

Reaction of the ethynyl radical, C_2H , with methylacetylene, CH_3CCH , under single collision conditions: Implications for astrochemistry

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The reaction between the ethynyl radical, $C_2H(X^2\Sigma^+)$, and methylacetylene (X^1A_1'), which yields ethynylallene, pentadiyne, and butadiyne, has been studied at the density functional (B3LYP/6-311+G**) and coupled cluster (coupled-cluster single double perturbative triple/cc-pVTZ) levels of theory. These results agree with data from crossed molecular beam experiments where ethynylallene (**10**) and pentadiyne (**13**) have been observed. The $C_2H(1)$ radical initially attacks the π system of methylacetylene (**2**) without an entrance barrier to form Z-1-ethynylpropen-2-yl (**3**) or Z-2-ethynylpropen-1-yl (**4**) in highly exothermic reactions. Geometric considerations as well as the computed enthalpies suggest Z-1-ethynylpropen-2-yl (**3**) to be the dominant initial intermediate. Assuming single collision conditions as found in cold molecular clouds in the interstellar medium and distinct planetary atmospheres, numerous rearrangements may ensue the initial reaction step before ejection of a hydrogen atom or a methyl group releases the accumulated reaction energy. © 2001 American Institute of Physics. [DOI: 10.1063/1.1331360]

I. INTRODUCTION

Reactions of small radicals with neutral molecules play a significant role in diverse environments such as combustion flames,¹ the interstellar medium (ISM),²⁻⁶ and planetary atmospheres⁷⁻⁹ such as Saturn's moon Titan.

Carbon chain radicals with the general formula C_nH have been identified in the interstellar medium (ISM).^{5,6} Tucker¹⁰ reported the observation of the ethynyl radical (C_2H) 1974 in the Orion nebula. Seven years later, 1981, Sastry *et al.*¹¹ were able to record its rotational spectrum in a terrestrial laboratory. Analogously, C_4H was also first observed by astronomers¹² and the laboratory identification¹³ followed. The physical and chemical properties of this series of compounds have been the subject of comprehensive experimental¹⁴⁻¹⁸ as well as theoretical¹⁹⁻²⁴ studies.

Due to the low temperature and extremely low pressure in the ISM,³ reactions must proceed without or with only a very small entrance barrier. Unfortunately, kinetic and ther-

modynamic data of reactions at low temperatures are rare. However, considering that an initially associative process results in a positive value for the entropy, low temperatures in fact favor the reaction. In a series of kinetic studies of the ethynyl radical (C_2H) with saturated and unsaturated hydrocarbons, Leone *et al.*^{14,16,17} most recently reported low-temperature rate coefficients for reactions of C_2H with the C_3H_4 isomers methylacetylene (CH_3CCH , propyne) and allene (CH_2CCH_2)¹⁴ under pseudo-first-order conditions ($[C_3H_4] \gg [C_2H]$). The temperature ranged between 155 and 298 K. Both reactions are fast ($k_{CH_3CCH} = 1.9 \pm 0.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; $k_{CH_2CCH_2} = 1.7 \pm 0.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), pressure independent over the range 2.8–12 kPa at room temperature, and show zero-to-slightly-negative temperature dependencies. However, kinetic studies neither account for reaction products nor do they reveal reaction paths.

For the reaction of the ethynyl radical with methylacetylene, hydrogen abstraction [Eq. (1)], addition, and addition/elimination [Eqs. (2)–(4)] are thermodynamically possible but only limited experimental data to define the reaction products are available.²⁵

The fast rates and zero-to-slightly-negative temperature dependencies are indicative of addition–elimination mecha-

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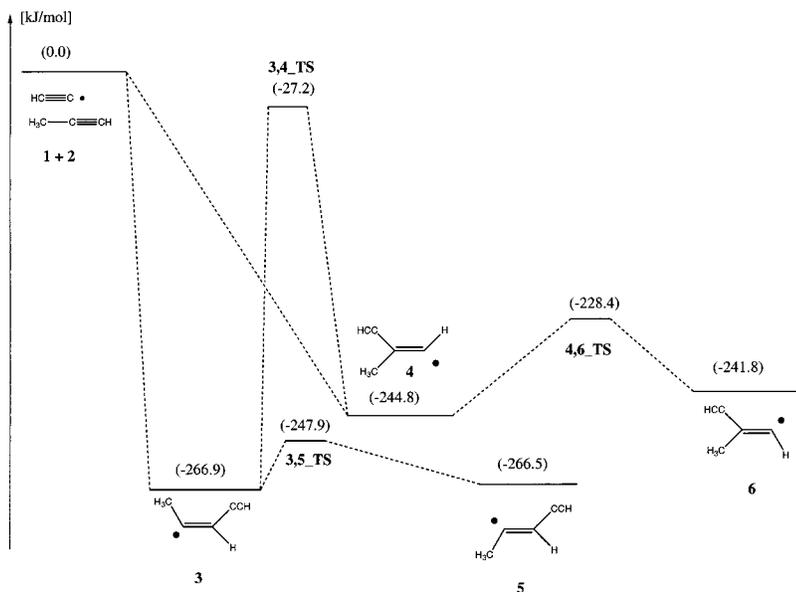
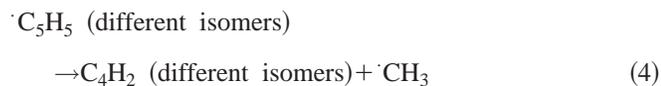
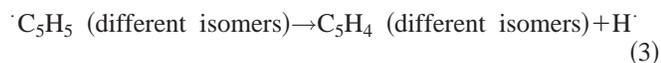
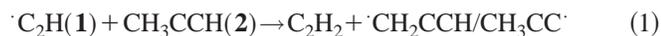


CHART 1. Schematic representation of part of the C₅H₅ potential energy surface (UB3LYP/6-311+G**): Initial intermediates and *cis/trans* isomerizations.

nism [Eqs. (2)–(4)] domination over hydrogen abstraction either from the methyl group or the acetylenic hydrogen [Eq. (1)]¹⁴ of methylacetylene. Furthermore, the high reaction rates at room temperature suggest the absence of an entry channel barrier.



Numerous theoretical studies have demonstrated the ability of C₂H to participate in barrierless reactions with neutral

molecules: Herbst and Woon²⁶ reported a limited *ab initio* study for the reaction of C₂H with acetylene (HCCH) [Eq. (5)]. They found no entrance barrier for this reaction and the exit-transition state for ejecting a hydrogen atom, exothermally yielding butadiyne (diacetylene, HCCCCH), is located below the reactants. Fukuzawa and Osamura²⁷ investigated comprehensive neutral–neutral reactions for the formation of cyanoacetylene (HCCCN), another prevalent species in ex-traterrestrial environments.^{8,9} They concluded that C₂H+HNC [Eq. (6)] and CN+HCCH [Eq. (8)] may proceed without an entrance barrier. Their CISD/DZ+P calculations predict the existence of a barrier for the reaction of C₂H+HCN [Eq. (7)], though only 6.3 kcal mol⁻¹ that further diminishes to 1.6 kcal mol⁻¹ at CCSD(T)/cc-pVTZ//CISD/DZ+P.

