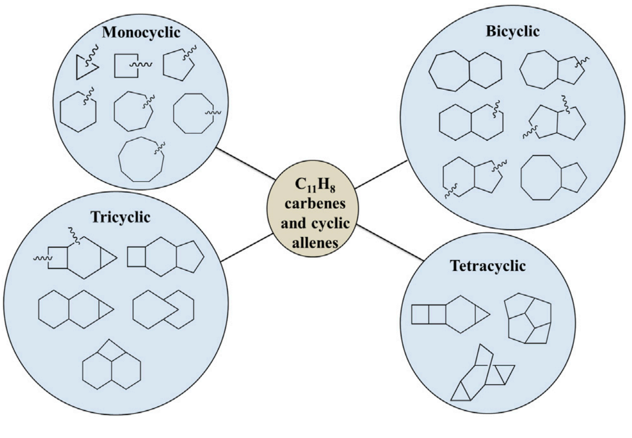


FIGURE 1 | Various types of skeletal representation of $C_{11}H_8$ cyclic carbene/allene isomers.

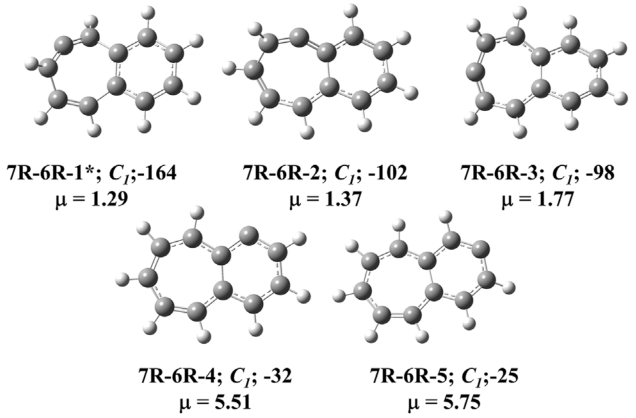


FIGURE 2 | All low-lying $C_{11}H_8$ carbenes/cyclic allenes isomers with seven-membered and six-membered fused ring system i.e., (7R-6R) group. ZPVE-corrected relative energies (in kJ mol^{-1}), absolute dipole moment values (in Debye) are calculated at the B3LYP/6-311 + G (d,p) level of theory. Experimentally detected isomers are marked with an asterisk symbol.

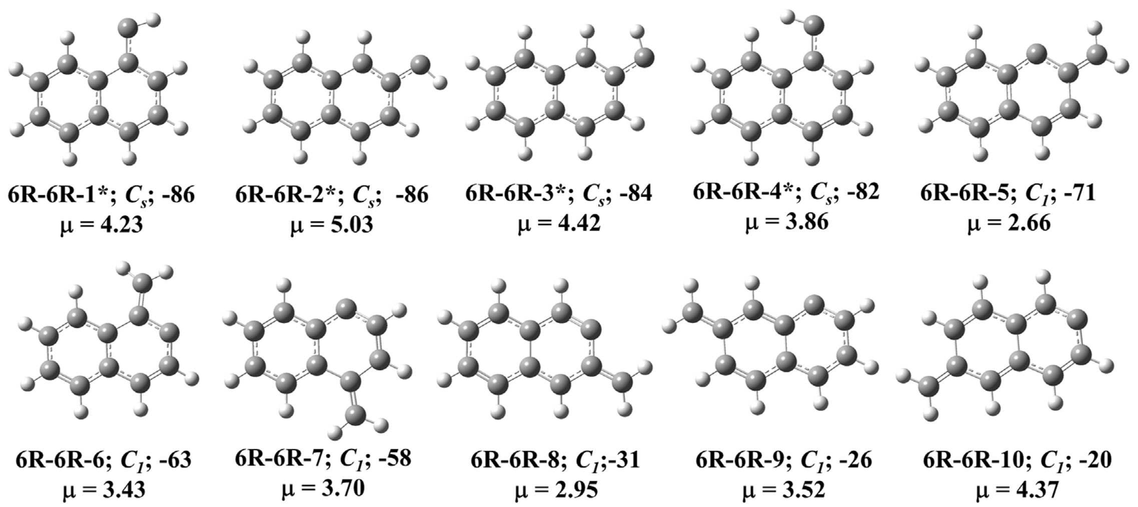
external electric and magnetic fields etc [17–20]. These experiments lead to the understanding of possible growth mechanism of the PAHs and soot formation in ISM. The cyclic and linear molecules of C_5H_n configuration have been found to be the possible routes of benzene formation [21–23]. For example, isoprene (C_5H_8) and the methyl-substituted 1,3-butadiene can form phenyl radical with very low activation energy [24]. Earlier, in 2001, Zhang et al. had proposed the formation of bicyclic PAHs from phenyl radicals reacting with cis-3-penten-1-yne [25]. Later, formation of naphthalene had been identified as a result of bimolecular recombination of para-tolyl and phenyl radicals using crossed molecular beam experiments and higher order PAHs like anthracene and phenanthrene had been prepared in low temperature environments [26–28].

Very recently, a large number of cyano-derivatives of cyclic organic molecules have been discovered in the dark molecular cloud of TMC-1 using precise rotational spectroscopic measurement methods [29–32]. Apart from this, the recent discovery of two of the carbene molecules of C_5H_2, ethynylcyclopropenylidene and pentatetraenylidene [33–36] have opened up the possibility of detecting more organic molecules in the dark, low-pressure and low-temperature regions in space. Recent theoretical investigations on C_5H_2 isomers suggest both acyclic and cyclic carbenes and diradicals as potential target molecules for laboratory spectroscopy [37, 38]. It is expected that reactive intermediates, e.g., free radicals and carbene molecules might have played an important role in the formation of such molecules [39]. Carbene molecules such as cyclopropenylidene (c-C_3H_2) [40], propadienylidene (C_3H_2) [35], butatrienylidene (C_4H_2) [41], hexapentaenylidene (C_6H_2) [42] etc. had been detected as early as late 20th century in the ISM. Other studies have suggested that the isomeric conversion of several radical PAHs can undergo via linear and cyclic carbene formation at the high temperature environment [43, 44].

PAHs are considered to be responsible for the unidentified infrared emission bands (UIRs) associated with a wide range of interstellar species such as free radicals, ions, carbenes, and neutral molecules from near-UV to the near IR region [45–47]. These UIRs generally show characteristic spectral signatures in the 3–14 μm wavelength range and the variation of the observed IR spectra can be correlated with the structural type of PAHs and population of the hydrocarbons from difference sources [48]. Rastogi et al. also successfully modeled the PAHs into different groups based on their ring sizes, number of carbon atoms present and found significant spectral changes associated with the structural changes of the PAHs [49]. Nevertheless, it is not very clear if these bands originate from any particular species, or a group of structurally similar molecules that are responsible for such emission bands. Therefore, we intended to identify molecules, which are structurally similar and studied their thermodynamic and spectroscopic properties for future identification either in laboratory or in the ISM.

In this study, carbene and allene isomers of molecular formula $C_{11}H_8$ have been theoretically investigated using Density Functional Theory (DFT) calculations. Although several low-lying neutral isomers of $C_{11}H_8$ have been investigated recently [50], such an account for reactive carbene intermediates are still missing in the literature. Closely related to $C_{11}H_8$ isomers, Maier and co-workers have detected $C_{11}H_9^+$ and $C_{11}H_9^\bullet$ isomers in neon matrices [51]. 2-naphthylmethylium and benzotropylium cations were detected and their electronic absorption spectra were recorded. After photobleaching of matrices containing $C_{11}H_9^+$, the corresponding neutral molecules were also characterized. Using ultraviolet population transfer spectroscopy, Zwier and co-workers have studied the excited state dynamics of $C_{10}H_8$ and probed the E/Z isomerization of 1-phenyl-1-buten-3-yne [52]. Moreover, the electronic spectroscopy of the indene-motif PAHs has been studied by Maier and co-workers [53].

