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Article

New Carbenes and Cyclic Allenes Energetically Comparable to Experimentally Known 1-Azulenylcarbene

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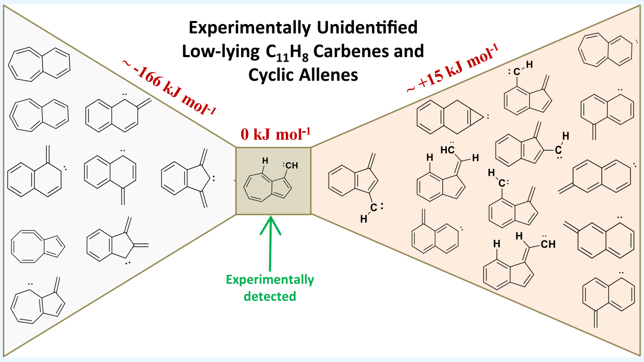

ABSTRACT: 1-Azulenylcarbene (**18**; 0 kJ mol^{-1}) is experimentally known as the key reactive intermediate for the rearrangement reactions of aryl carbenes in the laboratory. Here, using coupled-cluster methods up to the fc-CCSD(T)/cc-pVTZ//fc-CCSD(T)/cc-pVDZ level, thirteen new carbenes and one new cyclic allene are theoretically identified within the $C_{11}H_8$ elemental composition that either energetically lie below or very close to **18**. While the cyclic allene, bicyclo[5.4.0]undeca-2,3,5,7,9,11-hexene (**1**; −166 kJ mol^{-1}), is the experimentally known lowest energy isomer, three other cyclic allenes, bicyclo[5.4.0]undeca-1,2,4,6,8,10-hexene (**2**; −100 kJ mol^{-1}), bicyclo[5.4.0]undeca-1,3,4,6,8,10-hexene (**3**; −97 kJ mol^{-1}), and bicyclo[6.3.0]undeca-1,2,4,6,8,10-hexene (**13**; −42 kJ mol^{-1}), demand new experimental studies. In total, thirty-one isomers are studied in this work (within −166 to +15 kJ mol^{-1} from **18**) and all are found to be polar ($\mu \neq 0$). Among these, 1H-benzo[7]annulen-1-ylidene (**17**; −4 kJ mol^{-1}; μ = 5.24 D), bicyclo[5.4.0]undeca-2,4,6,8,11-pentaene-10-ylidene (**24**; 13 kJ mol^{-1}; μ = 7.59 D), 5-methylene-naphthalen-1-ylidene (**26**; 15 kJ mol^{-1}; μ = 5.32 D), 6-methylene-naphthalen-2-ylidene (**27**; −43 kJ mol^{-1}; μ = 6.60 D), and 8-methylene-naphthalen-2-ylidene (**28**; −39 kJ mol^{-1}; μ = 5.55 D) are competitively polar compared to **18** (μ = 5.39 D). Therefore, these carbene molecules are potential targets for rotational spectroscopists and radioastronomers. Considering the importance of naphthyl and azulenylcarbenes in reactive intermediate chemistry, mechanisms of different rearrangement reactions and plausible formation pathways of some of these new carbenes are studied in this work using density functional theory.

1. INTRODUCTION

Carbenes are key reactive intermediates not only in the laboratory[1−6] but also in the interstellar medium (ISM).[7,8] To date, six carbene molecules—cyclopropenylidene (c-C_3H_2),[9] propadienylidene (C_3H_2),[10] butatrienylidene (C_4H_2),[11] ethynylcyclopropenylidene (C_5H_2),[12] pentatetraenylidene (C_5H_2),[13] and hexapentaenylidene (C_6H_2)[7]—are identified in the ISM. As a follow-up study to understand the nature of carbenes, their structures, isomerization, and reactivity patterns, a considerable amount of theoretical and experimental work has been done on the homologous series C_nH_2 (n = 5,[2,3,6,14−25] 6,[2,7,26−29] 7,[30−33] 8,[5,28,29,34] and 9[5,14,23,35−41]). Potential target molecules to be identified in the laboratory have also been listed, but they remain as an open challenge to gas-phase molecular spectroscopists. Unequivocally, if a molecule is polar ($\mu \neq 0$), then the laboratory rotational transitions are a pre-requisite for potential confirmation of the same molecules many light-years away.[42−50] Thus, a firm experimental and theoretical understanding of carbene and its related chemistry has become necessary for many related fields such as astrochemistry, combustion, and soot formation.[51] Along the same lines, phenyl/naphthyl/azulenyl rings containing carbenes (arylcarbenes) have drawn considerable attention to the astrochemistry community because of their ease of thermal and photochemical transformations.[52−56] The recent discovery of four neutral molecules, cyclopentadiene (C_5H_6), two isomers of ethynylcyclopentadiene (C_7H_6), and indene (C_9H_8), along with two of the C_5H_2 carbenes aforementioned in the Taurus Molecular Cloud-1,[12,13,57] reinforces the possibility of polycyclic aromatic hydrocarbon (PAH) formation in space through resonance-stabilized carbene intermediates.[58−61] In this endeavor, $C_{11}H_8$ is the next higher homologue potentially suitable for laboratory and radioastronomical studies.[62] Our recent theoretical account on $C_{11}H_8$ isomers established a fact that six low-lying indene isomers (2aH-cyclopenta[*cd*]indene, 7-ethynyl-1*H*-indene, 4-ethynyl-1*H*-indene, 6-ethynyl-1Hindene, 5-ethynyl-1*H*-indene, and 7bH-cyclopenta[cd]-indene) remain elusive till date in the laboratory.[63] Very recently, we have also investigated all the possible $C_{11}H_8$ bicyclic carbene and allene isomers.[64] It is

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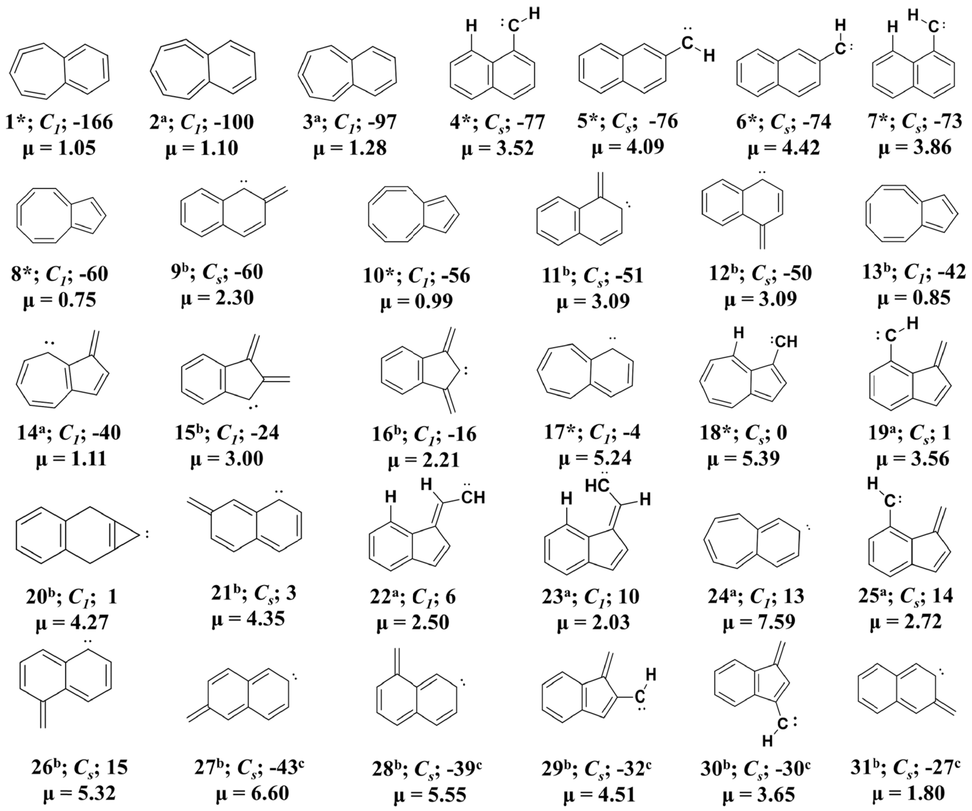