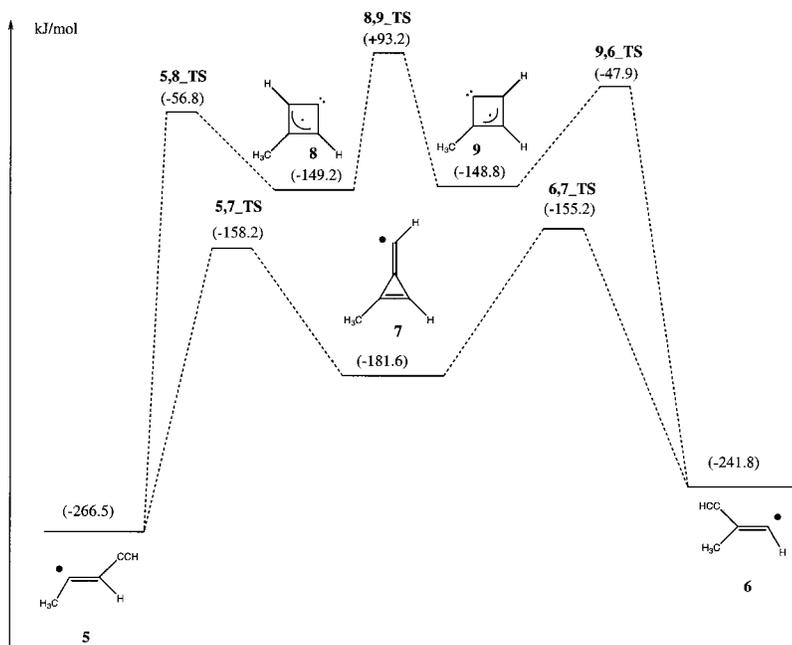
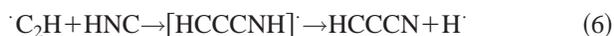


CHART 2. Schematic representation of part of the C₅H₅ potential energy surface (UB3LYP/6-311+G**): Cyclic intermediates connecting 5 and 6.



The following extensive density functional and *ab initio* study of the reaction of the ethynyl radical (C_2H) with methylacetylene (CH_3CCH) was carried out as part of an ongoing project within the international astrophysics network to investigate reactions of small radicals with neutral hydrocarbons under conditions found in extraterrestrial environments. Kaiser *et al.* studied the title reaction employing partially deuterated reactants C_2D and CD_3CCH using the crossed molecular beam technique at a collision energy of 39.8 kJ mol^{-1} and mass-spectroscopically identified products of the general formula C_5H_4 with an exothermicity of $100\text{--}130 \text{ kJ mol}^{-1}$.²⁸ To unravel the elusive reaction mechanism and explore alternative reaction paths we conducted a complementary theoretical study.

At this point we would like to emphasize that bulk experiments which involve ternary processes may give different results. In the following we assume that the reaction energy is accumulated in the individual intermediates and cannot be released via elastic collisions.

The remainder of the paper is structured as follows: The computational methods employed for this study are described in Sec. II, we briefly summarize all the investigated reaction paths in Sec. III, and a discussion of the most comprehensive paths together with a more precise examination of the reaction enthalpies follows in Sec. IV. Astrochemical implications, conclusions, and outlook, Sec. V, constitute the final section of this article.

II. COMPUTATIONAL METHODS

Geometries of stationary points were optimized with the 6-311+G** basis set²⁹⁻³¹ and Becke's³² three parameter hybrid functional in conjunction with the correlation functional of Lee, Yang, and Parr³³ (B3LYP) as implemented in the GAUSSIAN 98³⁴ program package. The spin-unrestricted formalism was employed for all species, spin-contamination turned out to be negligible. Harmonic vibrational frequencies and zero-point vibrational energy (ZPVE) corrections were computed at UB3LYP/6-311+G**. The latter were used unscaled to correct the UB3LYP/6-311+G** energies.

Note, the ethynyl radical (C_2H , **1**) in its ground state ($X^2\Sigma^+$)²³ is known to have a linear structure¹⁸ but it is incorrectly described as a second-order saddle point at UB3LYP/6-31G* and UB3LYP/6-31+G*. The linear form is correctly characterized as a minimum with the 6-311G** and 6-311+G** basis sets.

This unexpected behavior prohibits the use of the G2(B3LYP/MP2)³⁵⁻³⁷ model, which uses B3LYP/6-31G* geometries and ZPVEs, as employed earlier by our group in related studies^{38,39} to achieve chemical accuracy ($\pm 5 \text{ kJ mol}^{-1}$) for the reaction enthalpies. Alternatively, we computed coupled-cluster single double perturbative triple [CCSD(T)] single point energies using the

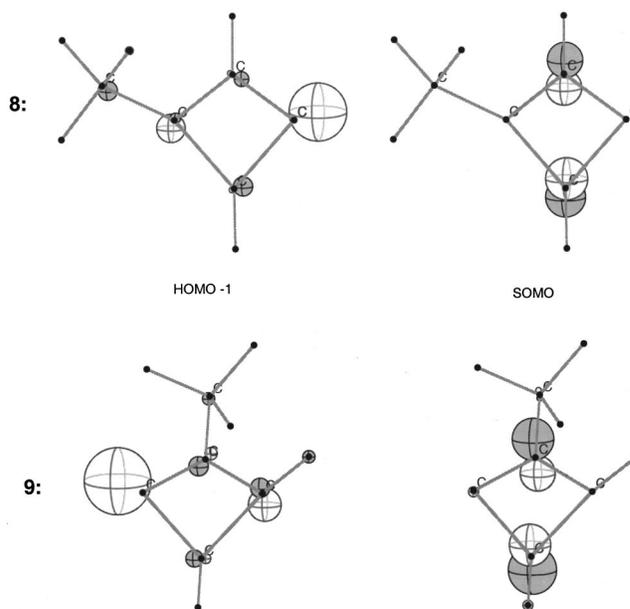


FIG. 1. Schematic representation of the highest two occupied molecular orbitals of the four-membered ring intermediates **8** and **9**, calculated at UB3LYP/6-311+G**.

UB3LYP/6-311+G** geometries and unscaled ZPVE. A TZ2P basis set, constructed from Dunning's triple- ζ C ($10s6p/5s3p$), H($5s/3s$) contraction⁴⁰ augmented with two sets of (2,1) contracted polarization functions with orbital exponents $\alpha_d(\text{C})=1.3751, 0.4073, 0.34$ and $\alpha_p(\text{H})=1.2203, 0.2839, 0.26$ as well as the correlation consistent cc-pVTZ basis set^{41,42} were utilized. The absence of multi-reference character for C_2H is indicated by T_1 diagnostics^{43,44} with a value of 0.0013 at CCSD(T)/cc-pVTZ. The ACES2 program suite⁴⁵ was utilized for the coupled cluster calculations.

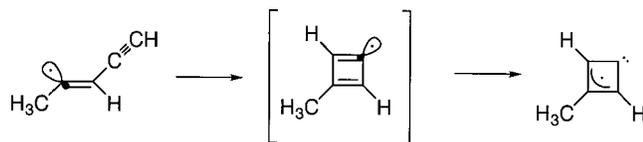
To probe aromaticity, GIAO-UB3LYP/6-311+G** nucleus independent chemical shifts (NICS)⁴⁶ were computed for selected structures.