As shown in **Figure 1**, various types of skeletal structures (monocyclo, bicyclo, tricyclo, tetracyclo, and linear) are possible, but, considering the importance of naphthyl, azulenyl, and indenyl group for the formation of PAHs in the ISM, we have



6R-6R-1*; C_s; -86 $\mu = 4.23$

6R-6R-2*; C_s; -86 $\mu = 5.03$

6R-6R-3*; C_s; -84 $\mu = 4.42$

6R-6R-4*; C_s; -82 $\mu = 3.86$

6R-6R-5; C_1; -71 $\mu = 2.66$

6R-6R-6; C_1; -63 $\mu = 3.43$

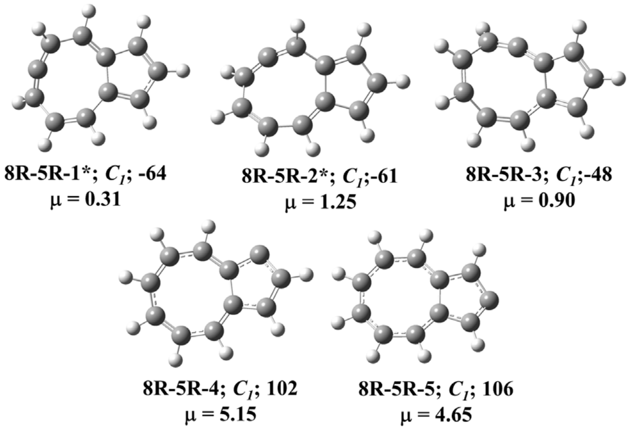
6R-6R-7; C_1; -58 $\mu = 3.70$

6R-6R-8; C_1;-31 $\mu = 2.95$

6R-6R-9; C_1; -26 $\mu = 3.52$

6R-6R-10; C_1; -20 $\mu = 4.37$

FIGURE 3 | First ten low-lying $C_{11}H_8$ carbenes/cyclic allenes isomers of (6R-6R) group. ZPVE-corrected relative energies (in kJ mol^{-1}), absolute dipole moment values (in Debye) are calculated at the B3LYP/6-311 + G (d,p) level of theory. Experimentally detected isomers are marked with an asterisk symbol.



8R-5R-1*; C_1; -64 $\mu = 0.31$

8R-5R-2*; C_1;-61 $\mu = 1.25$

8R-5R-3; C_1;-48 $\mu = 0.90$

8R-5R-4; C_1; 102 $\mu = 5.15$

8R-5R-5; C_1; 106 $\mu = 4.65$

FIGURE 4 | All low-lying $C_{11}H_8$ carbenes/cyclic allenes isomers of (8R-5R) group. ZPVE-corrected relative energies (in kJ mol^{-1}), absolute dipole moment values (in Debye) are calculated at the B3LYP/6-311 + G (d,p) level of theory. Experimentally detected isomers are marked with an asterisk symbol.

focused on nearly four hundred bicyclic carbene and allene isomers of $C_{11}H_8$. Most of these molecular structures have been identified through chemical intuition and/or by using a Python code for Aggregation and Reaction (PyAR), which is based on a tabu-search algorithm, developed and maintained by Anoop and co-workers [54].

THEORETICAL METHODOLOGY

A bottom-up approach is adopted in the current implementation of the PyAR software and thus the constituent atoms will be added sequentially in building isomers of the molecular formula C_nH_m, where $n = 1,2,3,\ldots 11$ and $m = 1,2,3,\ldots 8$ until the desired molecular formula ($C_{11}H_8$) is achieved. A tabu-based search algorithm is used to generate several trial geometries of $C_{11}H_8$ hydrocarbons with various combinations of C and H atoms. After screening the initial structures, geometry optimization and frequency calculations for all the carbene and allene isomers have been carried out using DFT at the B3LYP/6-311 + G (d,p) and ωB97XD/6-311 + G (d,p) levels of theory [55–62]. For singlet electronic states, restricted Hartree-Fock (HF) wavefunction have been used as reference in the DFT calculations, whereas, unrestricted HF (UHF) wavefunction at the UB3LYP/6-311 + G (d,p) and UωB97XD/6-311 + G (d,p) levels has been used for open-shell triplet electronic state calculations. Although one can use restricted open-shell HF (ROHF) as a reference to avoid spin-contamination, we have observed that in certain cases ROHF based calculations don't converge. Therefore, we have used UHF wavefunction throughout. We note that the spin-contamination is not too high for the triplet state, and most-often the value we got for $<S^2>$ is closer to the ideal value (2.00).

The infrared (IR) spectral frequencies and intensities have been captured from the frequency calculations on the optimized geometry. All calculations have been performed using the Gaussian 09 program [63].

RESULTS AND DISCUSSIONS

Depending upon the skeletal structures, we have sub-divided the resonance stabilized bicylic isomers into six different groups (**Figure 1**). For example, 8-membered and 5-membered fused ring containing carbenes are represented as (8R-5R)-group. Similarly, other isomers are categorized as (7R-6R), (7R-5R), (6R-6R), (6R-5R), and (5R-5R) groups depending on the size of the rings. In the present study, we have identified 5 isomers in the 7R-6R, 12 in 6R-6R, 5 in 8R-5R, 26 in 7R-5R, 149 in 6R-5R and 220 isomers in 5R-5R groups, respectively. We have not

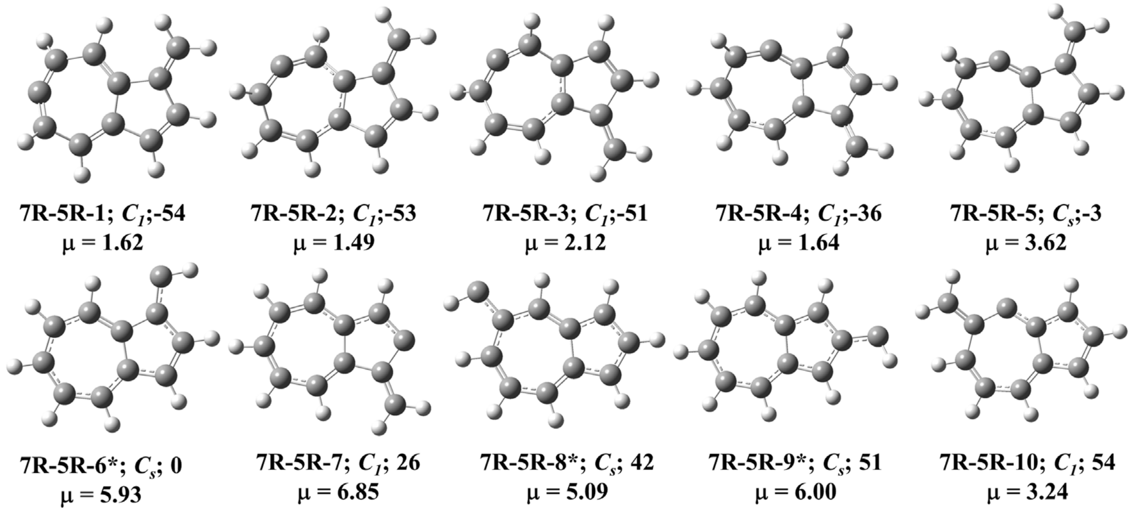


FIGURE 5 | First ten low-lying $C_{11}H_8$ carbenes/cyclic allenes isomers of (7R-5R) group. ZPVE-corrected relative energies (in kJ mol^{-1}), absolute dipole moment values (in Debye) are calculated at the B3LYP/6-311 + G (d,p) level of theory. Experimentally detected isomers are marked with an asterisk symbol.