Figure 1. Thirty-one low-lying isomers of $C_{11}H_8$ carbenes/cyclic allenes. ZPVE-corrected relative energies (in kJ mol^{-1}) and absolute dipole moment values (in Debye) are calculated at the fc-CCSD(T)/cc-pVDZ level of theory. *Experimentally detected isomers. ^{a}Theoretically isolated but no experimental evidence. ^{b}New isomer. ^{c}Single Point Energy calculated at the fc-CCSD(T)/cc-pVTZ//B3LYP/6-311+G(d,p) level of theory, and ZPVEs are obtained at the B3LYP/6-311+G(d,p) level.

noted here that using synchrotron-based vacuum ultraviolet ionization mass spectrometry, 1-ethynyl-1*H*-indene has been identified by Kaiser and co-workers.[62] Here, we focus on the arylcarbenes and cyclic allenes of $C_{11}H_8$ to further unravel the potential thermo- and photochemical transformations. While the synthesis, experimental detection, and characterization of such short-lived reactive intermediates are very challenging in the laboratory, computational studies of these new reactive intermediates are beneficial to discover them in the laboratory eventually and subsequently in the ISM.

The spectroscopic characterization of the reactive intermediates during the rearrangement of different arylcarbenes was studied in detail for a long time.[12,13,52,58,60,65−77] In 1993, Albrecht and McMahon could first characterize the photochemical rearrangement between 2-naphthylcarbene (**5** & **6**, Figure 1) and 2,3-benzobicyclo[4.1.0]hepta-2,4,6-triene spectroscopically using the matrix isolation technique.[53] Initial attempts to identify the rearrangement between 1-naphthylcarbene (**4** & **7**) and 2-naphthylcarbene (**5** & **6**) at 10 K in argon matrices were unsuccessful,[53] although later, the intermediates could be trapped in their triplet ground electronic state.[77−79] Flash Vacuum Pyrolysis (FVP) of either 1- or 2-naphthyldiazomethane produced mainly 1H-cyclobuta-[*de*]naphthalene and small amounts of an unknown compound, which was tentatively assigned to bicyclo[5.4.0]undeca-2,3,5,7,9,11-hexene (**1**).[72]

After unsuccessful attempts by Saito's group,[80] Sander and co-workers in 2012 first isolated 1-azulenylcarbene (**18**) in its singlet ground electronic state in argon or neon matrices at 3−10 K.[81] In 2016, they also trapped three regio-isomers (2-, 5-, and 6-azulenylcarbene) of **18** in their triplet ground electronic state but attempts made to trap 4-azulenylcarbene were unsuccessful.[82] The singlet electronic state of **18** is stabilized by the high electron density at the 1-position of the azulenyl system along with a favorable C...H interaction between the carbene carbon and the neighboring H-atom at the seven-membered ring.[82] Although Wentrup and co-workers have studied the isomerization of both azulenylcarbene and naphthylcarbenes by using falling solid-FVP (FS-FVP), a detailed analysis of the mechanism of these rearrangements is still missing in the literature.[56,79]

In this study, we have explored the potential energy surface (PES) of $C_{11}H_8$ in search of carbene reactive intermediates in their ground electronic state. We have studied the detailed structure, thermodynamic, and spectroscopic properties of thirty-one isomers within ∼−166 to +15 kJ mol^{-1} range from the experimentally identified **18** in their singlet and triplet electronic states. Theoretically, we report one new cyclic allene and thirteen new carbene reactive intermediates that are not reported before in the literature.

On the basis of relative energies obtained from density functional theory (DFT) and coupled-cluster (CC) calculations, the current theoretical study reveals that several molecules remain elusive, which energetically lie below the experimentally identified carbenes. Out of the thirty-one low-lying $C_{11}H_8$ carbene and allene isomers shown in Figure 1, only nine isomers, bicyclo[5.4.0]undeca-2,3,5,7,9,11-hexene (**1**),[72,83] (E)-1-naphthylcarbene (**4**),[84] (E)-2-naphthylcarbene (**5**),[84] (Z)-2-naphthylcarbene (**6**),[84] (Z)-1-naphthylcarbene (**7**),[84] bicyclo[6.3.0]undeca-1,3,4,6,8,10-hexaene (**8**),[82]

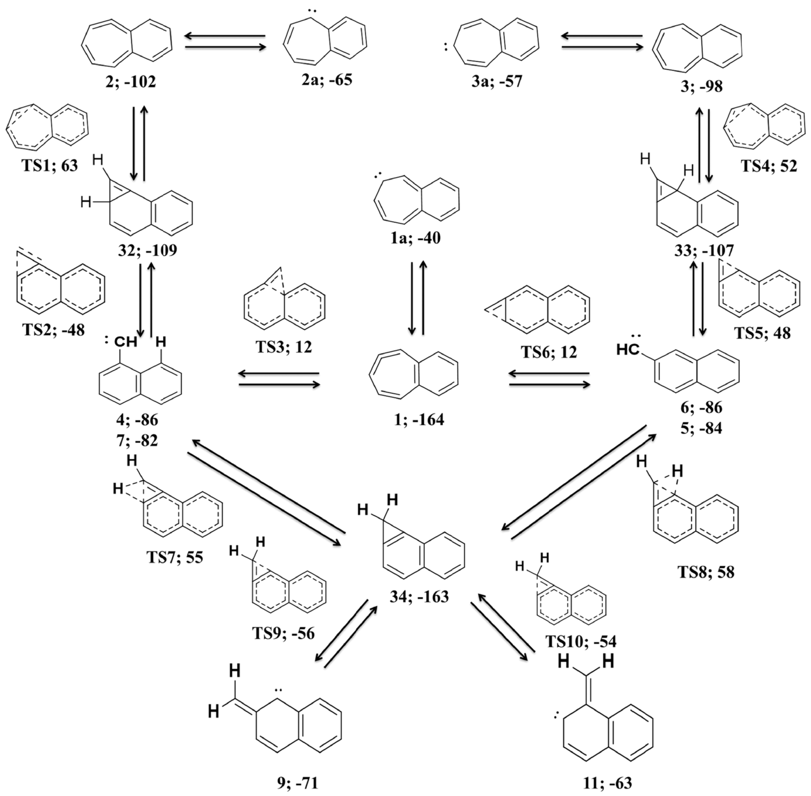

Figure 2. Plausible rearrangement mechanism of cyclic allenes (**1**, **2**, **3**) and carbenes (**9**, **11**) via the formation of 1- and 2-naphthylcarbenes calculated at the B3LYP/6-311+G(d,p) level of theory.