All energies referred to in the text are calculated at UB3LYP/6-311+G** using unscaled UB3LYP/6-311+G** ZPVE corrections unless noted otherwise.

III. REACTION CHANNELS ON THE DOUBLET C_5H_5 POTENTIAL ENERGY SURFACE

A. Initial reaction intermediates

The highly reactive ethynyl radical (**1**) attacks the π system of methylacetylene (**2**) without an entrance barrier to either give *Z*-1-ethynylpropen-2-yl (**3**) or *Z*-2-ethynylpropen-1-yl (**4**) in a highly exothermic reaction (*E/Z* defines the position of the ethynyl moiety relative to the substituent on the other end of the C–C double bond, cf. Chart 1). The absence of a barrier is stated by the experimental results.²⁸ Computationally we found only one stationary point for C_2H (**1**) approaching methylacetylene (**2**), which we identified as the transition state (**3,4**_TS) connecting the two minima **3** and **4**. The existence of this reaction channel was confirmed by intrinsic reaction coordinate (IRC) calculation

SCHEME 1. Formal cyclization reaction of **5**.

at UB3LYP/6-311+G^{**}. Furthermore we performed relaxed scans of the attack of **1** on **2** in which the energy constantly decreased.

In competition of the two entry channels, formation of **3** is favored over **4** by 22.1 kJ mol⁻¹. Intuitive geometric considerations also suggest C2 of **2** as less approachable due to its attached methyl group. This might also favor binding of the ethynyl radical (**1**) to C1 of propyne (methylacetylene, **2**) rather than to C2. *Cis-trans* isomerizations **3/5** via **3,5_TS** and **4/6** via **4,6_TS** proceed through very low lying barriers. Note that the transition state for *cis-trans* isomerization **3/5** is located below the relative reaction energy of **4**. Hence, an ultrafast rearrangement and a near equal distribution of **3** and **5** are anticipated.

B. Cyclization reactions of **5** and **6**

In both *trans* intermediates, E-1-ethynylpropen-2-yl (**5**) and E-2-ethynylpropenyl (**6**), the unpaired electron may attack the ethyne moiety undergoing cyclization to either three- or four-membered rings (Chart 2). The reaction path via formation of 1-methyl-3-methylenecyclopropene (**7**) connects **5** and **6** directly. Alternatively, the four-membered ring species **8** and **9** can be generated. The barrier for hydrogen shift between the latter is high above the energy of the separated reactants.

C. The nature of the four-membered ring intermediates, **8** and **9**, as well as their related transition states

Formally, attack of the unpaired vinylic electron at the terminal carbon atom of the ethyne moiety, followed by ring closure, would yield an antiaromatic 4π+1σ electronic arrangement (Scheme 1).

The system avoids this unfavorable planar structure by folding the ring. This results in an allyl system bridged by a

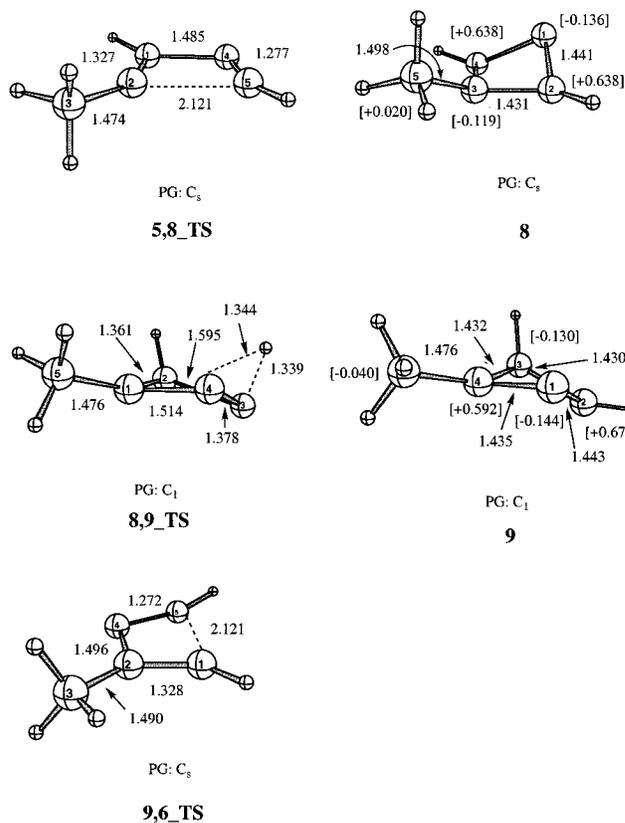


FIG. 2. Optimized geometries (UB3LYP/6-311+G^{**}) of **8** and **9** and related transition states, bond lengths are given in Å, spin densities in parentheses.

carbene-type carbon.³⁹ The latter is nicely depicted by the calculated molecular orbitals (Fig. 1). The highest doubly occupied molecular orbital (HOMO-1) shows the singlet carbene arrangement at the divalent carbon while the singly occupied molecular orbital (SOMO) is allyl-like. Analysis of the spin density also indicates the presence of an allyl system (Fig. 2). This electronic arrangement clarifies the height of the barrier for the 1,2-hydrogen shift, **8,9_TS**. Though **8** and **9** are puckered all the carbon atoms in the transition states forming the four-membered ring species, **5,8_TS** and **9,6_TS**, are in-plane. Hence, the molecular orbitals are characteristic for a diene π system and the SOMO characterizes the radical center attacking the triple bond (Fig. 3). The NICS

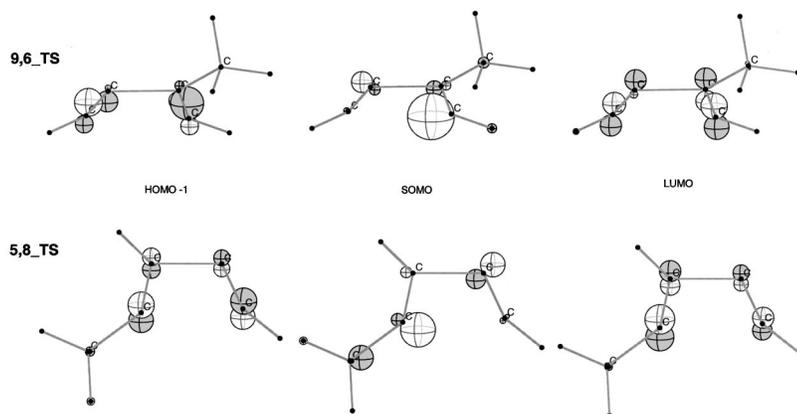


FIG. 3. Schematic representation of the highest two occupied and the lowest two unoccupied orbitals of the transition states forming the four-membered ring species **8** and **9**, calculated at UB3LYP/6-311+G^{**}.

TABLE I. Calculated NICS values (GIAO-UB3LYP/6-311+G**//UB3LYP/6-311+G**) at the geometrical centers and at points above (and below where applicable) for the four-membered ring intermediates **8** and **9**, and related transition states.