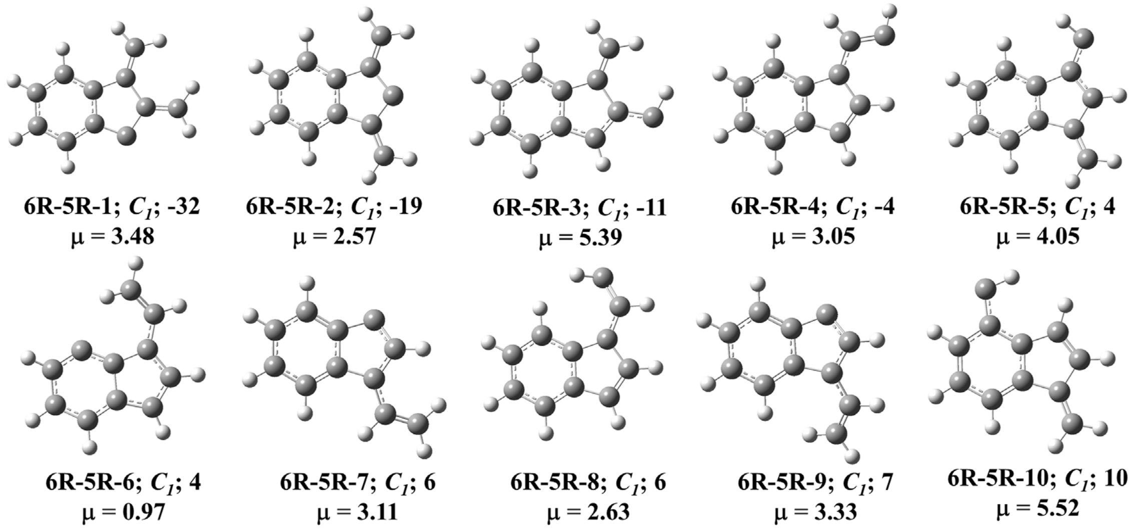


FIGURE 6 | First ten low-lying $C_{11}H_8$ carbenes/cyclic allenes isomers of (6R-5R) group. ZPVE-corrected relative energies (in kJ mol^{-1}), absolute dipole moment values (in Debye) are calculated at the B3LYP/6-311 + G (d,p) level of theory. Experimentally detected isomers are marked with an asterisk symbol.

considered the carbenes with less than five-membered ring because of higher relative energies due to lack of resonance stabilization or conjugation. The zero-point vibrational energy (ZPVE)-corrected relative energies of all isomers are scaled with respect to 1-azulenylcarbene, which is experimentally known [64]. On the basis of these relative energies, we found that the allene-like isomers of the (7R-6R) group are most stable, whereas, the isomers of the (5R-5R) group are high-lying isomers.

The current study reveals that several carbene and allene isomers remain elusive in the literature, some of which are more stable than the experimentally identified carbenes. The ZPVE-corrected relative energy, point group symmetry, and permanent dipole moments of each group have been listed along with their structures in **Figures 2–7** for few low-lying carbene or allene isomers. Molecular structures of rest of the isomers are listed in the Electronic Supporting Information (ESI). Experimentally detected isomers are represented with an asterisk symbol. We note that, some of the carbene isomers corresponding to the allene-like structures turned out to be local maxima on the $C_{11}H_8$ PES. These low-lying transition

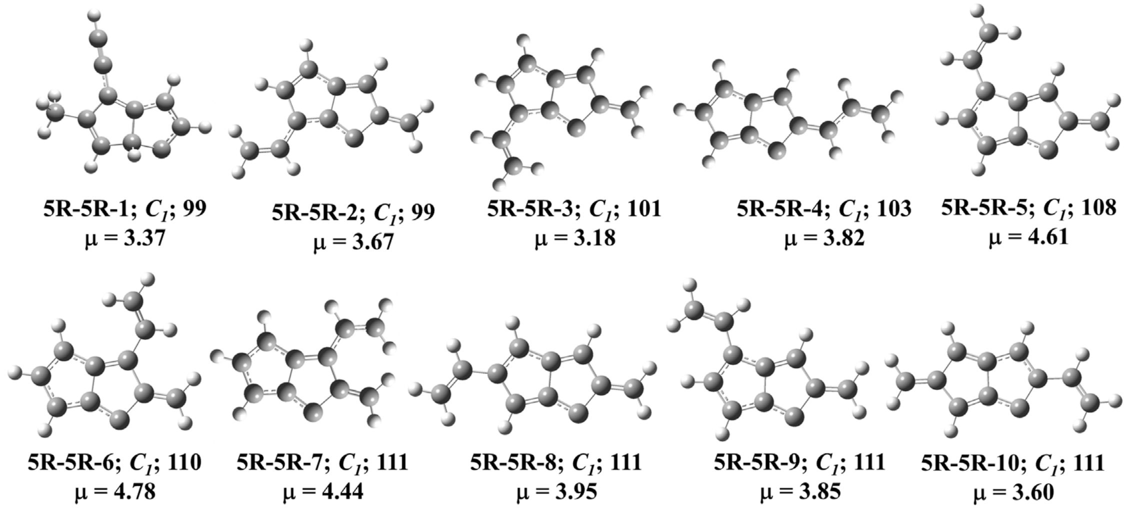


FIGURE 7 | First ten low-lying $C_{11}H_8$ carbenes/cyclic allenes isomers of (5R-5R) group. ZPVE-corrected relative energies (in kJ mol^{-1}), absolute dipole moment values (in Debye) are calculated at the B3LYP/6-311 + G (d,p) level of theory. Experimentally detected isomers are marked with an asterisk symbol.

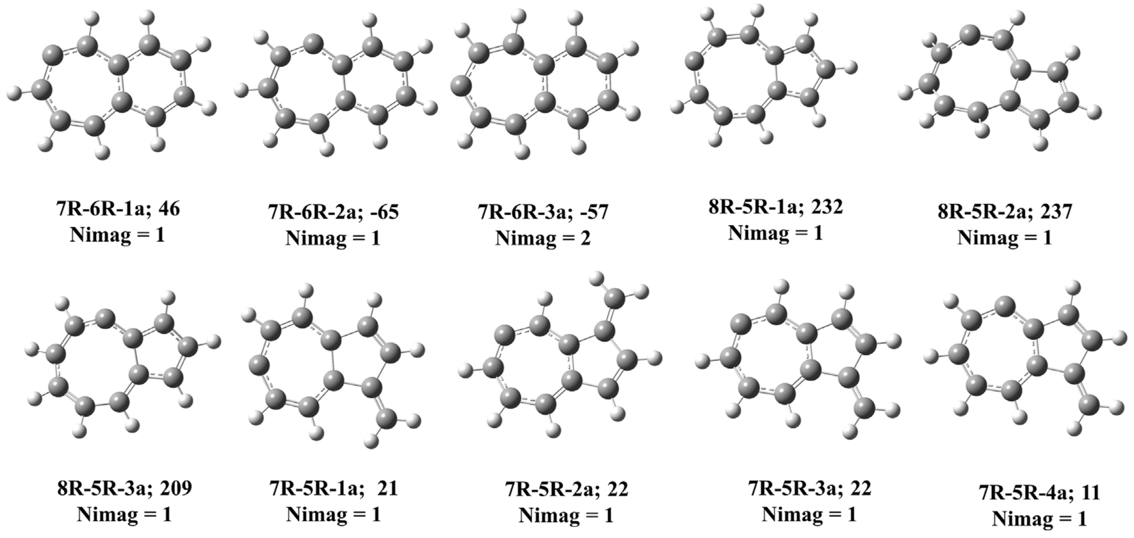


FIGURE 8 | Carbene counter parts of various cyclic allene isomers at local maxima in $C_{11}H_8$ potential energy surface. ZPVE-corrected relative energies (in kJ mol^{-1}), absolute dipole moment values (in Debye) are calculated at the B3LYP/6-311 + G (d,p) level of theory.

states or intermediate saddle point structures are shown separately in **Figure 8**, along with their relative energies. The detailed ZPVE-corrected relative energies, Gibbs free energies and singlet−triplet energy gaps of all the low-lying isomers are shown in **Tables 1–4** at the B3LYP/6-311+G (d,p) and ωB97XD/6-311+G (d,p) levels of theory. Energy details for all other isomers, along with useful spectroscopic parameters, such as, rotational constants, inertial axis dipole moments, and centrifugal distortion constants are listed in the ESI.