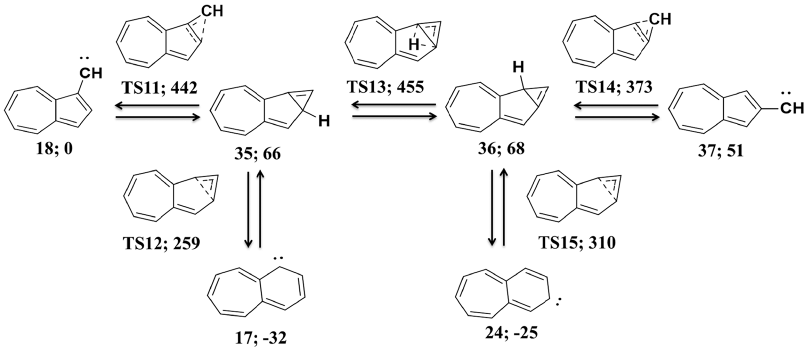

Figure 3. Plausible rearrangement mechanism of 1- and 2-azulenylcarbene calculated at the B3LYP/6-311+G(d,p) level of theory.

bicyclo[6.3.0]undeca-2,3,5,7,9,11-hexaene (**10**),[82] 1H-benzo[7]annulen-1-ylidene (**17**),[81,82] and 1-azulenylcarbene (**18**),[81,82] have been experimentally detected in the laboratory. While some of the molecules had been predicted in earlier theoretical studies, carbene isomers **9**, **11**, **12**, **15**, **16**, **20**, **21**, **26**, **27**, **28**, **29**, **30**, and **31** (i.e., methylene-naphthalene-ylidenes, dimethylene-1H-inden-ylidenes, and methylene-1H-inden-yl-methylidene) and the cyclic allene **13** are still elusive in the literature. Apart from this, we have proposed low-energy thermal rearrangement schemes between 1- and 2-naphthylcarbene (Figure 2), 1- and 2-azulenylcarbene (Figure 3), the formation of 1H-cyclopenta[*cd*]indene (the global minima of $C_{11}H_8$ PES, **40**, Figure 4) from experimentally identified 1-azulenylcarbene (**18**, 0 kJ mol^{-1}), and a plausible rearrangement scheme for the formation of unidentified methylene substituted carbenes (Figure 5) based on thermodynamically favorable energy considerations. Although several other research groups have studied the rearrangement processes between 1- and 2-napthylcarbene and 1- and 2-azulenylcarbene,[53,75,77,79,81−83] we have proposed pathways here for the formation of some of these new carbenes that might progress through several allene-like $C_{11}H_8$ intermediates, which had not been identified earlier.

2. RESULT AND DISCUSSION

The valence-bond structures for thirty-one low-lying isomers of $C_{11}H_8$ within −166 to +15 kJ mol^{-1} from **18** have been shown in Figure 1. Because **18** had been synthesized and isolated in the laboratory,[79,81,82] we have considered this carbene as the reference of energy for all the molecules studied in this work. The zero-point vibrational energy (ZPVE) corrected relative energy, point group symmetry, and permanent dipole moments of the molecules are listed along with the structures in Figure 1. Experimentally detected isomers are represented with an asterisk symbol. The detailed ZPVE corrected relative energies, Gibbs free energies, and singlet−triplet energy gaps at

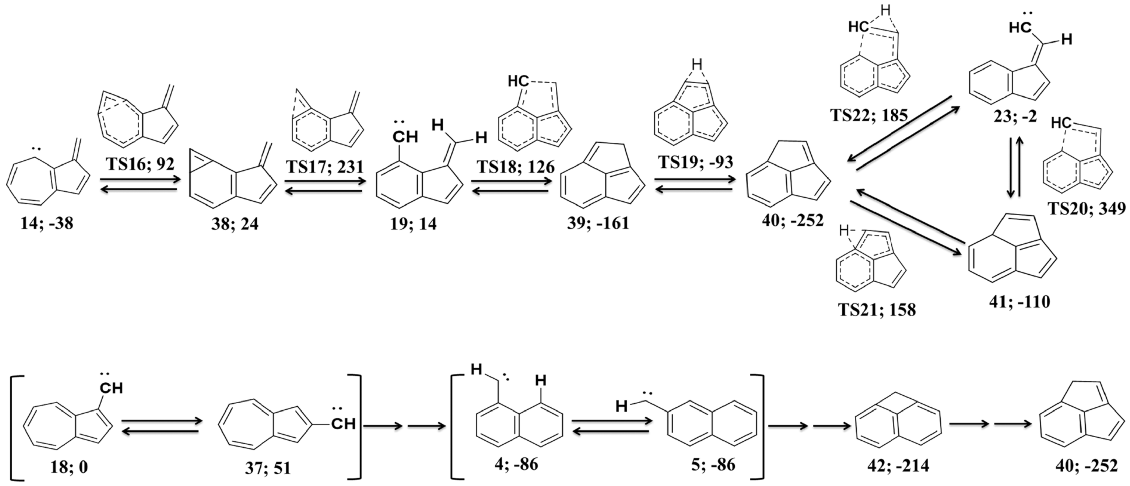

Figure 4. Overall rearrangement scheme for the formation of $C_{11}H_8$ global minima from some low-lying carbene/allene isomers calculated at the B3LYP/6-311+G(d,p) level of theory.

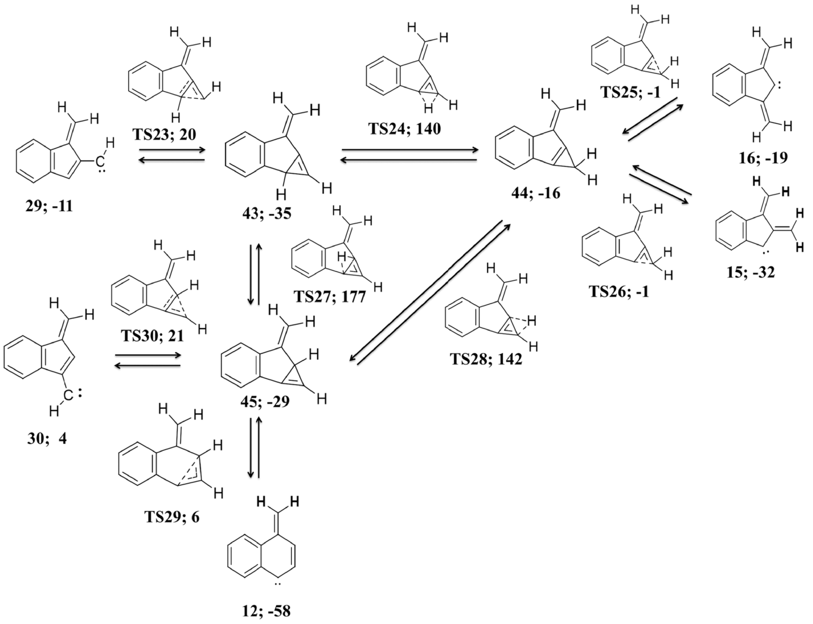

Figure 5. Plausible rearrangement scheme for the formation of unidentified methylene-substituted carbenes calculated at the B3LYP/6-311+G(d,p) level of theory.

