

Isomerization Mechanisms of C₅H₂ on the Triplet and Singlet Potential Energy Surfaces

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Density functional theory calculations with the B3LYP functional are used to study the structure and stabilities of C₅H₂ isomers and possible isomerization mechanisms on the triplet and singlet potential energy surfaces. Calculated results show that isomerization of C₅H₂ is likely to occur on the triplet potential energy surface while direct conversions of the singlet C₅H₂ isomers via 1,3-hydrogen migration transition states are extremely difficult dynamically. In such isomerization processes, the hydrogen transfer processes in carbon chains are the rate-determining steps. The triplet species except the linear ground state X³Σ_g⁻ are rather less stable than their singlet forms, although the singlet and triplet species have similar geometries.

Keywords C₅H₂, isomerization, DFT calculation

Introduction

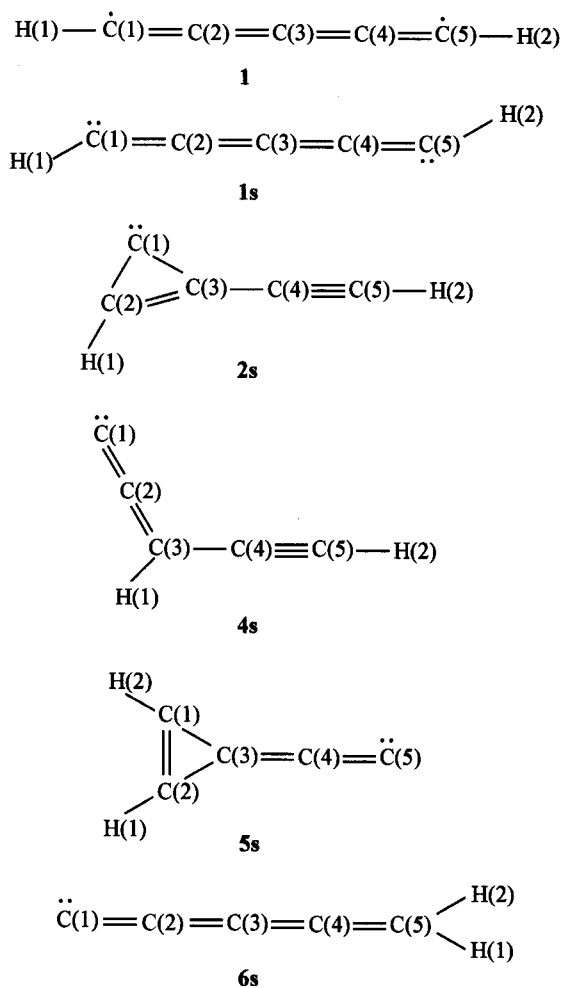
Simple carbon-rich systems C₃H₂, C₅H₂, C₇H₂ are of a widely astronomical interest because lots of carbon molecules have been detected in space.¹⁻³ Recently, the generation and characterization of such species are the subject of intensive investigation both experimentally and theoretically.⁴⁻⁸

Using matrix isolation and mass selection techniques, Maier and coworkers measured the electronic spectra of linear forms of HC_{2n+1}H (n = 2–7).⁴ Their experimental observations show that specific carbon chains are plausible candidates as carriers of the diffuse interstellar bands. By negative ion chemical ionization mass spectrometry in the gas phase, Bowie and co-workers synthesized the isomers C₄CH₂[·], C₂CHC₂H[·] and HC₅H[·]. Combining their experiments and theoretical calculations, they conclude that the neutrals C₄CH₂, C₂CHC₂H and HC₅H can exist as stable species.⁵

Using sophisticated coupled-cluster calculations, Seburg and co-workers predicted five isomers of the carbon-rich molecule C₅H₂ (Scheme 1). The most stable forms of C₅H₂ are linear triplet pentadiynylidene (**1**) and singlet ethynylcyclopropenylidene (**2s**).⁶ Such isomers of C₅H₂ were detected

by the microwave spectra of McCarthy *et al.* and they were found fairly stable.^{7,8} Furthermore, these experiments reveal a fairly close correlation of the abundances of C₅H₂ isomers

Scheme 1



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with the relative energies predicted by Seburg *et al.*, although each isomer is presumably formed from different mechanisms. This suggests that there is a thermodynamical equilibrium connecting isomers of C_5H_2 . In order to gain insight into conversion mechanisms among C_5H_2 isomers, density functional theory and *ab initio* calculations are applied to investigate structures, relative stabilities, and possible isomerization processes.