The detailed energetics of each skeletal group have been discussed in the following:

(7R-6R) Group

The $C_{11}H_8$ carbene and allene like structures having one 7-membered and one 6-membered fused ring systems are listed in this group. As shown in **Figure 2**, total five minimum energy isomers are possible in this group and two transition states (7R-6R-1a and 7R-6R-2a) and one second order saddle point (7R-6R-3a) (**Figure 8**). Relative energies are shown in **Table 1**.

Bicyclo [5.4.0]undeca-2,3,5,7,9,11-hexaene (7R-6R-1) has been identified by West et al. in 1986 [65] and spectroscopically characterized by McMahon's group in the year of 2000 through matrix isolation method [66]. According

TABLE 1 | ZPVE-Corrected Relative Energies (ΔE_0; in kJ mol^{-1}), Gibbs Free Energies ($\Delta G_{298.15}$; in kJ mol^{-1}), and Singlet-Triplet Energy Gaps (ΔE_{ST}; in kJ mol^{-1}) of low-lying $C_{11}H_8$ carbene/cyclic allene isomers calculated at Different Levels.

Group	Isomer, point group	IUPAC Name	B3LYP/6-311+G (d,p)			ωB97XD/6-311+G (d,p)		
			ΔE_0	$\Delta G_{298.15}$	ΔE_{ST}	ΔE_0	$\Delta G_{298.15}$	ΔE_{ST}
7-6 Group	7R-6R-1, C_1	Bicyclo [5.4.0]undeca-2,3,5,7,9,11-hexaene	-164	-159	79	-180	-174	86
	7R-6R-2, C_1	Bicyclo [5.4.0]undeca-1,2,4,6,8,10-hexaene	-102	-99	13	-105	-101	4
	7R-6R-3, C_1	Bicyclo [5.4.0]undeca-1,3,4,6,8,10-hexaene	-98	-94	16	–103	-98	7
	7R-6R-4, C_s	Bicyclo [5.4.0]undeca-1,3,5,7,9-pentaene-11-ylidene	–32	–34	–39	–29	–28	–50
	7R-6R-5, C_s	Bicyclo [5.4.0]undeca-2,4,6,8,11-pentaene-10-ylidene	–25	–24	–40	–12	–14	–65
6-6 Group	6R-6R-1, C_s	(E)-2-naphthylcarbene	–86	–85	–26	–99	–99	–32
	6R-6R-2, C_s	(E)-1-naphthylcarbene	–86	–85	–22	–98	–97	–28
	6R-6R-3, C_1	(Z)-2-naphthylcarbene	–84	–84	–25	–96	–96	–30
	6R-6R-4, C_s	(Z)-1-naphthylcarbene	–82	–81	–27	–95	–93	–33
	6R-6R-5, C_1	2-methylene-naphthalen-1-ylidene	–71	–72	–39	–80	–80	–43
	6R-6R-6, C_s	1-methylene-naphthalen-2-ylidene	–63	24	–45	–72	–70	–53
	6R-6R-7, C_s	4-methylene-naphthalen-1-ylidene	–58	–58	–47	–64	–64	–58
	6R-6R-8, C_1	3-methylene-naphthalen-2-ylidene	–31	55	–77	–23	–25	–97
	6R-6R-9, C_1	7-methylene-naphthalen-1-ylidene	–26	–27	–80	–17	–18	–102
	6R-6R-10, C_s	6-methylene-naphthalen-2-ylidene	–20	–21	–86	–1	–2	–120
	6R-6R-11, C_s	5-methylene-naphthalen-1-ylidene	–18	68	–85	–8	–9	–111
	6R-6R-12, C_1	8-methylene-naphthalen-2-ylidene	–14	–15	–89	4	4	–124
8-5 Group	8R-5R-1, C_s	Bicyclo [6.3.0]undeca-1,3,4,6,8,10-hexaene	–64	–63	87	–74	–73	102
	8R-5R-2, C_s	Bicyclo [6.3.0]undeca-2,3,5,7,9,11-hexaene	–61	–60	86	–70	–68	98
	8R-5R-3, C_1	Bicyclo [6.3.0]undeca-1,2,4,6,8,10-hexaene	–48	–48	74	–57	–56	88
	8R-5R-4, C_s	(4Z,6Z,8Z)-1H-cyclopenta [8]annulen-1-ylidene	102	–18	56	–21	–31	68
	8R-5R-5, C_1	(4Z,6Z,8Z)-2H-cyclopenta [8]annulen-2-ylidene	106	–11	44	–9	–13	51

TABLE 2 | Same as **Table 1**, low-lying $C_{11}H_8$ carbene isomer of (7R-5R) group calculated at different levels.

Group	Isomer, Point group	IUPAC Name	B3LYP/6-311+G (d,p)			ωB97XD/6-311+G (d,p)		
			ΔE_0	$\Delta G_{298.15}$	ΔE_{ST}	ΔE_0	$\Delta G_{298.15}$	ΔE_{ST}
7-5 Group	7R-5R-1, C_1	10-methylenebicyclo [5.3.0]deca-1,3,4,6,8-pentaene	–54	–56	46	–64	–65	53
	7R-5R-2, C_1	10-methylenebicyclo [5.3.0]deca-2,3,5,7 (1),8-pentaene	–53	–55	46	–64	–65	51
	7R-5R-3, C_1	8-methylenebicyclo [5.3.0]deca-2,3,5,7 (1),9-pentaene	–51	–53	44	–63	–63	51
	7R-5R-4, C_1	8-methylenebicyclo [5.3.0]deca-1,2,4,6,9-pentaene	–36	–38	30	–41	–42	34
	7R-5R-5, C_1	10-methylenebicyclo [5.3.0]deca-1,2,4,6,8-pentaene	–3	–40	–7	–6	–7	–3
	7R-5R-6, C_s	1-azulenylcarbene	0	0	2	0	0	2
	7R-5R-7, C_s	1-methylene-1,2-dihydroazulen-2-ylidene	26	22	–3	27	24	–9
	7R-5R-8, C_1	5-azulenylcarbene	42	38	–21	45	42	–32
	7R-5R-9, C_1	2-azulenylcarbene	51	42	–48	52	48	–33
	7R-5R-10, C_1	5-methylene-4,5-dihydroazulen-4-ylidene	54	47	–54	57	52	–60
	7R-5R-11, C_1	6-methylene-5,6-dihydroazulen-5-ylidene	58	51	–56	68	62	–72
	7R-5R-12, C_1	7-methylene-1,7-dihydroazulen-1-ylidene	59	55	–19	61	58	–27
	7R-5R-13, C_1	5-methylene-1,5-dihydroazulen-1-ylidene	59	56	–21	61	57	–28
	7R-5R-14, C_1	7-methylene-4,7-dihydroazulen-4-ylidene	61	57	–58	70	66	–70
	7R-5R-15, C_1	5-methylene-5,6-dihydroazulen-6-ylidene	62	56	–63	72	67	–78
	7R-5R-16, C_s	2-methylene-2,6-dihydroazulen-6-ylidene	62	56	–76	77	72	–94
	7R-5R-17, C_1	2-methylene-1,2-dihydroazulen-1-ylidene	64	61	–37	72	67	–78
	7R-5R-18, C_1	6-azulenylcarbene	66	75	–92	80	77	–94
	7R-5R-19, C_s	2-methylene-2,4-dihydroazulen-4-ylidene	80	–60	86	86	80	–98
	7R-5R-20, C_1	4-azulenylcarbene	81	75	–64	91	84	–83
	7R-5R-21, C_1	8-methylene-5,8-dihydroazulen-5-ylidene	82	–18	–102	96	87	–80
	7R-5R-22, C_s	6-methylene-2,6-dihydroazulen-2-ylidene	97	92	–64	107	101	–81
	7R-5R-23, C_1	8-methylene-1,8-dihydroazulen-1-ylidene	113	107	–62	116	108	–70
	7R-5R-24, C_1	4-methylene-2,4-dihydroazulen-2-ylidene	116	109	–69	120	114	–83
	7R-5R-25, C_1	6-methylene-1,6-dihydroazulen-1-ylidene	118	112	–73	119	110	–75
	7R-5R-26, C_1	4-methylene-1,4-dihydroazulen-1-ylidene	120	112	–62	116	109	–60