various levels for all the thirty-one low-lying isomers are shown in Table 1. To evaluate the multireference character of these isomers, T_1 diagnostic values have been calculated at the CCSD/6-311+G(d,p)//B3LYP/6-311+G(d,p) level of theory.[85] Rotational constants, inertial axis dipole moments along with their components, and the centrifugal distortion constants for isomers **1**−**31** are shown in Table S2 (see the Supporting Information) at the fc-CCSD(T)/cc-pVDZ level of theory. NICS (1 Å) values calculated for each ring of the low-lying isomers are shown in Table 2. For brevity, total energies, ZPVEs, rotational constants, singlet−triplet energy gaps, NICS (1 Å), and T_1 diagnostic values calculated using CC and DFT for all isomers, and final optimized Cartesian coordinates are given in the ESI.

2.1. Energetics. 1H-cyclopenta[*cd*]indene (**40**) is the global minimum isomer for $C_{11}H_8$.[82] In the early 1970s, **40** was isolated by different groups.[86,87] However, when we consider $C_{11}H_8$ carbene and allene isomers, bicyclo[5.4.0]-undeca-2,3,5,7,9,11-hexene (**1**) turns out to be the lowest energy isomer among the thirty-one isomers that are currently studied within the $C_{11}H_8$ PES. Isomer **1** is more stabilized because of the fact that one benzene ring is annulated with cycloheptatetraene. For the last few decades, **1** has been known as the key intermediate in the rearrangement of 1- and 2-naphthylcarbenes (isomers **4** and **5**).[75] In 1986, West et al. observed isomer **1** as a minor product in the rearrangement of 1- and 2-napthylcarbene.[72] In 2000, McMahon's group has studied the spectroscopic characterization and photochemical reactivity of **1** through matrix isolation.[83] However, to the best of our knowledge, isomer **2** (bicyclo[5.4.0]undeca-1,2,4,6,8,10-hexene) and isomer **3** (bicyclo[5.4.0]undeca-1,3,4,6,8,10-hexene) have not been detected experimentally. Isomers **1**, **2**, and **3** are cyclic allene-like neutral molecules that are 166, 100, and 97 kJ mol^{-1} lower in energy than experimentally identified 1-azulenylcarbene, respectively. All attempts to optimize the carbenes **1a**, **2a**, **3a**, **8a**, **10a**, and **13a** (see Figure S1 in the

Table 1. ZPVE-Corrected Relative Energies (ΔE_0; in kJ mol^{-1}), Gibbs Free Energies ($\Delta G_{298.15}$; in kJ mol^{-1}), Singlet−Triplet Energy Gaps (ΔE_{ST}; in kJ mol^{-1}), and T_1 Diagnostic Values of 31 Low-Lying Isomers of $C_{11}H_8$ Calculated at Different Levels

		fc-CCSD(T)/cc-pVDZ	B3LYP/6-311+G(d,p)			ωB97XD/6-311+G(d,p)			fc-CCSD(T)/cc-pVTZ[a,b]	
isomer	state	ΔE_0	ΔE_0	$\Delta G_{298.15}$	ΔE_{ST}	ΔE_0	$\Delta G_{298.15}$	ΔE_{ST}	ΔE_0	T_1[c]
1, C_1	$\tilde{X}_1A$	−166	−164	−159	79	−180	−174	86	−167[a]	0.012
2, C_1	$\tilde{X}_1A$	−100	−101	−99	13	−105	−101	4	−100[a]	0.015
3, C_1	$\tilde{X}_1A$	−97	−98	−94	16	−103	−98	7	−98[a]	0.014
4, C_s	$\tilde{X}_1A'$	−77	−86	−85	−26	−99	−99	−32	−77[a]	0.013
5, C_s	$\tilde{X}_1A'$	−76	−86	−85	−22	−98	−97	−28	−76[a]	0.013
6, C_s	$\tilde{X}_1A'$	−74	−84	−84	−25	−96	−96	−30	−74[a]	0.013
7, C_s	$\tilde{X}_1A'$	−73	−82	−81	−27	−95	−93	−33	−72[a]	0.013
8, C_1	$\tilde{X}_1A$	−60	−64	−63	87	−74	−73	102	−62[a]	0.013
9, C_s	$\tilde{X}_1A'$	−60	−71	−72	−39	−80	−80	−43	−59[a]	0.014
10, C_1	$\tilde{X}_1A$	−56	−61	−60	86	−70	−68	98	−59[a]	0.013
11, C_s	$\tilde{X}_1A'$	−51	−63	24	−45	−72	−70	−53	−52[a]	0.024
12, C_s	$\tilde{X}_1A'$	−50	−58	−58	−47	−64	−64	−58	−50[a]	0.023
13, C_1	$\tilde{X}_1A$	−42	−48	−48	74	−57	−56	88	−45[a]	0.013
14, C_1	$\tilde{X}_1A$	−40	−3	−40	−7	−6	−7	−3	−39[a]	0.014
15, C_s	$\tilde{X}_1A'$	−24	−44	−48	1	−32	−36	6	−26[a]	0.014
16, C_s	$\tilde{X}_1A'$	−16	−34	−54	−15	−19	−24	−12	−13[a]	0.013
17, C_1	$\tilde{X}_1A$	−4	−32	−34	−39	−29	−28	−50	−6[a]	0.020
18, C_s	$\tilde{X}_1A'$	0	0	0	2	0	0	2	0[a]	0.014
19, C_s	$\tilde{X}_1A'$	1	26	21	−32	12	7	−37	1[a]	0.014
20, C_1	$\tilde{X}_1A$	1	10	10	187	−34	−34	271	1[a]	0.011
21, C_s	$\tilde{X}_1A'$	3	−26	−27	−80	−17	−18	−102	2[a]	0.055
22, C_1	$\tilde{X}_1A$	6	−4	−10	−60	−9	−15	−71	4[a]	0.021
23, C_1	$\tilde{X}_1A$	10	6	−8	−66	4	−2	−81	6[a]	0.023
24, C_1	$\tilde{X}_1A'$	13	−25	−24	−40	−12	−14	−65	9[a]	0.044
25, C_s	$\tilde{X}_1A'$	14	14	9	−26	−1	−6	−31	11[a]	0.013
26, C_s	$\tilde{X}_1A'$	15	−18	68	−85	−8	−9	−111	14[a]	0.080
27, C_s	$\tilde{X}_1A'$		−20	−21	−86	−1	−2	−120	−43[b]	0.047
28, C_s	$\tilde{X}_1A'$		−14	−15	−89	4	4	−124	−39[b]	0.067
29, C_s	$\tilde{X}_1A'$		−11	−16	−31	−21	−26	−39	−32[b]	0.014
30, C_s	$\tilde{X}_1A'$		4	−24	−40	−12	−14	−65	−30[b]	0.013
31, C_s	$\tilde{X}_1A'$		−23	−25	−97	−31	55	−77	−27[b]	0.076

[a] Calculated at the fc-CCSD(T)/cc-pVTZ//fc-CCSD(T)/cc-pVDZ level of theory. ZPVE values are taken from the fc-CCSD(T)/cc-pVDZ level. [b] Calculated at the fc-CCSD(T)/cc-pVTZ//B3LYP/6-311+G(d,p) level of theory. ZPVE values are taken from B3LYP/6-311+G(d,p). [c] Calculated at the CCSD/6-311+G(d,p)//B3LYP/6-311+G(d,p) level of theory.