Computational details

Geometries, vibrational frequencies, and relative energetics of C_5H_2 isomers and transition state structures have been investigated by DFT calculations with the B3LYP functional^{9,10} and 6-31G* basis set in the *Gaussian 98* program package.¹¹ Analytic DFT frequency calculations were used to determine the intermediates and transition states of C_5H_2 . To calibrate DFT calculations on carbon-ring systems considered here, a comparison of DFT with previous CCSD calculations is given in Table 1. As Table 1 shows, DFT optimized geometries and relative energies are in good agreement with CCSD(T) calculations by Seburg *et al.*⁶

Results and discussion

Optimized geometries of intermediates and transition states on the triplet potential energy surfaces (PES) of C_5H_2 are shown in Fig. 1. Fig. 2 gives optimized geometries of 1, 3-hydrogen migration transition states on the singlet PES.

Figs. 3–5 display PES profiles along relevant isomerization paths.

Isomerization mechanism on the triplet PES

Potential energy surface profiles of isomerization processes from the intermediate **4** to the triplet linear ground state **1** and from **4** to the intermediate **6** are displayed in Fig. 3 and Fig. 4, respectively. In Fig. 3, the triplet intermediate **4** is less stable than the most stable species **1** by 204.12 kJ/mol. The triplet **4** is higher in energy than corresponding singlet **4s** by 111.72 kJ/mol. The closed-shell carbene **4s** is detected in the laboratory.^{7,8} The triplet **4** is presumably formed by either the direct $S_0 \rightarrow T_1$ excitation or by intersystem crossing (ISC) from $S_n \rightarrow T_1$ in **4s**. The $S_0 \rightarrow T_1$ transition is formally spin forbidden, but it can be enhanced by spin-orbit perturbation. Furthermore, the triplet **4** has geometry quite similar to the singlet **4s**, which will result in a large Frank-Condon factor for the $S_0 \rightarrow T_1$ transition.

In the isomerization path from **4** to **1**, first, **4** proceeds to the intermediate **3** through a hydrogen transfer transition state **TS1** with a barrier of 131.46 kJ/mol, followed by conversion from **3** to a more stable intermediate **2** via the carbon-ring transition state **TS2** with a neglectable barrier. Finally, **2** is converted to **1** through the carbon-ring opening **TS3** with a barrier of 29.28 kJ/mol.

The triplet intermediate **2** is only stable carbon-ring form on the triplet PES of C_5H_2 . **2** has a non-planar structure, in which the bond lengths of C(1)—C(2), C(2)—C(3), and C(1)—C(3) in the carbon-ring are 0.1308, 0.1531, and

Table 1 A comparison of B3LYP/6-31G* with CCSD(T)/cc-pVTZ calculations for selected C_5H_2 isomers

Species	1s		1		2s		4s		6s	
Method	DFT	DFT	CCSD(T)	DFT	CCSD(T)	DFT	CCSD(T)	DFT	CCSD(T)	
Symmetry	C_s	$D_{\infty h}$	$D_{\infty h}$	C_s	C_s	C_s	C_s	C_s	C_{2v}	
State	$^1A'$	$^3\Sigma_g^-$	$^3\Sigma_g^-$	$^1A'$	$^1A'$	$^1A'$	$^1A'$	1A_1	1A_1	
Relative energy (kJ·mol ⁻¹)	71.8 ^a	0.0 ^a	0.0 ^b	37.4 ^a	8.4 ^b	92.8 ^a	70.5 ^b	61.3 ^a	58.0 ^b	
Bond length (nm)										
C(1)—C(2)	0.1286	0.1244	0.1237	0.1286	0.1286	0.1289	0.1288			
C(1)—C(3)				0.1337	0.1331					
C(2)—C(3)	0.1282	0.1309	0.1308	0.1452	0.1433	0.1343	0.1337	0.1303	0.1300	
C(3)—C(4)	0.1315			0.1390	0.1394	0.1411	0.1413	0.1269	0.1266	
C(4)—C(5)	0.1243			0.1212	0.1209	0.1213	0.1211	0.1321	0.1322	
C(3)—H(1)	0.1095	0.1084								
C(1)—H(1)	0.1084									
C(5)—H(2)	0.1071	0.1066	0.1059	0.1067	0.1059	0.1068	0.1060	0.1090	0.1092	
Bond angle (°)										
C(1)-C(2)-C(3)							179.7	177.5		
C(2)-C(3)-C(4)				148.7	148.3	124.4	124.3			
C(3)-C(4)-C(5)				179.7	178.8	178.4	177.9			
C(1)-C(2)-C(4)				150.6	148.6	119.5	119.7			
H(2)-C(5)-C(4)				179.8	180.0	178.8	178.5	121.8	120.8	

^a DFT/B3LYP, ^b CCSD(T) from Ref. 6.