to our theoretical calculation at B3LYP/6-311 + G (d,p) level of theory, this allene-like molecule (7R-6R-1) is the lowest energy isomer on the $C_{11}H_8$ carbenes potential energy surface (PES). It is ~164 kJ mol^{-1} lower in energy than the experimentally identified 1-azulenylcarbene. In 1- and 2-naphthylcarbene rearrangement, 7R-6R-1 has been considered as the potential

TABLE 3 | Same as **Table 1**, low-lying $C_{11}H_8$ isomer of (6R-5R) Group within ~30 kJ mol^{-1} energy range calculated at different levels.

Group	Isomer, Point group	IUPAC Name	B3LYP/6-311+G (d,p)			ωB97XD/6-311+G (d,p)		
			ΔE_0	ΔG_{298}	ΔE_{ST}	ΔE_0	ΔG_{298}	ΔE_{ST}
6-5 Group	6R-5R-1, C_1	2,3-dimethylene-1H-inden-1-ylidene	–32	–36	6	–44	–48	1
	6R-5R-2, C_1	1,3-dimethylene-1H-inden-2-ylidene	–19	–24	–12	–34	–54	–15
	6R-5R-3, C_1	(1-methylene-1H-inden-2-yl)methylidene	–11	–16	–31	–21	–26	–39
	6R-5R-4, C_1	(E)-2-(1H-inden-1-ylidene)ethan-1-ylidene	–4	–10	–60	–9	–15	–71
	6R-5R-5, C_1	(1-methylene-1H-inden-3-yl)methylidene	4	–24	–40	–12	–14	–65
	6R-5R-6, C_s	(3Z)-3-vinyl-4H-inden-4-ylidene	4	–5	–26	–99	–99	–32
	6R-5R-7, C_s	(3E)-3-vinyl-1H-inden-1-ylidene	6	1	–22	1	–4	–60
	6R-5R-8, C_1	(Z)-2-(1H-inden-1-ylidene)ethan-1-ylidene	6	–8	–66	4	–2	–81
	6R-5R-9, C_1	(3Z)-3-vinyl-1H-inden-1-ylidene	7	3	–46	1	–3	–57
	6R-5R-10, C_1	(1-methylene-1H-inden-4-yl)methylidene	10	–72	–39	–80	–80	–43
	6R-5R-11, C_1	(2Z)-2-vinyl-1H-inden-1-ylidene	13	6	–39	7	1	–49
	6R-5R-12, C_1	(7E)-1-methylene-7-indenylcarbene	14	9	–26	–1	–6	–31
	6R-5R-13, C_1	(7E)-7-vinyl-1H-inden-1-ylidene	14	9	–37	6	1	–48
	6R-5R-14, C_1	(2E)-2-vinyl-1H-inden-1-ylidene	14	8	–38	8	3	–48
	6R-5R-15, C_1	(3E)-3-vinyl-4H-inden-4-ylidene	15	6	–73	24	15	–94
	6R-5R-16, C_s	(1Z)-1-vinyl-4H-inden-4-ylidene	15	8	–69	23	16	–90
	6R-5R-17, C_1	(1Z)-1-vinyl-2H-inden-2-ylidene	16	12	–50	14	11	–60
	6R-5R-18, C_1	(5E)-5-vinyl-4H-inden-4-ylidene	17	10	–54	21	15	–68
	6R-5R-19, C_s	(3E)-3-vinyl-5H-inden-5-ylidene	18	11	–70	25	18	–91
	6R-5R-20, C_1	(7Z)-7-vinyl-1H-inden-1-ylidene	19	13	–41	11	5	–50
	6R-5R-21, C_1	(3Z)-3-vinyl-5H-inden-5-ylidene	19	13	–68	25	19	–88
	6R-5R-22, C_s	(2Z)-2-vinyl-4H-inden-4-ylidene	21	13	–56	25	17	–78
	6R-5R-23, C_1	(6E)-6-vinyl-4H-inden-4-ylidene	21	13	–54	24	18	–69
	6R-5R-24, C_1	(5Z)-5-vinyl-1H-inden-1-ylidene	21	14	–43	14	4	–53
	6R-5R-25, C_1	(1E)-1-vinyl-4H-inden-4-ylidene	21	14	–72	28	21	–92
	6R-5R-26, C_1	(6E)-6-vinyl-1H-inden-1-ylidene	22	16	–43	16	9	–53
	6R-5R-27, C_1	(5Z)-5-vinyl-4H-inden-4-ylidene	23	16	–55	28	21	–70
	6R-5R-28, C_1	(5E)-5-vinyl-1H-inden-1-ylidene	23	15	–44	17	11	–54
	6R-5R-29, C_1	(6Z)-6-vinyl-1H-inden-1-ylidene	25	17	–44	17	10	–54
	6R-5R-30, C_1	(4E)-4-vinyl-1H-inden-1-ylidene	26	18	–43	18	12	–54
	6R-5R-31, C_1	(7Z)-1-methylene-7-indenylcarbene	26	21	–32	12	7	–37
	6R-5R-32, C_1	(2E)-2-vinyl-4H-inden-4-ylidene	26	15	–62	29	20	–78
	6R-5R-33, C_1	(1E)-1-vinyl-2H-inden-2-ylidene	27	23	–54	25	22	–65
	6R-5R-34, C_1	(1E)-1-vinyl-5H-inden-5-ylidene	27	17	–81	35	27	–103
	6R-5R-35, C_1	(1E)-2-methylene-1-indenylcarbene	27	21	–66	28	23	-80
	6R-5R-36, C_1	(2Z)-2-vinyl-5H-inden-5-ylidene	28	21	–61	30	23	–77

key intermediate [67]. Isomers 7R-6R-2 (bicyclo [5.4.0]undeca-1,2,4,6,8,10-hexaene) and 7R-6R-3 (bicyclo [5.4.0]undeca-1,3,4,6,8,10-hexaene) are elusive in the laboratory till date. Both of them are lower in energy than 1-azulenylcarbene. 7R-6R-1a (benzo [7]annulen-6-ylidene, υ_i = 1,461.75i cm^{-1}), 7R-6R-2a (benzo [7]annulen-5-ylidene, υ_i = 217.77i cm^{-1}), and 7R-6R-3a (benzo [7]annulen-7-ylidene, υ_i = 134.77i cm^{-1}, 119.63i cm^{-1}) are the carbene counterparts of the stable allenes and they lie as the local maxima on the $C_{11}H_8$ PES. Bicyclo [5.4.0]undeca-1,3,5,7,9-pentaene-11-ylidene (7R-6R-4) and bicyclo [5.4.0] undeca-2,4,6,8,11-pentaene-10-ylidene (7R-6R-5) are also lower in energy than 1-azulenylcarbene by 32 and 25 kJ mol^{-1}, respectively.