Supporting Information) in their singlet ground electronic state directly led to their allene counterparts **1**, **2**, **3**, **8**, **10**, and **13**, respectively. One imaginary frequency is obtained for each isomers **1a** (benzo[7]annulen-6-ylidene, ν_i = 1461.75i cm^{-1}), **2a** (benzo[7]annulen-5-ylidene, ν_i = 217.77i cm^{-1}), **3a** (benzo[7]annulen-7-ylidene, ν_i = 134.77i cm^{-1}, 119.63i cm^{-1}), **8a** ((4Z,7Z,9Z)-cyclopenta[8]annulen-6-ylidene, ν_i = 377.36i cm^{-1}), **10a** ((3aZ,6Z,8Z)-cyclopenta[8]annulen-5-ylidene, ν_i = 507.32i cm^{-1}), and **13a** ((5Z,7Z,9Z)-cyclopenta[8]annulen-4-ylidene, ν_i = 292.69i cm^{-1}) at the B3LYP/6-311+G(d,p) level; thereby, they represent the transition state in the $C_{11}H_8$ PES.

Isomers **4**, **5** and **6**, **7** are the *anti*- and *syn*-conformer of 1- and 2-naphthylcarbene, respectively. The triplet state geometry of 1- and 2-naphthylcarbene is more stable than the singlet one. However, because of the presence of a very small singlet-triplet energy gap (ΔE_{ST}), the naphthylcarbene rearrangement chemistry was established in their singlet electronic state. In the early 1965, Trozzolo and co-workers have tried to determine the structures of (E)-1-naphthylcarbene (**4**), (E)-2-naphthylcarbene (**5**), (Z)-2-naphthylcarbene (**6**), and (Z)-1-naphthylcarbene (**7**) through electron paramagnetic resonance spectroscopy but only triplet 2-naphthylcarbenes (**5** and **6**) were identified (via ESR spectroscopy) in their respective ground electronic state.[84] Bicyclo[6.3.0]undeca-1,3,4,6,8,10-hexene (**8**), bicyclo[6.3.0]undeca-2,3,5,7,9,11-hexene (**10**), and bicyclo[6.3.0]undeca-1,2,4,6,8,10-hexene (**13**) are the cyclic allenes having one eight-membered ring and one five-membered ring fused together. They are 60, 56, and 42 kJ mol^{-1} lower in energy than **18**, respectively. In 2016, the allenes **8** and **10** were both identified by Sander's group,[82] and they are formed by the ring expansion reaction of 5-azulenylcarbene.

Other carbenes such as 2-methylene-naphthalen-1-ylidene (**9**), 4-methylene-naphthalen-1-ylidene (**12**), 7-methylene-naphthalen-1-ylidene (**21**), and 5-methylene-naphthalen-1-ylidene (**26**) are the methylene-substituted naphthalene ring containing carbene derivatives where the carbene carbon is present at the first position of the naphthalene ring, whereas in 1-methylene-naphthalen-2-ylidene (**11**), 6-methylene-naphthalen-2-ylidene (**27**), 8-methylene-naphthalen-2-ylidene (**28**), and 3-methylene-naphthalen-2-ylidene (**31**), the carbene carbon is present at the second position of the naphthalene ring. The isomers where the methylene carbon and carbene carbon are in the same six-membered ring (for example, **9**, **11**, and **12**) are lower in energy than **18**, whereas for carbenes with

Table 2. NICS (1 Å) (in Ppm) Values of Low-Lying $C_{11}H_8$ Isomers Calculated at the B3LYP/6-311+G(d,p) Level of Theory

	NICS (1 Å)		
isomer	left ring	right ring	center ring
1	−5.78	−10.07	N/A
2	−7.29	−4.71	N/A
3	−9.22	−7.51	N/A
4	−9.50	−7.79	N/A
5	−9.67	−7.84	N/A
6	−9.69	−8.40	N/A
7	−10.72	−7.01	N/A
8	−3.53	−7.43	N/A
9	−7.97	−7.58	N/A
10	−3.21	−6.28	N/A
11	−10.35	−7.18	N/A
12	−8.74	−8.20	N/A
13	−2.61	−6.65	N/A
14	−8.91	−3.96	N/A
15	−8.61	−7.09	N/A
16	−9.20	−6.70	N/A
17	−3.6	−16.62	N/A
18	−7.75	−10.73	N/A
19	−7.51	−1.62	N/A
20	−9.73	−17.07	−1.23
21	−0.98	−9.35	N/A
22	−6.77	3.66	N/A
23	−7.48	2.76	N/A
24	−2.20	−9.59	N/A
25	−7.27	−1.66	N/A
26	−1.20	−10.38	N/A
27	5.37	−1.71	N/A
28	4.03	13.08	N/A
29	9.31	1.73	N/A
30	9.37	0.76	N/A
31	6.30	9.09	N/A

the methylene carbon in the other six-membered ring than the carbene carbon (for example, **21** and **26**), they are comparatively higher in energy. This is due to the fact that **9**, **11**, and **12** are more stabilized by resonance. 4-methylene-1,4-dihydronaphthalene (derivative of **12**) was experimentally identified by Griffth and co-workers in 1989.[88] The hydrocarbon derivative of **9** (2-methylene-1,2-dihydronaphthale) and **11** (*l*-methylene-1,2-dihydronaphthale) have been experimentally identified by Scott and co-workers in 1978.[89] To the best of our knowledge, the parent isomers of **9** and **11** and the other new isomers **12**, **21**, **26**, **27**, **28** and **31** that are identified theoretically in this work remain elusive in the laboratory till date.