	0.0 ^a	+0.5 (-0.5)	+1.0 (-1.0)	+1.5 (-1.5)	+2.0 (-2.0)
5,8_TS	+4.1	+5.8	+5.1	+3.1	+1.8
8	-9.8	-23.1 (+4.1)	-12.8 (+1.1)	-5.7 (-0.8)	-2.8 (-0.9)
9,6_TS	+4.6	+6.2	+5.3	+3.2	+1.9
9	-13.1	-24.4 (+2.4)	-12.5 (+0.6)	-5.3 (-1.0)	-2.6 (-1.0)
8,9_TS	-16.7	-22.5 (-2.2)	-9.9 (-1.2)	-3.9 (-1.3)	-1.9 (-0.9)
cyclo-butadiene	+26.5	+26.3	+17.6	+8.7	+4.3

^aThe NICS point 0.0 is located in the geometrical center of the ring atoms, the direction indicated with a positive sign is defined to which the divalent carbon atom points (distances are given in Å).

values^{46,47} of these structures are also instructive (Table I). We computed significantly negative NICS at the geometrical centers of both rings, **8** and **9**, and even larger values 0.5 Å above (the direction to which the divalent carbon points) while an antiaromatic cyclobutadiene would produce large positive values.⁴⁶ In the other direction, though, the NICS values diminish more rapidly. Hence, the large negative values arise from the electron density from the lone pair of the carbene-type carbon. Even in transition states **5,8_TS** and **9,6_TS** with all carbon atoms in-plane, NICS values are only modestly positive, and no significantly paratropic ring current is sustained.

D. Reaction paths from Z-1-ethynylpropen-2-yl (**3**)

As we already pointed out, *cis*-/*trans*-isomerization **3/5** proceeds through the lowest barrier of only 19 kJ mol⁻¹. Besides this reaction path Z-1-ethynylpropen-2-yl (**3**) can undergo two types of 1,2-hydrogen shifts or immediately lose a hydrogen atom from its methyl group to give ethynylallene (**10**) (Chart 3). The barriers for C–H bond rupture via a productlike transition state, **3,10_TS** (Fig. 5), and 1,2-hydrogen shift yielding Z-1-ethynylallyl radical (**11**) are calculated to lie within 3 kJ mol⁻¹. Formation of **11**, however, is highly exothermic while the exit channel from the C₅H₅ to

the C₅H₄ PES (**10**) is endothermic but well below the total available energy of the reaction. The alternative 1,2-hydrogen shift to give E-1-ethynylpropen-1-yl (**12**) exhibits the highest barrier but nevertheless is exothermic. Note that the ethynyl substituent in **12** is almost collinear with the formal double bond (Fig. 4) and is only slightly bent, *trans* to the methyl group. Hence, the unpaired electron is mostly delocalized throughout the double bond–triple bond conjugated π system. This electronic situation is reflected in the calculated spin densities and in the short C1–C4 bond and the elongated formal triple bond between C4 and C5 (Fig. 4). Both hydrogen and methyl groups at C2 in **12** can be expelled; the corresponding reaction paths have been confirmed by IRC calculations. The Z-1-ethynylallyl radical (**11**) can react in several ways. It can undergo cyclization reactions (discussed in the following paragraph), a 1,2-hydrogen shift, or it can eject the vinylic hydrogen atom. The barriers for the 1,2-hydrogen shift and the exit channel are calculated to be within 3.3 kJ mol⁻¹ of one another, yielding 3-ethynylpropen-2-yl (**14**) and ethynylallene (**10**), respectively (Chart 3). Two different products are accessible from **14**, release of a hydrogen from the terminal CH₂ group yields penta-1,4-diyne (**16**), while C–H bond rupture at C3 results in ethynylallene (**10**).

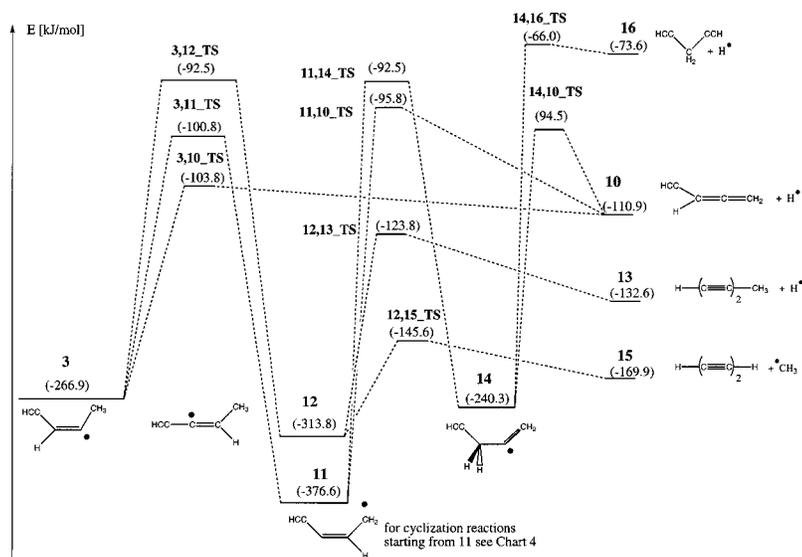


CHART 3. Schematic representation of part of the C₅H₅ potential energy surface (UB3LYP/6-311+G**): Reaction paths starting from Z-1-ethynylpropen-2-yl (**3**).