(6R-6R) Group

This group of carbenes have naphthalene moiety and 12 resonance stabilized naphthalene ring-containing isomers are possible for $C_{11}H_8$. Ten low-energy carbenes in this group have been shown in **Figure 3** and their relative energies have been shown in **Table 1**. The most stable isomer in this group is (E)-1-naphthylcarbene (6R-6R-1), which is 86 kJ mol^{-1} lower in energy than 1-azulnylcarbene. (6R-6R-1), (E)-2-naphthylcarbene (6R-6R-2), (Z)-2-naphthylcarbene (6R-6R-3) and (Z)-1-naphthylcarbene (6R-6R-4) are the *anti*- and *syn*-conformer of 1- and 2-naphthylcarbenes, respectively. Though the singlet-triplet energy gap (ΔE_{ST}) of 1- and 2-naphthylcarbenes is relatively low (~25 kJ mol^{-1}), the triplet isomer state is more stable than the singlet isomer. Many years ago, in 1965, Trozzolo and co-workers have identified 2-naphthylcarbene (isomer 6R-6R-1 and 6R-6R-3) in its triplet ground electronic state *via* ESR spectroscopy [68]. Based on our chemical intuition, by varying the position of methylene group and carbene carbon, we have identified total eight methylene substituted naphthalene ring containing $C_{11}H_8$ carbene isomers. 2-methylene-naphthalen-1-ylidene (6R-6R-5), 1-methylene-naphthalen-2-ylidene (6R-6R-6), 4-methylene-naphthalen-1-ylidene (6R-6R-7), 3-methylene-naphthalen-2-ylidene (6R-6R-8), 7-methylene-naphthalen-1-ylidene (6R-6R-9), 6-methylene-naphthalen-2-ylidene (6R-6R-10), 5-methylene-naphthalen-1-ylidene (6R-6R-11), and 8-methylene-naphthalen-2-ylidene (6R-6R-12) are 71, 63, 58, 31, 26, 20, 18, and 14 kJ mol^{-1} lower in

TABLE 4 | Same as **Table 1**, low-lying $C_{11}H_8$ isomer of (5R-5R) group with in ~120 kJ mol^{-1} energy range calculated at different levels.

Group	Isomer, point group	IUPAC Name	B3LYP/6-311 + G (d,p)			ωB97XD/6-311 + G (d,p)		
			ΔE_0	ΔG_{298}	ΔE_{ST}	ΔE_0	ΔG_{298}	ΔE_{ST}
5-5 Group	5R-5R-1, C_1	(Z)-2-allylidene-1,2-dihydropentalen-1-ylidene	99	89	−6	103	92	−14
	5R-5R-2, C_1	(6E)-2-methylene-6-vinyl-1,2-dihydropentalen-1-ylidene	99	89	−22	100	90	1
	5R-5R-3, C_1	(6Z)-2-methylene-6-vinyl-1,2-dihydropentalen-1-ylidene	101	88	−23	100	88	−12
	5R-5R-4, C_1	(E)-2-allylidene-1,2-dihydropentalen-1-ylidene	103	93	−2	106	95	−13
	5R-5R-5, C_1	(4Z)-2-methylene-4-vinyl-1,2-dihydropentalen-1-ylidene	108	95	−29	108	99	−4
	5R-5R-6, C_s	(3E)2-methylene-3-vinyl-1,2-dihydropentalen-1-ylidene	110	98	12	107	97	−8
	5R-5R-7, C_s	(3Z)2-methylene-3-vinyl-1,2-dihydropentalen-1-ylidene	111	100	28	110	101	−17
	5R-5R-8, C_1	(5Z)-2-methylene-5-vinyl-1,2-dihydropentalen-1-ylidene	111	99	−28	112	99	−22
	5R-5R-9, C_1	(4E)2-methylene-4-vinyl-1,2-dihydropentalen-1-ylidene	111	97	22	112	102	1
	5R-5R-10, C_1	(2Z)-5-methylene-2-vinyl-1,5-dihydropentalen-1-ylidene	111	99	−17	114	−102	40
	5R-5R-11, C_1	(3-ethynyl-1,2-dihydropentalen-2-yl)methylidene	111	107	74	61	57	94
	5R-5R-12, C_1	(Z)-5-allylidene-1,5-dihydropentalen-1-ylidene	112	98	−23	116	105	−29
	5R-5R-13, C_1	(E)-5-allylidene-1,5-dihydropentalen-1-ylidene	112	99	8	117	106	−13
	5R-5R-14, C_1	(3Z)-5-methylene-3-vinyl-1,5-dihydropentalen-1-ylidene	112	100	−6	112	103	−17
	5R-5R-15, C_1	(6Z)-5-methylene-6-vinyl-1,5-dihydropentalen-1-ylidene	113	103	−20	111	100	−19
	5R-5R-16, C_s	(3E)-5-methylene-3-vinyl-1,5-dihydropentalen-1-ylidene	115	103	−15	116	103	23
	5R-5R-17, C_1	(5E)-2-methylene-5-vinyl-1,2-dihydropentalen-1-ylidene	115	100	−36	116	105	−14
	5R-5R-18, C_1	(E)-2-allylidene-1,2-dihydropentalen-1-ylidene	117	105	−6	119	108	−19
	5R-5R-19, C_s	(2E)-5-methylene-2-vinyl-1,5-dihydropentalen-1-ylidene	118	105	−28	121	108	23
	5R-5R-20, C_1	(6E)-5-methylene-6-vinyl-1,5-dihydropentalen-1-ylidene	120	109	−27	118	109	175
	5R-5R-21, C_1	(Z)-2-allylidene-1,2-dihydropentalen-1-ylidene	120	109	−27	118	109	−29

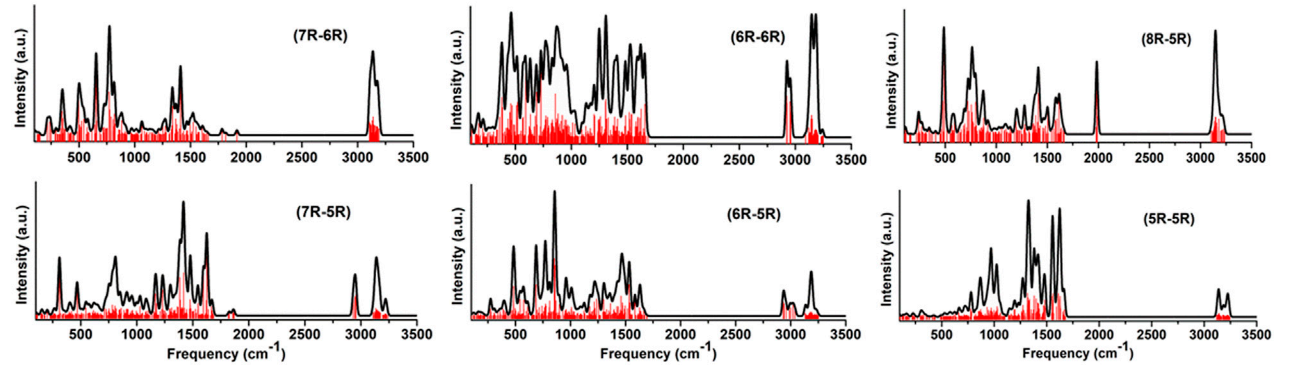


FIGURE 9 | Convoluted vibrational spectra of low-lying carbene/cyclic allene isomers of various groups.

energy than 1-azulenylcarbene, respectively. The hydrocarbon derivatives of 6R-6R-5, 6R-6R-6, and 6R-6R-7 have been detected experimentally [69, 70]. According to our knowledge, parent carbene isomers 6R-6R-8, 6R-6R-9, 6R-6R-10, 6R-6R-11, and 6R-6R-12 are absent in the laboratory till date.