Isomer **13** is an allene-like neutral molecule and still obscure in the laboratory. To the best of our knowledge, 1-methyleneazulene-8-ylidene (**14**) is the new carbene isomer in the $C_{11}H_8$ PES. However, the allene counterpart of **14**, that is, 10-methylenebicyclo[5.3.0]deca-1,2,4,6,8-pentene, was experimentally detected from the diazosalt.[82] The mechanism for the conversion of the latter from **18** through the quantum mechanical tunneling (QMT) process was also established elsewhere.[81] 2,3-dimethylene-1H-inden-1-ylidene (**15**) and 1,3-dimethylene-1H-inden-2-ylidene (**16**) are the bi-methylene-substituted indene derivatives having carbene carbon at the first and second position of the indenyl ring, respectively. Both of them are thermodynamically more stable than **18** and also unidentified in the laboratory till date. In 1988, the 2,2-bimethyl derivative of **16** has been experimentally determined through the Wittig reaction.[90] 1H-benzo[7]annulen-1-ylidene (**17**) and bicyclo[5.4.0]undeca-2,4,6,8,11-pentaene-10-ylidene (**24**) have same the skeletal structure but differs on their carbene carbon center. **17** is 4 kJ mol^{-1} lower in energy, but **24** is 13 kJ mol^{-1} higher in energy than **18**. Isomer **17** has been identified elsewhere in the literature.[81] However, isomer 24 is still unidentified in the laboratory. (7Z)-1-methylene-7-indenylcarbene (**19**) and (7E)-1-methylene-7-indenylcarbene (**25**) are 1 and 14 kJ mol^{-1} higher in energy, respectively, than **18**. Henkel et al. have theoretically identified isomer **25** as a reactive intermediate for the formation of $C_{11}H_8$ global minima from **18**.[82] However, the experimental evidence of **19** and **25** are still absent in the laboratory. 1H-cyclopropa[*b*]naphthalen-1-ylidene (**20**) is a tricyclic ring containing carbene isomers where two six-membered and one three-membered rings are fused together, and the carbene center is present in the strained three-membered ring. Isomer **20** is still elusive in the laboratory. The hydrocarbon derivatives of (E)-2-(1H-inden-1-ylidene)ethan-1-ylidene (**22**) and (Z)-2-(1H-inden-1-ylidene)-ethan-1-ylidene (**23**) are basically formed through the intramolecular Heck reaction.[91] However, the experimental evidence for **22** (6 kJ mol^{-1} higher in energy than **18**) and **23** (10 kJ mol^{-1} higher in energy than **18**) are still missing in the literature. (1-methylene-1H-inden-2-yl)methylidene (**29**) and (1-methylene-1H-inden-3-yl)methylidene (**30**) are the methylene-substituted indenyl ring containing methylidene derivatives. Both of them are elusive in the laboratory to date. For isomers **27**, **28**, **29**, **30**, and **31**, calculations are carried out at the fc-CCSD(T)/cc-pVTZ//B3LYP/6-311+G(d,p) level of theory. Also, we have studied the possible rotamers of **18**, **29**, and **30** and included their structures in the Supporting Information (Figure S3).

2.2. Rearrangement Scheme. We have divided the whole rearrangement scheme into four parts: (i) rearrangement of 1- and 2-naphthylcarbene (Figure 2), (ii) rearrangement of 1- and 2-azulenylcarbene (Figure 3), (iii) rearrangement reaction for the formation of global minima from other low-lying carbene/allene isomers (Figure 4), and (iv) Rearrangement of unidentified methylene-substituted carbenes (Figure 5). We have identified appropriate transition states and intermediates involved in the rearrangement process, and the corresponding activation energies are shown in the form of a relative potential energy diagram.

2.2.1. Rearrangement of 1- and 2-Naphthylcarbene. There is no experimental evidence to prepare 1-naphthylcarbene (**4**) from the reversible ring-closer reaction of 2-naphthylcarbene (**5**) in the solution phase.[92−96] At the high-temperature gas-phase reaction condition (360−375 °C), the conversion of **5** into **4** was postulated from their diazo precursor using the pyrolysis method.[97] Either through flash vacuum pyrolysis of 1- or 2-naphthyldiazomethane[70,98,99] or thermal reaction of atomic carbon with naphthalene,[76] cyclobuta[*de*]naphthalene (**42**) has been formed as a final product. Based on these experimental observations, we have proposed a detailed rearrangement scheme of 1- and 2-napthylcarbene and the formation of new methylene-naphthalen-ylidenes in this work, as shown in Figure 2.

The rearrangement between 1- and 2-napthylcarbene takes place via allene-like reactive intermediate bicyclo[5.4.0]-undeca-2,3,5,7,9,11-hexene (**1**). **2a** (benzo[7]annulen-5-ylidene, ν_i = 217.77i cm^{-1}), the allene counterpart of **2**, acts as a transition state to form **2** through the carbene−allene interconversion rearrangement process. Furthermore, a ring-closing rearrangement takes place at **2** to form a three-membered strained ring containing 1aH-cyclopropa[*a*]-naphthalene (**32**), which is 7 kJ mol^{-1} lower in energy than **2**. This reaction goes through the transition state (**TS1**) with an activation energy (E_a) of 165 kJ mol^{-1}. **TS1** has one imaginary frequency (ν_i) at 433.32i cm^{-1}, which corresponds to the ring-closing reaction in **2** to form **32**. Ring-opening reaction of **32** leads to the formation of 1-naptylcarbene (**4**) through **TS2** (E_a = 61 kJ mol^{-1}, ν_i = 323.87i cm^{-1}).

In a similar fashion, the reaction intermediate **3a** (benzo[7]-annulen-7-ylidene, ν_i = 134.77i cm^{-1}, 119.63i cm^{-1}) and the carbene counterpart of **3** can undergo similar ring-closing and ring-opening reactions to form 2-naphthylcarbene (**5**) through the formation of highly strained cyclopropenes (7bH-cyclopropa[*a*]naphthalene, **33**) as a product intermediate. Two transition states **TS4** (E_a = 150 kJ mol^{-1}, ν_i = 422.54i cm^{-1}) and **TS5** (E_a = 155 kJ mol^{-1}, ν_i = 334.28i cm^{-1}) have been identified for these two steps for the rearrangement from **3** to **5**.

A ring-closing and ring-opening reaction can take place simultaneously either from 1-naphthylcarbene (**4**) or from 2-naphthylcarbene (**5**) to form **1**, which is 78 kJ mol^{-1} lower in energy than both **4** and **5**. These rearrangements can proceed through **TS3** (ν_i = 253.92i cm^{-1}) and **TS6** (ν_i = 349.31i cm^{-1}) with an approximately similar activation energy of (E_a) 98 kJ mol^{-1}. Again, **1** can also be formed from its carbene counterpart **1a** (benzo[7]annulen-6-ylidene, ν_i = 1461.75i cm^{-1}), which is not a minimum in $C_{11}H_8$ PES.

Although experimental groups are yet to identify, two low-lying methylene-naphthalen-ylidenes (methylene-substituted naphthalene ring containing carbene derivatives, isomers **9** and **11**) can also be prepared from 1- and 2-naphthylcarbene rearrangement reaction. A hydrogen transfer and ring-closing reaction can take place simultaneously from **4** to form 1H-cyclopropa[*a*]naphthalene (**34**), which is 163 kJ mol^{-1} lower in energy than **18**. This reaction goes through **TS7** (E_a = 55 kJ mol^{-1}, ν_i = 1556.17i cm^{-1}). Again, **34** can also be obtained from **5** via similar simultaneous hydrogen transfer and ring-closing reaction. **TS8** (E_a = 58 kJ mol^{-1}, ν_i = 1565.53i cm^{-1}) can be a possible transition state for this reaction. Again ring-opening reaction of **34** can lead to the formation of low-lying isomers **9** and **11** through **TS9** (E_a = −56 kJ mol^{-1}, ν_i = 363.03i cm^{-1}) and **TS10** (E_a = −54 kJ mol^{-1}, ν_i = 346.33i cm^{-1}), respectively.