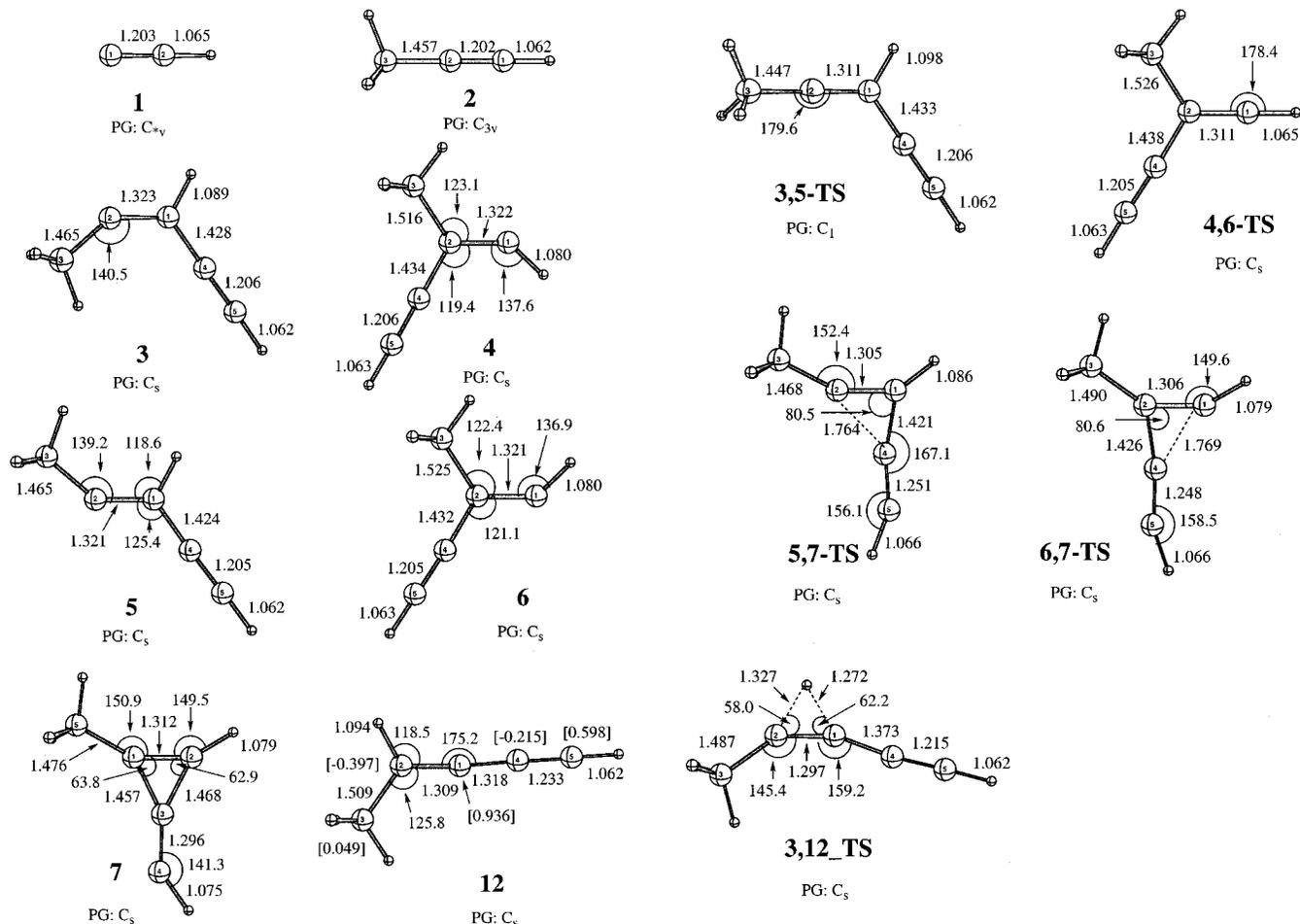


FIG. 4. Optimized geometries (UB3LYP/6-311+G**) of reactants, intermediates, and transition states for the most probable paths of the reaction of C₂H with CH₃CCH (bond length are given in Å, bond angles in degrees).

E. Cyclizations following the Z-1-ethynylallyl radical (11)

Three different cyclization reactions of the Z-1-ethynylallyl radical (11) are conceivable (Chart 4). The tran-

sition states for the formation of 3-methyl-ethylcyclobutene (17) and cyclopenta-1,3-dien-2-yl (18) are calculated to be within 1 kJ mol⁻¹ though 18 is 90.2 kJ mol⁻¹ more stable than 17. Alternatively, a three-

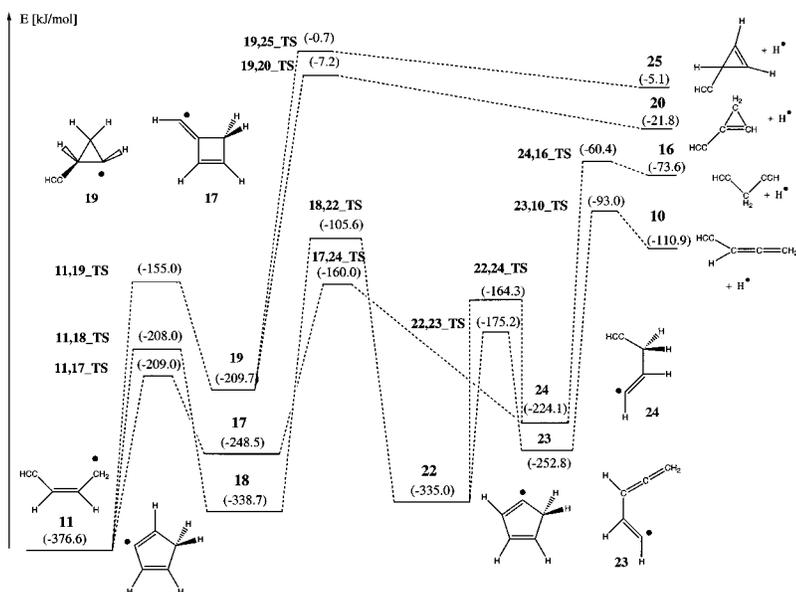


CHART 4. Schematic representation of part of the C₅H₅ potential energy surface (UB3LYP/6-311+G**): Reaction paths for cyclizations starting from Z-1-ethynylallyl radical (11).

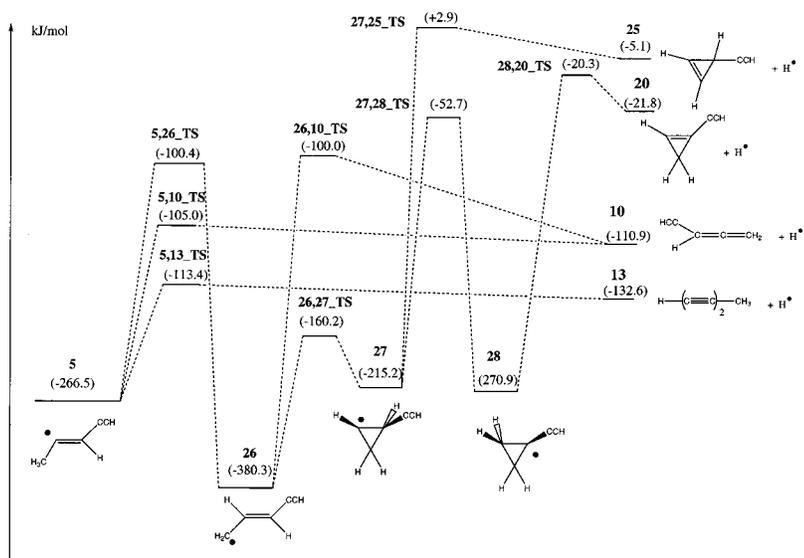


CHART 5. Schematic representation of part of the C_5H_5 potential energy surface (UB3LYP/6-311+G**): Reaction paths starting from E-1-ethynylpropen-2-yl (5).

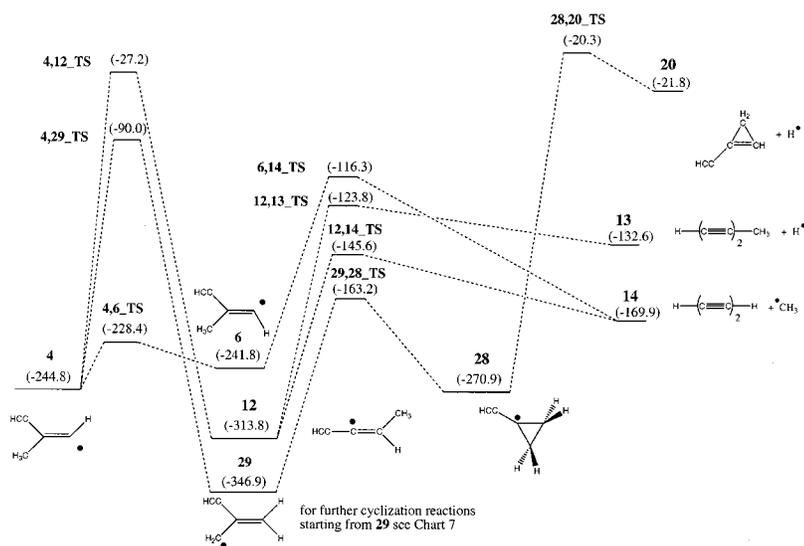


CHART 6. Schematic representation of part of the C_5H_5 potential energy surface (UB3LYP/6-311+G**): Reaction paths starting from Z-2-ethynylpropen-1-yl (4).