(8R-5R) Group

Total eight isomers are possible containing one eight-membered and one five-membered ring including carbene counter part of the low-lying cyclic allenes (**Figures 4**, **9**). Out of these eight isomers, bicyclo [6.3.0]undeca-1,3,4,6,8,10-hexaene (8R-5R-1), bicyclo [6.3.0]undeca-2,3,5,7,9,11-hexaene (8R-5R-2), and bicyclo [6.3.0]undeca-1,2,4,6,8,10-hexaene (8R-5R-3) are 64, 61 and 48 kJ mol^{-1} lower in energy than 1-azulenylcarbene, respectively. Ring expansion reaction of 5-azulenylcarbene gives 8R-5R-1 and 8R-5R-2. In 2016, these two cyclic allenes were identified for the first time by Sander and co-workers in 2016 [71]. Bicyclo [6.3.0]undeca-1,2,4,6,8,10-hexaene (8R-5R-3) has not been unidentified in the laboratory till date. The carbene counterparts of these cyclic allenes (shown in **Figure 8**) are not minima on the $C_{11}H_8$ PES. 8R-5R-1a [(4Z,7Z,9Z)-cyclopenta [8] annulen-6-ylidene, υ_i = 377.36i cm^{-1}], 8R-5R-2a [(3aZ,6Z,8Z)-cyclopenta [8]annulen-5-ylidene, υ_i = 507.32i cm^{-1}], and 8R-5R-3a [(5Z,7Z,9Z)-cyclopenta [8]annulen-4-ylidene, υ_i = 292.69i cm^{-1}] have one imaginary frequency each, therefore, they represent local maxima or transition states on the $C_{11}H_8$ PES. 8R-5R-4 [(4Z,6Z,8Z)-1H-cyclopenta [8]annulen-1-ylidene] and 8R-5R-5 [(4Z,6Z,8Z)-2H-cyclopenta [8]annulen-2-ylidene] are 102 and 106 kJ mol^{-1} higher in energy than 1-azulenylcarbene, respectively.

(7R-5R) Group

This type of $C_{11}H_8$ carbene/cyclic allene isomers contains fused seven and five membered moiety along with one substituent. Total twenty-six minima have been identified including carbene and allene like structures, out of which, 10 low-lying structures are shown in **Figure 5**, and energies of all the isomers are listed in **Table 2**. 10-methylenebicyclo [5.3.0]deca-1,3,4,6,8-pentaene (7R-5R-1), 10-methylenebicyclo [5.3.0]deca-2,3,5,7 (1),8-pentaene (7R-5R-2), 8-methylenebicyclo [5.3.0]deca-2,3,5,7 (1),9-pentaene (7R-5R-3) and 8-methylenebicyclo [5.3.0]deca-1,2,4,6,9-pentaene (7R-5R-4) are cyclic allene like structures. They are 54, 53, 51, and 36 kJ mol^{-1} lower in energy than 1-azulenylcarbene (7R-5R-6), respectively. All of them are elusive in the literature till date. The carbene counterparts of these allenes are not minima on the $C_{11}H_8$ PES (**Figure 8**). 1-methylene-1,6-dihydroazulen-6-ylidene (7R-5R-1a, υ_i = 405.80i cm^{-1}), 3-methylene-3,5-dihydroazulen-5-ylidene (7R-5R-2a, υ_i = 384.13i cm^{-1}), 1-methylene-1,5-dihydroazulen-5-ylidene (7R-5R-3a, υ_i = 394.10i cm^{-1}) and 1-methylene-1,4-dihydroazulen-4-ylidene (7R-5R-4a, υ_i = 362.01i cm^{-1}) are 21, 22, 22, and 10 kJ mol^{-1} higher in energy than 7R-5R-6. Five azulenylcarbenes (1-, 2-, 4-, 5-, and 6-azulenylcarbene) are present in this group. Among them 1-azulenylcarbene (7R-5R-6), 2-azulenylcarbene (7R-5R-9), 5-azulenylcarbene (7R-5R-8), and 6-azulenylcarbene (7R-5R-18) have already been detected experimentally [71] except 4-azulenylcarbene (8R-5R-20). 8R-5R-6 had been isolated by Sander's group in 2012, through low-temperature argon matrix in its singlet ground electronic state [64]. But the other regio-isomers of 8R-5R-6 have been trapped at their triplet ground electronic state [71]. In this group, 21 low-lying methylene substituted azulenyl ring containing carbene/cyclic allene like $C_{11}H_8$ isomers are also present. Out of these 21 isomers, 1-methyleneazulene-8-ylidene (7R-5R-5) is 3 kJ mol^{-1} lower in energy than experimentally identified isomer 7R-5R-6. Isomer 7R-5R-5 is still elusive in the literature. The other methylene substituted azulenyl ring containing carbene-derivatives are higher in energy than 7R-5R-6. All of them are missing in the laboratory till date.

(6R-5R) Group

One six and one five membered fused indenyl ring along with one or two substituent containing $C_{11}H_8$ carbene isomers are mainly present in this group. We have identified one hundred forty-nine isomers in this group. Only 10 lowest energy carbene molecules are shown in **Figure 6**, rest of them are listed in the ESI. Energies of lowest thirty-six isomers (up to ~28 kJ mol^{-1}) have been shown in **Table 3**, rest is listed in ESI. 2,3-dimethylene-1H-inden-1-ylidene (6R-5R-1) and 1,3-dimethylene-1H-inden-2-ylidene (6R-5R-2) are the bi-methylene substituted indene derivative having carbene carbon at first and second position of the indenyl ring respectively. 6R-5R-1 is the most stable $C_{11}H_8$ carbene isomer with having one indenyl ring and it is 32 kJ mol^{-1} lower in energy than 1-azulenylcarbene. (1-methylene-1H-inden-2-yl) methylidene (6R-5R-3) and (E)-2-(1H-inden-1-ylidene)ethan-1-ylidene (6R-5R-4) are 11 and 4 kJ mol^{-1} lower in energy than 1-azulenylcarbene, respectively. (1-methylene-1H-inden-3-yl)methylidene (6R-5R-5), (3Z)-3-vinyl-4H-inden-4-ylidene (6R-5R-6), (3E)-3-vinyl-1H-inden-1-ylidene (6R-5R-7), (Z)-2-(1H-inden-1-ylidene)ethan-1-ylidene (6R-5R-8), (3Z)-3-vinyl-1H-inden-1-ylidene (6R-5R-9) and (1-methylene-1H-inden-4-yl)methylidene (6R-5R-10) are within 10 kJ mol^{-1} higher in energy than 1-azulenylcarbene. To the best of our knowledge, most of the carbene isomers listed in this group are still elusive in the laboratory.