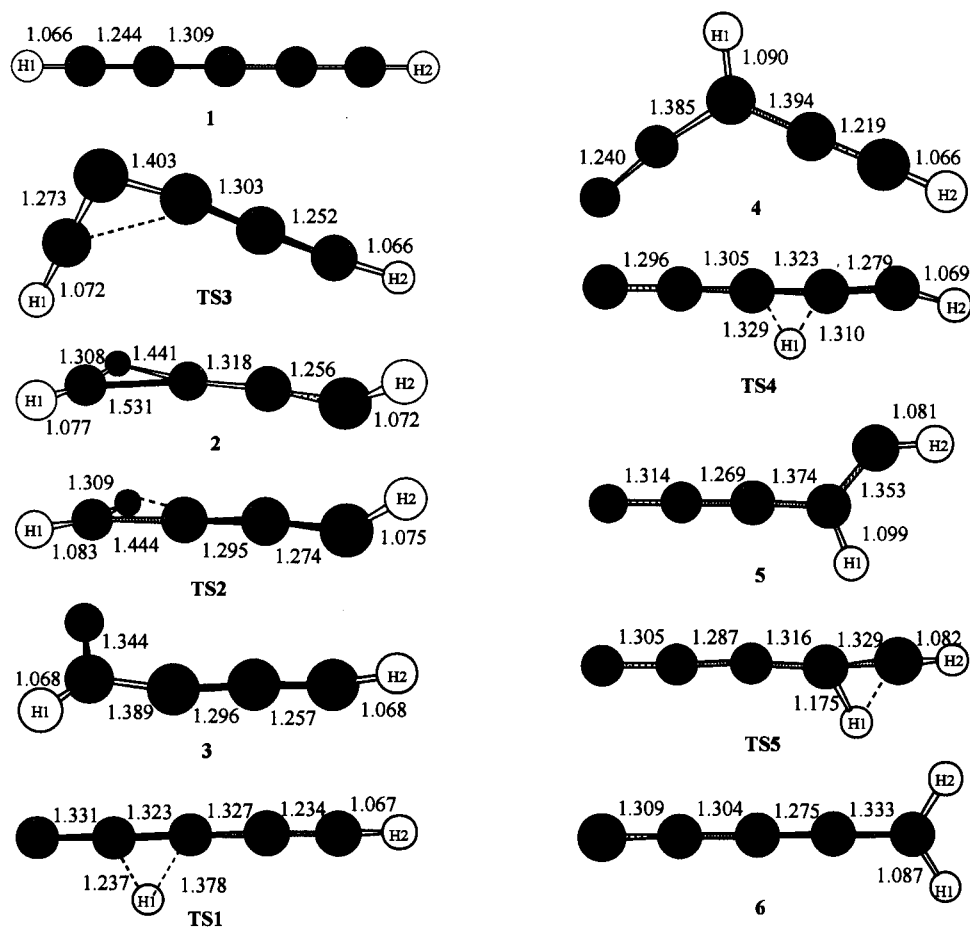


Fig. 1 Optimized geometries of intermediates and transition states of C_5H_2 on the triplet PES.



Fig. 2 Optimized geometries of 1,3-hydrogen migration transition states on the singlet PES.

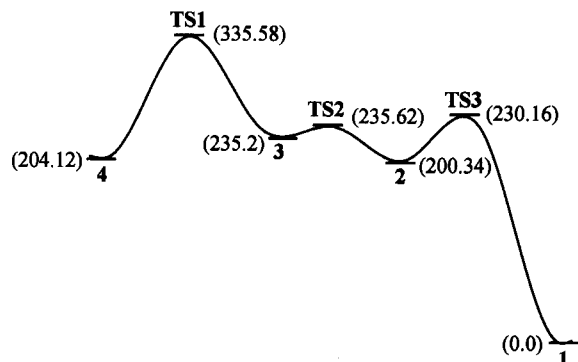


Fig. 3 Potential energy surface profile (kJ/mol) for conversion from 4 to 1.