2.2.2. Rearrangement of 1- and 2-Azulenylcarbene. Using the flash vacuum pyrolysis method, the diazo precursor of **18** (that is, 1-azulenyldiazomethane) produces 1H-cyclopenta-[*cd*]indene (**40**), which is the global minima on the $C_{11}H_8$ PES.[79] At similar conditions, 5-(2-azulenyl)tetrazole (precursor of 2-azulenylcarbene) also yields **40**.[79] Earlier reports indicated a pathway where 1- and 2-azulenylcarbene have been connected together through bicyclo-[5.4.0]undeca-1,3,5,7,10-pentaen-10-ylidene (**24**).[82] However, at 10 K temperature, this irradiation did not lead to 1- and 2-azulenylcarbene rearrangement under matrix isolation conditions.

In a previous study,[63] we have identified two types of ring-closing rearrangement *via* the carbene carbon of **18**; (i) ring-closing within the five-membered ring and (ii) ring-closing reaction toward the neighboring seven-membered ring. In both cases, the final product was the global minimum (**40**). As an alternative pathway, during the rearrangement between **18** to form 2-azulenylcarbene (**37**), **18** might undergo ring-closing reaction within the five-membered ring to form a strained three-membered propene ring containing 7aH-cyclopropa[*a*]-azulene (**35**, 66 kJ mol^{-1} higher energy than **18**). **TS11** (E_a = 442 kJ mol^{-1}, ν_i = 375.27i cm^{-1}) acts as the ring-closing transition state for this rearrangement. From **35**, the rearrangement can proceed through two possible pathways: (i) ring-opening reaction to form relatively more stable (98 kJ mol^{-1}) isomer bicyclo[5.4.0]undeca-1,3,5,7,9-pentaene-11-ylidene (**17**) through transition state **TS12**, (E_a = 193 kJ mol^{-1}, ν_i = 496.41i cm^{-1}) or (ii) hydrogen transfer reaction to form 1aH-cyclopropa[*a*]azulene (**36**), which requires relatively high activation energy (**TS13**, E_a = 389 kJ mol^{-1}, ν_i = 1192.70i cm^{-1}). Again, 2-azulenylcarbene (**37**) undergoes ring-closing reaction to form relatively less stable (17 kJ mol^{-1}) isomer 1aH-cyclopropa[*a*]azulene (**36**) through **TS14** (E_a = 322 kJ mol^{-1}, ν_i = 595.80i cm^{-1}). From **36**, the rearrangement can proceed through two possible pathways: (i) ring-opening reaction to form relatively more stable (93 kJ mol^{-1}) isomer bicyclo[5.4.0]undeca-2,4,6,8,11-pentaene-10-ylidene (**24**) through transition state **TS15** (E_a = 242 kJ mol^{-1}, ν_i = 494.63i cm^{-1}) or (ii) hydrogen transfer reaction to form 7aH-cyclopropa[*a*]azulene (**35**), which requires relatively high activation energy (**TS13**, E_a = 387 kJ mol^{-1}, ν_i = 1192.70i cm^{-1}). Thus, from this rearrangement scheme, we can easily conclude that 1- and 2-azulenylcarbenes are connected together through **35** and **36**, unlike the rearrangement between 2- to 1-naphthylcarbene, where **17** and **24** are the two side products.

2.2.3. Rearrangement Reaction for the Formation of Global Minima from Other Low-lying Carbene Isomers. The rearrangement **18** via 1-naphthylcarbene (**4**) and cyclobuta-[*de*]naphthalene (**42**) ultimately produces the $C_{11}H_8$ global minima 1H-cyclopenta[*cd*]indene (**40**). Detailed discussion and the plausible rearrangement schemes can be found elsewhere in our study.[63] In this section, we discuss a possible rearrangement scheme for the formation of global minimum (**40**) on the $C_{11}H_8$ PES from other low-lying carbenes **14** and **23**, which are thermodynamically more stable than **18** according to the B3LYP/6−311(+)G(d,p) level of calculations.

1-Methyleneazulene-8-ylidene (**14**) is a seven-membered carbene-like structure that can undergo ring-closing reaction to form 6-methylene-1a,6-dihydrocyclopropa[*e*]indene (**38**) through **TS16** (E_a = 130 kJ mol^{-1}, ν_i = 425.18i cm^{-1}). As the three-membered ring is much stained, ring-opening reaction will take place to form relatively less stable (10 kJ mol^{-1}) (7Z)-1-methylene-7-indenylcarbene (**19**). This ring-opening reaction goes through **TS17** (E_a = 207 kJ mol^{-1}, ν_i = 584.26i cm^{-1}). Again, ring-closing reaction of carbene **19** led to the formation of 2H-cyclopenta[*cd*]indene (**39**), which is a prototropic tautomer of $C_{11}H_8$ global minima (**40**). **TS18** (E_a = 112 kJ mol^{-1}, ν_i = 363.76i cm^{-1}) acts as a transition state for this ring-closing reaction. A hydrogen transfer rearrangement takes place from **39** to form **40** (1H-cyclopenta[*cd*]indene). The hydrogen transfer reaction goes through the transition state **TS19** (E_a = 68 kJ mol^{-1}, ν_i = 1534.24i cm^{-1}).

(Z)-2-(1H-inden-1-ylidene)ethan-1-ylidene (**23**) can undergo ring-closing rearrangement through two possible pathways: (i) a ring-closing rearrangement to form a more stable (108 kJ mol^{-1}) 4aH-cyclopenta[*cd*]indene (**41**) and followed by hydrogen transfer takes place to form **42**. This pathway might go through **TS20** (E_a = 351 kJ mol^{-1}, ν_i = 230.79i cm^{-1}) and **TS21** (E_a = 268 kJ mol^{-1}, ν_i = 1118.18i cm^{-1}). (ii) An alternative pathway would be simultaneous ring-closing and hydrogen transfer to form **40**, which might proceed through **TS22** (E_a = 183 kJ mol^{-1}, ν_i = 306.55i cm^{-1}). A simultaneous ring-closing and hydrogen transfer pathway might be thermodynamically more favorable because of lower activation energy.