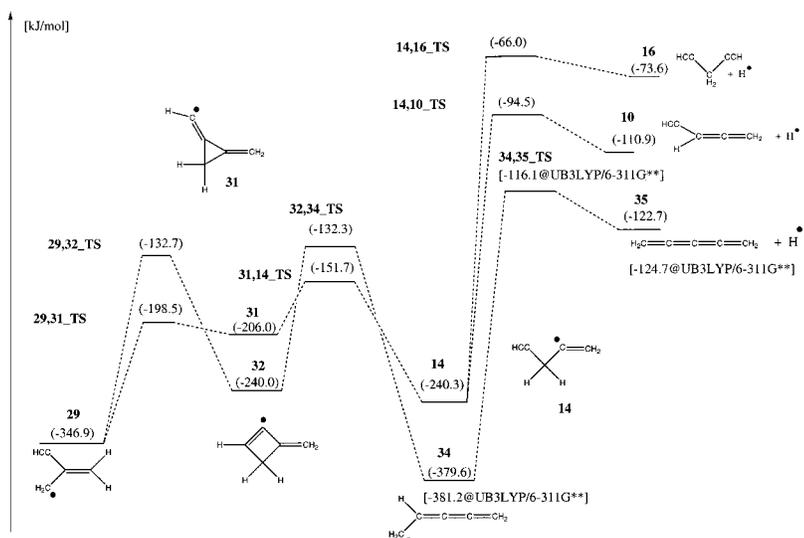


CHART 7. Schematic representation of part of the C_5H_5 potential energy surface (UB3LYP/6-311+G**): Cyclization reactions starting from the 2-ethynylallyl radical (29).

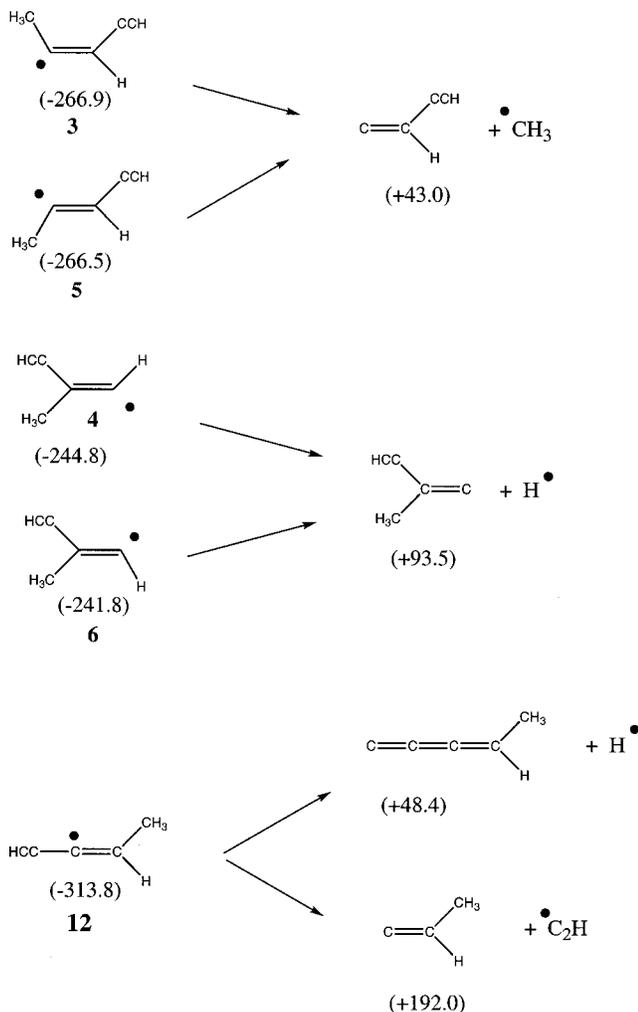


CHART 8. Relative energies kJ mol^{-1} of some singlet carbene species and their precursors, calculated at UB3LYP/6-311+G**.

membered ring, 2-ethynylcyclopropanyl (19), can be formed but is energetically less favorable than 17 or 18. The relative *cis* arrangement of the vinylic hydrogens in 11 is preserved in 19 and therefore a possible suprafacial 1,2-hydrogen shift

is degenerate. C–H bond rupture at C2 leads to 1-ethynylcyclopropene (20) and ejection of the *trans* hydrogen from C3 yields 3-ethynylcyclopropene (25). Both reaction channels are high in energy but, nevertheless, calculated to be below the total available energy of the reaction. Pent-1-en-4-in-1-yl (24) is accessible from ring opening of 3-methylenecyclobuten (17) and can itself eject the hydrogen atom *trans* to the unpaired electron yielding pent-1,4-diyne (16). Cyclopenta-1,3-dien-2-yl (18) first has to undergo a 1,2-hydrogen shift to 22 over a relatively high barrier before ring opening to either 2-allenylethenyl (23) or pent-1-en-4-in-1-yl (24) can take place. Hydrogen loss from C4 of 23 constitutes another exit channel giving ethynylallene (10).

F. Reaction paths following E-1-ethynylpropen-2-yl (5)

E-1-ethynylpropen-2-yl (5) can expel a hydrogen atom immediately via two different reaction channels (Chart 5). Penta-1,3-diyne (13) is obtainable through the energetically most favorable path by loss of the vinylic hydrogen atom. Alternatively, a hydrogen from the methyl group can be ejected resulting in ethynylallene (10). The allyl system corresponding to 5, E-1-ethynylallyl (26), is accessible via a 1,2-hydrogen shift. This has the highest barrier of all paths away from 5. Also 26 can eject a hydrogen to form ethynylallene (10). Furthermore the CH₂ group of the allyl system can attack C1 to give *trans*-2-ethynylcyclopropanyl (27). Besides a degenerate suprafacial 1,2-hydrogen shift, a nondegenerate hydrogen shift is possible, yielding 1-ethynylcyclopropanyl (28). Alternatively, a hydrogen from C3 can be expelled to form 3-ethynylcyclopropene (25). The transition state for this process is computed to be slightly above the energy of the reactants. 1-Ethynylcyclopropene (20) is feasible via hydrogen loss from 28.

G. Reaction paths from Z-2-ethynylpropen-1-yl (4)

The rearrangements following C2 attack of the ethynyl radical (1) on methylacetylene (2) are less diverse than for the previously discussed C1 attack. As we described previ-

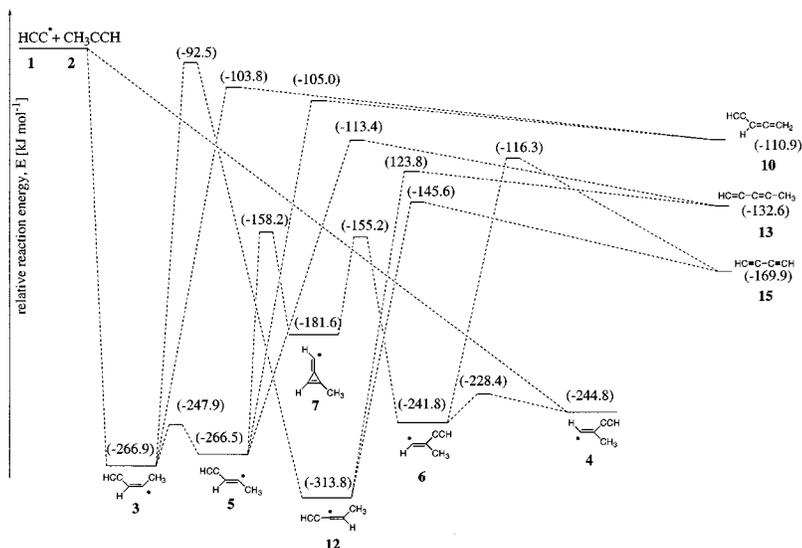


CHART 9. Potential energy surface for the reaction of C₂H with CH₃CCH describing the most probable reaction paths involved under single collision conditions, calculated at UB3LYP/6-311+G**.