(5R-5R) Group

This group of molecules contain two five membered fused ring along with mono-, di- or tri-substituted fragments. We have identified total two hundred twenty-seven carbene isomers in the $C_{11}H_8$ elemental composition. All these isomers are relatively higher in energy (within +98 to +435 kJ mol^{-1}) from 1-azulenylcarbene. Only 10 isomers in this group have been shown in **Figure 7**, rest of the isomers is tabulated in the ESI. Although the lowest energy isomer, (Z)-2-allylidene-1,2-dihydropentalen-1-ylidene (5R-5R-1) is 98 kJ mol^{-1} higher in energy than the reference, ~20 isomers lie within ~20 kJ mol^{-1} in energy with respect to 5R-5R-1 (**Table 4**). Most of the isomers in this group are unidentified in the laboratory till date.

Stability of Carbenes Based on Hückel's Rule

In this work, we have studied a large number of bicyclo-$C_{11}H_8$ isomers, most of which are carbenes. Previous studies [72] suggest that carbenes can be considered as a carbon atom with doubly occupied orbital in the molecular plane and an empty orbital perpendicular to the molecular plane. Therefore, the π-electron system in carbene is equivalent to a carbocation without any charge and usual rules for stabilization based on aromaticity could be applied to carbenes also. The doubly occupied orbital for carbenes having two nonbonded electrons can be either spin-paired (singlet state) or in parallel-spin (triplet state), whereas, in case of allenes, the electrons are always in paired form, therefore more stable than its carbene counterpart. Out of the six skeletal structures, (7R-6R) and (6R-6R) groups show better stability due to the presence of aromatic benzylic carbenes. In (7R-6R) group, 7R-6R-1, 7R-6R-2, and 7R-6R-3 show better stability due to their puckered cyclic-allene geometry where the electrons are always spin-paired, therefore, the singlet state geometry is more stable compared to triplet one. Likewise, one can explain the energetics of (8R-5R) group and (7R-5R) group, where the eight or seven membered cyclic allene like structure gives the better stability than the carbene isomers. Antiaromatic (8π electron) structure of eight membered ring containing carbene isomers (8R-5R-4 and 8R-5R-5) in (8R-5R) group led to high-energy isomers. Aryl carbenes along with its planar geometrical structure gives maximum delocalization between the vacant p-orbital of the carbene carbon with the neighboring arene π-system. Therefore, in case of (6R-6R) group, the electronic delocalization explains the stability of 6R-6R-1 to 6R-6R-4 where the carbene carbon is attached with an aromatic naphthyl ring. Isomer 6R-6R-5 to 6R-6R-8 has intact delocalized benzene rings, which leads to better stabilization of these compounds, whereas, in 6R-6R-9 and 6R-6R-10, methylene group breaks the delocalization. In similar manner, one can explain the energetics of (6R-5R) group. 6R-5R-10 contains 8π electrons in the cyclic conjugated system; the antiaromatic behavior of this isomer leads to instability. Most of the isomers in (5R-5R) groups are less conjugated structure and none of them fully satisfy the Huckel's (4n+2) π-electron rule of aromaticity/antiaromaticity which explains why the (5R-5R) carbenes are so thermodynamically high in energy.

SPECTROSCOPIC PROPERTIES

Based on the permanent dipole moments obtained at the B3LYP/6-311+G (d,p) level, it is quite clear that many of these molecules are suitable targets for rotational spectroscopy. For example, the dipole moments of 7R-6R-4, 7R-6R-5, 6R-6R-10, 7R-5R-7, and 8R-5R-3 are greater than 5 Debye but they still remain elusive in the laboratory. These polar molecules are very good targets and lack of laboratory rest frequencies of these highly polar molecules may only lead to further complications in successfully resolving confirmation of molecules in the ISM.

To understand the astronomical emission features, computational modeling is commonly done along with laboratory experiments. In this regard, an IR spectroscopic database for a large number of PAH molecules have been created by NASA Ames Research Center [73, 74]. Considering the importance of the bicyclic carbene and cyclic allene isomers of $C_{11}H_8$ in the ISM, we have simulated the key IR spectroscopic signatures of the low energy isomers for each skeletal group. The vibrational frequencies and their intensities for each low-lying isomers have been computed using harmonic approximation at B3LYP/6-311 + G (d,p) level of theory as implemented in the Gaussian 09 software [63] without introducing any scaling factor. Considering a very crude model, all the vibrational frequencies along with their intensities are combined for a particular skeletal group and convoluted using a Gaussian profile with a full width at half maximum (FWHM) of 25 cm^{-1}. The convoluted vibrational spectrum for each group is shown in **Figure 9**. Although from quantum chemistry perspective, some high-energy molecules may have stronger emission features, such effects have not been incorporated in this model.

From the spectral features, it can be easily identified that the common stretching frequencies of C-H symmetric and asymmetric vibrations in ~3,000–3,200 cm^{-1} range. All of the isomers are resonance stabilised, therefore the C=C starching frequency can also be identified at ~1,500 cm^{-1} for every group. Apart from the common features, the groups containing allene like isomers, (7R-6R), (8R-5R) and (7R-5R) group in particular, show characteristic vibrational stretching frequency at ~1,800–2,000 cm^{-1} range. The fingerprint regions below 1,000 cm^{-1} are almost similar for all groups and no characteristic features can be highlighted to identify the skeletal difference (different ring size) between the bicyclo groups.

SUMMARY AND FUTURE STUDIES

In summary, more than 400 isomers of $C_{11}H_8$ have been computationally identified using chemical intuition and tabu-search algorithm implemented in PyAR. All the stationary points have been obtained at the B3LYP/6-311 + G (d,p) level of theory initially and calculations are also done at the ωB97XD/6-311 + G (d,p) level to see effect of empirical dispersion corrections. It is noted here that we did not find huge changes in structures or energetics whether the calculations are done with or without empirical dispersion corrections. ZPVE-corrected relative energies, dipole moments, and point group symmetry of all molecules are collected at the B3LYP/6-311++G (d,p) level of theory. High-level electron-correlation effects have not been incorporated through coupled-cluster methods considering a huge set of isomers. However, we had done such calculations for few selective low-lying isomers in the past. The dipole moments of 7R-6R-4, 7R-6R-5, 6R-6R-10, 7R-5R-7, and 8R-5R-3 are greater than 5 Debye but they still remain elusive in the laboratory. It is noted here that $C_{11}H_8$ isomers are important key reactive intermediates for the formation of PAHs. Therefore, further experimental investigations are warranted. To the best of our knowledge, so far none of the isomers of $C_{11}H_8$ are characterized by rotational spectroscopy though they are having a permanent dipole moment ($\mu \neq 0$).

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/**Supplementary Material**, further inquiries can be directed to the corresponding authors.

AUTHOR CONTRIBUTIONS

TR: Structure prediction, Theoretical calculations, Data analysis and interpretation. SS: Structure prediction, Theoretical calculations, Data analysis and interpretation. VT: Data analysis and interpretation, Critical revision of the article, Final approval of the version to be published. SG: Conception or design of the work, Data analysis and interpretation, Drafting the article, Final approval of the version to be published.

ACKNOWLEDGMENTS

SG thanks Govt. of India (GoI) for grant no DST/NSM/R&D_HPC_Applications/2021/21 for the Paramshakti HPC facilities at IIT Kharagpur and doctoral fellowship for SS Computational facilities in NITD supported by EMR/2017/002653 and support provided at SDSU (for VT) by DURIP grant W911NF-10-1-0157 from the U.S. Department of Defense and by NSF CRIF grant CHE-0947087 is gratefully acknowledged. TR thanks NITD for doctoral fellowship. We thank the reviewers for insightful comments to enrich this manuscript.

SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fphy.2022.907466/full#supplementary-material

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.