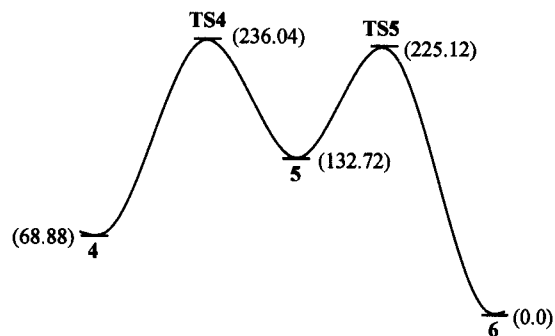


Fig. 4 Potential energy surface profile (kJ/mol) for conversion from 4 to 6.

0.1442 nm, respectively. **2** is higher in energy than its singlet form **2s** by 162.96 kJ/mol, and it may decay to the more stable singlet **2s** by spin quenching. The singlet **2s** is found to

lie above the linear isomer **1** by a small energy 37.24 kJ/mol at the B3LYP/6-31G* level, which is in agreement with the CCSD(T)/cc-pVTZ result of 8.41 kJ/mol.

Fig. 4 presents relative energetics of isomerization from **4** to **6**. The reaction from **4** to **6** may proceed by generation of the intermediate **5** through the hydrogen shift transition state **TS4** with a barrier of 167.16 kJ/mol, followed by conversion from **5** to **6** via a hydrogen shift transition state **TS5** with a barrier of 92.40 kJ/mol. The triplet **6** is less stable than its corresponding singlet **6s** by 73.92 kJ/mol. Since **6** has a geometry similar to **6s**, the triplet **6** may decay to the singlet **6s** within a Frank-Condon region by spin-orbit interaction. The singlet **6s** was detected in laboratory by McCarthy *et al.*^{7,8}

In the isomerization processes shown in Fig. 3 and Fig. 4, the hydrogen transfers to the neighbour carbon atom generally require high activation energies, whereas the barriers for the carbon chain cyclization and carbon-ring opening processes are relatively low. Therefore, the hydrogen transfer processes are the rate-determining step in such isomerizations on the triplet PES.

Isomerization mechanism on the singlet PES

To make sure if there are direct isomerization processes connecting the singlet isomers, we explored the feature of the singlet PES of C_5H_2 . Fig. 5 displays the PES profile for conversion of the singlet C_5H_2 isomers from **1s** to **6s**. Notably, all attempts to locate carbon-ring transition states similar to the triplet mechanisms failed at first, and current calculations located two 1,3-hydrogen migration transition states **TS6** and **TS7** accounting for direct conversions from **1s** to **4s** and from **4s** to **6s**, respectively. However, such isomerizations on the singlet PES have substantially high activation energies, and they are extremely unfavored dynamically on the singlet PES.

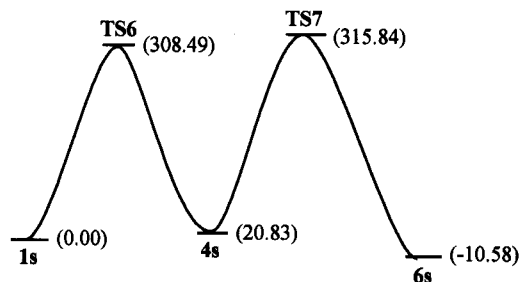


Fig. 5 Potential energy surface profile (kJ/mol) for isomerization from **1s** to **6s**.

Conclusion

Stable singlet and triplet forms and plausible isomerization mechanisms of C_5H_2 isomers are studied by the DFT approach. Present calculations show that the conversion of C_5H_2 isomers on the triplet PES is dynamically favored than the sin-

glet isomerization mechanism. Stable triplet intermediates are generally less stable than their singlet forms, although the triplet and its singlet partner have similar geometries. The metastable triplet species may be formed via the singlet-triplet transitions and intersystem crossings from the low-lying singlet excited states, and these triplet isomers may decay to their more stable singlet forms through spin quenching due to favorable Frank-Condon overlap. Generally, the hydrogen transfer in the carbon chain has relatively high barrier while the carbon chain cyclization and carbon-ring opening easily proceeds.

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