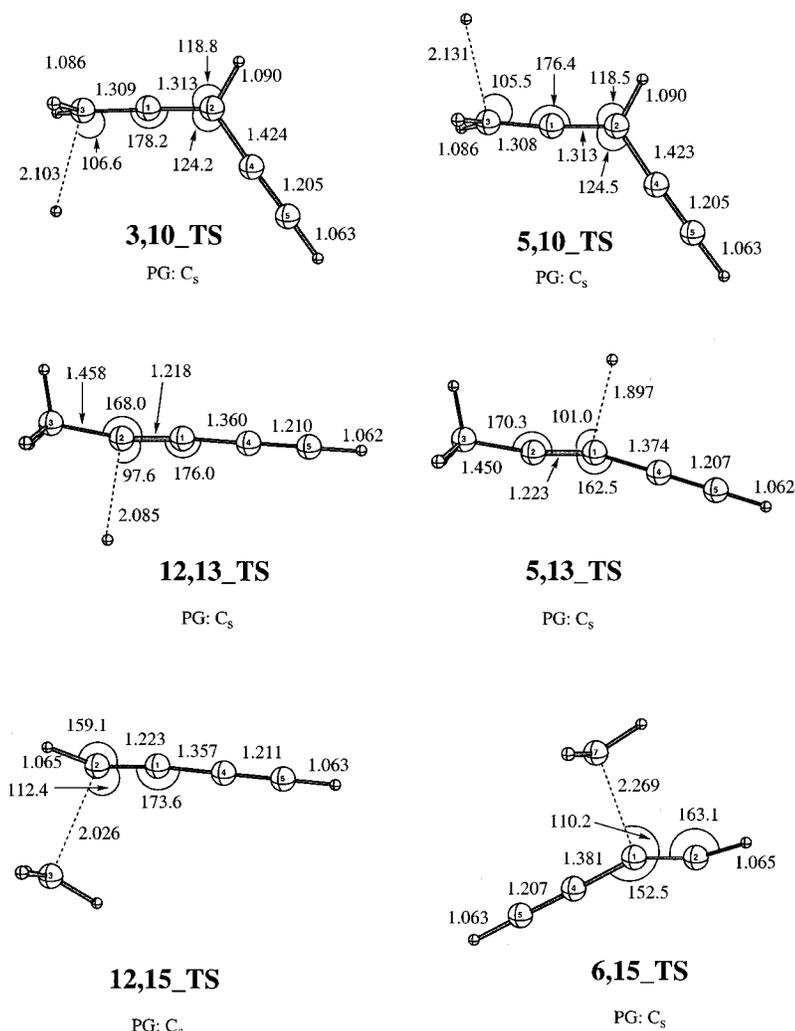


FIG. 5. Optimized geometries (UB3LYP/6-311+G**) for the exit channels of the most probable reaction paths.

ously, *cis/trans* isomerization **4/6** demands little energy. The only conceivable reaction channel for E-2-ethynylpropen-1-yl (**6**), besides the previously discussed cyclizations, is ejecting its methyl group to yield butadiyne (**15**) (Chart 6).

Starting from the initial intermediate, 2-ethynylpropen-1-yl (**4**), 1,3-hydrogen shift and 1,2-methyl group migration are imaginable (Chart 6). Both reaction paths proceed via relatively high barriers, leading to 1-ethynylpropen-1-yl (**12**) and the 2-ethynylallyl radical (**29**). Consecutive reactions for **12** have already been pointed out previously. The allyl radical **29** may form cyclic intermediates by attacking either the methylene group or the ethyne moiety. The first path yields 1-ethynylcyclopropan-1-yl (**28**) for which further reactions already were described previously.

H. Cyclization reactions of the 2-ethynylallyl radical (**29**)

1-methylenyl-2-methylenecyclopropane (**31**) and 4-methylenecyclobut-1-en-1-yl (**32**) constitute cyclization products of **29** where the allylic CH_2 group attacks its ethynyl "tail" (Chart 7). The barrier for formation of **32** is higher, though the product itself is lower in energy compared to **31**. Ring opening of **31** proceeds through a relatively low barrier yielding **14** for which successive reactions were al-

ready described previously. Ring cleavage of **32** generates pent-2,3,4-triene-1-yl (**34**), which can lose a hydrogen atom to give 4-cumulene (**35**). We encountered difficulties in the self-consistent field (SCF) procedure during optimization of the transition state for this process. Nevertheless, we were able to obtain SCF and geometric convergence at unrestricted Hartree-Fock/6-31G*, UB3LYP/6-31G*, and UB3LYP/6-311G** and confirmed the structures at each level as being the desired transition state by frequency analysis. Despite trying every available algorithm, all attempts to augment the basis with a diffuse function lead to nonconvergence in the SCF iterations. At UB3LYP/6-311G** we computed a relative energy of $-116.1 \text{ kJ mol}^{-1}$ for **34,35_TS** which is only 6.6 kJ mol^{-1} above the separated products at this level (Chart 7). The barrier with respect to **34** is $265.1 \text{ kJ mol}^{-1}$.

I. Carbenes as possible reaction products

From several of the previously described reaction intermediates different carbenes are accessible via C-H or C-C bond rupture. Density functional theory, especially use of the B3LYP method, is proven to be a powerful low cost tool to treat carbenes accurately.⁴⁸ We examined only a few carbenes in this study since the internal energy of the reactants