2.2.4. Rearrangement of Unidentified Methylene-Substituted Carbenes. The experimental evidence and theoretical predictions for the formation of low-lying bi-methylene-substituted indene ring containing carbene derivatives (**15** and **16**) and methylene-substituted naphthalene ring containing carbene derivative (isomer **12**) are still elusive in the literature. We have proposed a plausible rearrangement scheme for the formation of isomers **12**, **15**, and **16** in Figure 5. These isomers can be synthesized from **29** (1-methylene-1H-inden-2-yl), which is 11 kJ mol^{-1} lower in energy than **18**. A ring-closing reaction can take place from **29** to form 6-methylene-1a,6-dihydrocyclopropa[*a*]indene (**43**). A low activation barrier (E_a = 31 kJ mol^{-1}) is required to complete this reaction via **TS23** (ν_i = 290.09i cm^{-1}). Again, 1,2-H sifting rearrangement from **43** goes through two possible pathways: (i) hydrogen shifting takes place from the five-membered ring to the neighboring three-membered ring to form 6-methylene-1,6-dihydrocyclopropa[*a*]indene (**44**) through **TS24** (E_a = 175 kJ mol^{-1}, ν_i = 1605.96i cm^{-1}) and (ii) hydrogen shifting takes place within the same five-membered ring to form 6-methylene-6,6a-dihydrocyclopropa[*a*]indene (**45**) via **TS27** (E_a = 212 kJ mol^{-1}, ν_i = 1192.80i cm^{-1}). Ring-opening reaction from the strained three-membered ring of **44** can lead to the formation of isomers **15** and **16** through **TS25** (E_a = 15 kJ mol^{-1}, ν_i = 442.28i cm^{-1}) and **TS26** (E_a = 15 kJ mol^{-1}, ν_i = 409.20i cm^{-1}), respectively. Again, another 1,2-H sifting rearrangement from the five-membered ring to the neighboring three-membered ring can take place from **45** to form **44**. Relatively high activation energy is required for this conversion via **TS28** (E_a = 171 kJ mol^{-1}, ν_i = 1574.31i cm^{-1}). Ring-opening reaction from **45** goes through two possible pathways: (i) ring-opening of three-membered ring leads to the formation of two six-membered ring containing methylene substituted carbene (**12**) through **TS29** (E_a = 35 kJ mol^{-1}, ν_i = 452.21i cm^{-1}) and (ii) another ring-opening reaction of three-membered ring forms (1-methylene-1H-inden-3-yl)-methylidene (**30**) via **TS30** (E_a = 50 kJ mol^{-1}, ν_i = 280.01i cm^{-1}).

2.3. Aromatic Characteristics. All carbene/cyclic allene-like structures presented in this study have gained stability through resonances. Therefore, to determine the aromatic stability, NICS values have been calculated at 1 Å above the plane of each ring for the low-lying isomers of $C_{11}H_8$ at the B3LYP/6-311+G(d,p) level. Ghost atoms are placed approximately at the center position of each ring. These calculations have been carried out using the optimized equilibrium geometries at the same level. Most of the NICS values obtained have been found to be negative, indicating their aromatic nature (Table 2). Except isomer **20**, all the isomers are bicyclic in nature; thus, two NICS values have been calculated corresponding to the two rings. Likewise, for isomer **20** (tricyclic), three NICS values have been calculated. Among the low-lying isomers, because of the presence of the aromatic naphthyl-ring, one could see higher NICS values for isomers **4** (−9.50, −7.79 ppm), **5** (−9.67, −7.84 ppm), **6** (−9.69, −8.40 ppm), and **7** (−10.72, −7.01 ppm). Also, the tricyclic isomer **20** shows higher aromatic character with NICS (1 Å) values of −9.73, −1.23, and −17.07 ppm respectively, for six-, six-, and three-membered rings.

3. CONCLUSIONS

In summary, low-lying carbene/cyclic allene isomers of $C_{11}H_8$ have been theoretically investigated using DFT and CC methods. Geometry optimizations and frequency calculations have been carried out at the B3LYP/6-311+G(d,p) and ωB97XD/6-311+G(d,p) levels of theory. Furthermore, geometry optimization and frequency calculations have been performed by incorporating high-level electron correlation effect in the CC method at the fc-CCSD(T)/cc-pVDZ level. Out of the 31 low-lying isomers, only nine isomers (**1**, **4**, **5**, **6**, **7**, **8**, **10**, **17**, and **18**) have been detected experimentally in the literature. The remaining twenty-two isomers (**2**, **3**, **9**, **11**, **12**, **13**, **14**, **15**, **16**, **19**, **20**, **21**, **22**, **23**, **24**, **25**, **26**, **27**, **28**, **29**, **30**, and **31**) are still elusive in the laboratory. Thermodynamically favorable low-energy thermal rearrangement schemes have been investigated theoretically. Here, four special carbene-carbene rearrangement schemes (i) rearrangement of 1- and 2-naphthylcarbene, (ii) rearrangement of 1- and 2-azulenylcarbene, (iii) rearrangement of unidentified methylene-substituted carbenes, and (iv) an overall rearrangement scheme have been discussed for the formation of global minimum from various low-lying carbene/cyclic allene isomers. All the appropriate transition states involved in these rearrangement schemes have been identified and verified through intrinsic reaction coordinate calculations at the B3LYP/6-311+G(d,p) level. Our theoretical data may aid synthetic organic chemists and molecular spectroscopists in identifying new low-lying $C_{11}H_8$ carbene/cyclic allene isomers in the laboratory. Moreover, the spectroscopic data (rotational constants and centrifugal distortion constants) of these isomers at higher-level quantum chemical calculation might be crucial to identifying new $C_{11}H_8$ carbene/cyclic allene isomers in the ISM. It is noted here that they are considered to be key reactive intermediates for the formation of PAHs in the ISM.

4. COMPUTATIONAL METHODOLOGY

For all isomers, both geometry optimization and frequency calculations have been carried out using CC singles and doubles (CCSD)[100] and CCSD with quasi perturbative triple excitation [CCSD(T)][101,102] methods to incorporate higher-level treatment of electron-correlation effects. In all CCSD and CCSD(T) calculations, the correlation-consistent polarized valence double zeta basis set of Dunning's (cc-pVDZ) has been used.[103] For $C_{11}H_8$, the latter basis set consists of 194 basis functions. Frozen-core approximation is utilized in all these calculations (i.e., the carbon 1s orbitals are frozen). For all stationary points obtained at the fc-CCSD(T)/cc-pVDZ level, harmonic vibrational frequencies were determined by the analytical calculation of second derivatives,[104] and single-point energy calculations have been carried out at the fc-CCSD(T)/cc-pVTZ//fc-CCSD(T)/cc-pVDZ level.

The mechanism for different rearrangement reactions has been studied using DFT. Therefore, geometry optimization and frequency calculations for all the transition states and carbene/allene isomers considered in this work have been carried out at the B3LYP[105,106]/6-311+G(d,p)[107,108] level. As the relative energies calculated by the B3LYP functional have been challenged for hydrocarbons,[109,110] the geometry optimization and frequency calculations have also been performed using the ωB97XD[111] hybrid functional with an identical basis set that incorporates empirical dispersion corrections.[112] All the transition states reported in this study have been identified after several trial calculations and verified through the intrinsic reaction coordinate (IRC) calculations.[113] The transition states connect the reactants to the products through the IRCs in the $C_{11}H_8$ PES.

Nuclear independent chemical shift (NICS) values[114−116] for all ring isomers have been calculated at the B3LYP/6-311+G(d,p) level at 1 Å above the plane of each ring for the low-lying isomers. To assess the multireference character of $C_{11}H_8$ isomers, T_1 diagnostic values[85] have been calculated at the CCSD/6-311+G(d,p)//B3LYP/6-311+G(d,p) level for all isomers. Both optimization and frequency calculations for all triplet electronic states are carried out at the UB3LYP/6-311+G(d,p) and UωB97XD/6-311+G(d,p) levels. All ab initio calculations have been carried out using the CFOUR program package,[117] whereas all DFT calculations have been performed using the Gaussian suite of program.[118]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c03224.

> Cartesian coordinates of the optimized geometries; total electronic energies; ZPVEs; dipole moments; rotational constants; NICS (1°A) values; and T_1 diagnostic values calculated at different levels (PDF)

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Notes

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