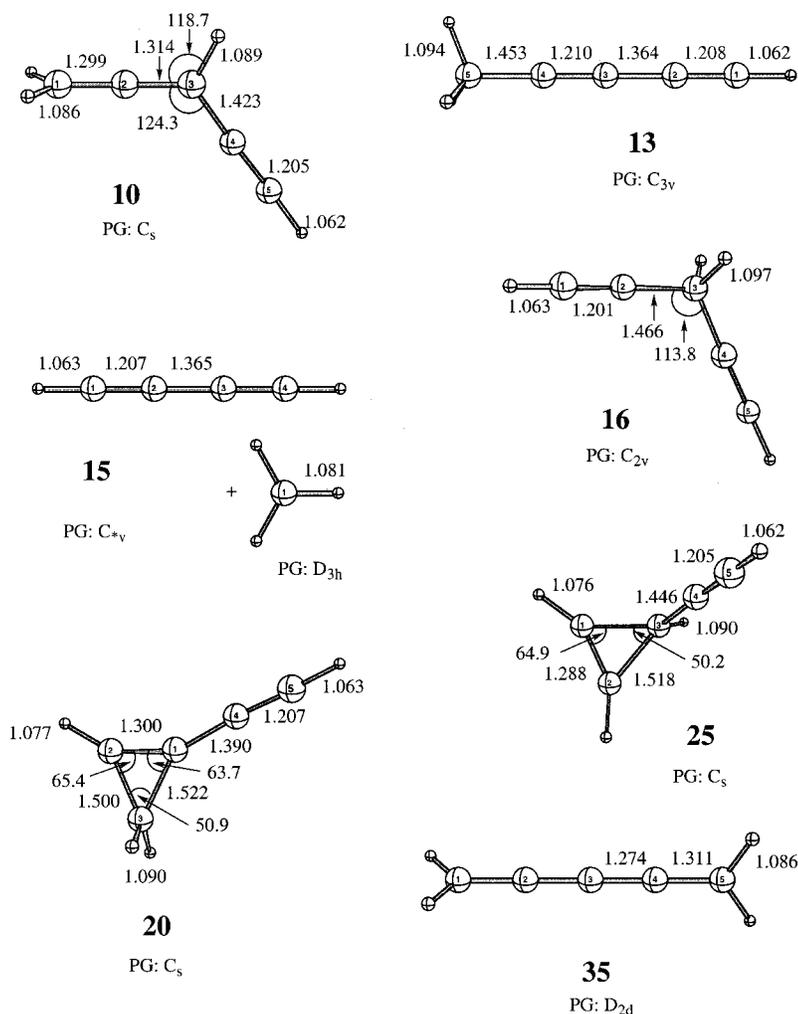


FIG. 6. Optimized geometries (UB3LYP/6-311+G**) of possible reaction products.

in the ISM is negligible and therefore only exothermic reactions need to be considered. All calculated reaction enthalpies leading to carbenes (Chart 8) are endothermic and the relative energies of the involved barriers are expected to be even higher. We therefore conclude that at low temperatures as in the ISM carbenes are unlikely products of the reaction of C₂H with CH₃CCH. However, we would like to recall that in circumstellar envelopes of carbon-rich AGB stars higher temperatures exist close to the photosphere of the central star. Therefore, the CCCC(CH₃)H carbene might be formed in these high temperature environments as well.

IV. THE MOST PROBABLE REACTION PATHS

Considering all the computed reaction intermediates one can extract a few which will most likely dominate the reaction (Chart 9). The initial process of the ethynyl radical (1) binding to methylacetylene (2), yielding Z-1-ethynylpropen-2-yl (3) or Z-2-ethynylpropen-1-yl (4), is highly exothermic. With reaction conditions where ternary processes are unlikely to happen, as in parts of the ISM and in distinct planetary atmospheres, e.g., Saturn's largest moon Titan, the total amount of reaction energy is accumulated in the intermedi-

TABLE II. Relative reaction energies for the products in kJ mol⁻¹ including unscaled UB3LYP/6-311+G** ZPVE corrections (without ZPVE correction in parentheses).

	UB3LYP/6-311+G**	CCSD(T)/TZ2P// UB3LYP/6-311+G**	CCSD(T)/cc-pVTZ// UB3LYP/6-311+G**
10+H [•]	-110.9 (-98.9)	-74.9 (-63.0)	-107.2 (-95.3)
13+H [•]	-132.6 (-122.9)	-97.1 (-87.4)	-135.1 (-125.4)
15+CH ₃	-169.9 (-163.7)	-144.8 (-138.6)	-156.4 (-150.2)
16+H [•]	-73.6 (-63.2)	-56.7 (-46.2)	-85.6 (-75.1)
20+H [•]	-21.8 (-11.5)	+8.9 (+19.3)	-29.1 (-18.7)
25+H [•]	-5.1 (+6.4)	+18.3 (+29.8)	-17.9 (-6.4)
35+H [•]	-122.7 (-109.4)	-62.9 (-49.5)	-101.2 (-87.9)

ates. Consequently, paths which transform the excess energy into kinetic energy rapidly are most likely to be pursued. Hence, complex reaction mechanisms involving many steps are of less importance under those conditions.

Following the initial reaction step, *cis/trans* isomerization proceeds via low barriers so that an even distribution of both isomers can be expected. However, due to geometric hindrance at C2 of methylacetylene (**2**), C1 attack is anticipated as the main reaction channel (Fig. 4). Immediate loss of a hydrogen atom from the methyl group of **3** to give ethynylallene (**10**) marks the most direct reaction path (Fig. 5). Shifting the vinylic hydrogen from C1 to C2 in **3** results in 1-ethynyl-propyn-1-yl (**12**), which itself can expel both a hydrogen atom or its methyl group. The *trans* isomers (**5,6**) of the initial reaction intermediates (**3,4**) can transform into each other via the three-membered ring intermediate **7**. Furthermore **5** can dismiss its vinylic hydrogen or one from its methyl substituent. Butadiyne (**15**) is also obtainable from **6** by loss of its methyl group.

Reaction products. Our theoretical study reveals seven different products for the reaction of methylacetylene (**2**) with the ethynyl radical (**1**) under single collision conditions. We calculated single point energies at the coupled cluster level of theory including single and double excitations and a perturbative treatment of triples, CCSD(T), for the UB3LYP/6-311+G** optimized geometries of the reactants and products (see Fig. 6). The energies obtained with the TZ2P basis set are in rather poor agreement with the density functional theory results (Table II). The use of the larger cc-pVTZ basis set which includes *f* functions for carbon, however, drastically changes the results and produces energies that reasonably correspond to the ones obtained from the much more economical UB3LYP/6-311+G** computations (Table II).

V. ASTROCHEMICAL IMPLICATIONS

The title reaction meets the most important prerequisite for a reaction to occur in the interstellar medium (ISM): An entrance barrier is absent and both reactants, C₂H(**1**) and methylacetylene (**2**), have been detected unambiguously in the ISM.⁴⁹ Our study reveals exothermic reaction pathways without entrance barrier to form more complex molecules from the two neutral species **1** and **2**. The most probable reaction products include the polyynes, butadiyne (**15**) and pentadiyne (**13**). Pentadiyne (**13**) has been observed in Saturn's moon Titan⁷⁻⁹ and **15** has been detected in the interstellar medium.^{5,49} Altogether we found seven different products which might be involved in the generation of larger, more complex molecules, like polycyclic aromatic hydrocarbons, in space.

VI. CONCLUSIONS AND OUTLOOK

We have presented a detailed study of the reaction of the ethynyl radical with methylacetylene. Following the entrance channel without barrier, numerous rearrangements on the doublet C₅H₅ potential energy surface were investigated. Among proposed radical-neutral reactions occurring in the interstellar medium, we focused particularly on exit channels

involving hydrogen or methyl loss. Seven different reaction products were located for which all reaction paths proceed below the energy of the separated reactants. We are currently investigating the kinetics of the title reaction, including all the calculated paths using the Rice-Ramsperger-Kassel-Marcus theory.

The reaction of the ethynyl radical with allene, an isomer of methylacetylene also detected in the ISM and planetary atmospheres, will be the subject of a future study. Does allene (also studied by Leone *et al.*¹⁴) lead to the same products or are divergent paths on the common doublet C₅H₅ potential energy surface pursued?

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