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Generation of Two Isomers of C_5H from the Corresponding Anions. A Theoretically Motivated Mass Spectrometric Study

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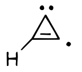
Molecular orbital calculations have predicted the stability of a range of connectivities for the radical C_5H potential surface. The most energetically favorable of these include the linear C_4CH geometry and two ring-chain structures HC_2C_3 and C_2C_3H. The corresponding anions are also shown to be theoretically stable, and furthermore, a fourth isomer, C_2CHC_2, is predicted to be the most stable anion connectivity. These results have motivated experimental efforts. Methodologies for the generation of the non-ring-containing isomeric anions C_4CH and C_2CHC_2 have been developed utilizing negative ion mass spectrometry. The absolute connectivities of the anions have been established using deuterium labeling, charge reversal, and neutralization reionization techniques. The success of the latter experiment confirms theoretical predictions of stability of the corresponding neutral species. This is the first reported observation of the neutral C_2CHC_2 species that calculations predict to be substantially less stable than the C_4CH connectivity but still bound relative to isomerization processes.

Introduction

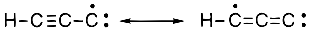
The history of the homologous hydrocarbon series C_nH is an interesting one. The discovery of these species in interstellar and circumstellar clouds in many cases predates their characterization in the laboratory. This has led to them to being broadly categorized, along with a number of other species, as "nonterrestrial" molecules.[1] The homologues with an even number of carbons, C_2H and C_4H, were the first to be detected in both galactic features as well as in the laboratory.[2−5] It was later discovered that the odd carbon species, C_3H and C_5H, were also present in circumstellar envelopes, detected virtually simultaneously in both astrophysical and terrestrial experiments.[6−9] It has been shown that C_nH species of odd n are generally less abundant in the galactic environment, sometimes by an order of magnitude or more than their even n homologues.[10] It has been suggested that the even members of the series are relatively stable, formed from removal of a single hydrogen atom from an acetylenic chain. In contrast, the odd members are likely to be much more reactive with up to three incomplete valencies.[8]

A range of theoretical and experimental studies have attempted to characterize and structurally elucidate this fascinating group of molecules. Traditionally, microwave spectroscopy of electrical dc discharges in atmospheres containing acetylene and diacetylene has been the method of choice for generation and detection of C_nH radicals. More recently, however, Fourier transform microwave spectroscopy of pulsed supersonic molecular beams has proved very successful, with linear chains up to $C_{14}H$ now characterized.[11] A recent study by Neumark and co-workers has demonstrated the possibility of generating the anions $C_{2n}H$ (where $n = 1-4$) by pulsing a supersonic molecular beam generated from acetylene with an electrical discharge.[12] The utility of this anionic approach is demonstrated by the measured photoelectron spectra, which have been used to determine not only the electron affinities of these radicals but also the assignment of their ground states. The adiabatic electron affinity of C_3H has also been determined [$AEA(C_3H) = 1.858 \pm 0.023$ eV] in a photoelectron experiment. This was carried out on the corresponding anion generated from a dc electrical discharge in a propene/oxygen atmosphere.[13] Theoretical interest in C_nH radicals has also been high; a number of studies have been concerned with the structures and electronic nature of the linear $C_{n-1}CH$ connectivities.[14−17]

Astrophysical detection of the cyclic C_3H structural isomer (**A**) has also been reported,[18] with the ratio of cyclic (**A**) to linear (**B**) varying from unity in some cold molecular clouds to around 0.2 in circumstellar envelopes.[19] Theoretical studies have attempted to predict the structures and relative energies of the linear[14,16,17] and cyclic[18,20,21] isomers. Further, the anion[17,22,23] and cation[14,24] structures have also been investigated theoretically. Ikuta has established a stability trend across all three surfaces.[25] His studies using the CCSD(T) and multireference CI approaches have suggested that neutral cyclic C_3H (now denoted c-C_3H) is more stable than linear C_3H (now denoted l-C_3H) by only 1 kcal mol^{-1}. For the anion surface, c-C_3H is less energetic by 7 kcal mol^{-1}, while for the corresponding cations, l-C_3H is lower in energy by some 17 kcal mol^{-1}. It should be noted that all three c-C_3H charge states can be described as aromatic, adhering to Hückel's $(4n + 2)$ π rule ($n = 0$). Calculations indicate that the π-electron populations on the C_3 ring decrease from the integer value of 2 in the order c-C_3H^-, c-C_3H, and c-C_3H^+. This observation suggests a decrease in aromatic stabilization and has been used to account for the relative energies of cyclic to linear structures across the three potential surfaces.



A



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The neutrals C_3H and C_3H_2 are the only interstellar hydrocarbon species thus far to be detected with more than one structural connectivity. This is largely because of the strong astrophysical bias toward detection of linear species with large

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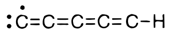
dipole moments. The interplay between isomers in these environments is not yet fully resolved; however, it has been demonstrated that both isomers may be formed in the binary collision between triplet carbon and acetylene.[19,26] Further, ab initio studies point to the possibility of isomerization of the linear to the cyclic structure via electron attachment. Electron capture by linear C_3H should result in sufficient energy gain to overcome the isomerization barrier on the anion surface; subsequent ejection of an electron gives neutral *c*-C_3H.[27]

By comparison with C_3H, isomeric studies of the higher C_nH homologues are relatively few. At this stage no experimental studies have shown the existence of a C_nH radical ($n > 3$), which is not the linear connectivity. Previous theoretical studies have addressed the linear C_4CH neutral structure but only recently have predictions emerged suggesting potentially stable nonlinear geometries. The isomers **1**−**7** have all been shown to be stable on the neutral potential surface.[28] The ring−chain species HC_2C_3 (**2**) and C_2C_3H (**3**) are of particular significance, since they are extensions of the *c*-C_3H geometry. By analogy with the *c*-C_3H radical, these species are surprisingly stable with respect to linear C_4CH (**1**); **2** and **3** are predicted to be more energetic than **1** by only 4.9 and 22.0 kcal mol^{-1}, respectively. A number of other intriguing geometries have been proposed as minima on this surface including the comparatively unstable C_2CHC_2 (**4**) geometry, predicted to be around 45 kcal mol^{-1} above C_4CH.



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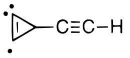

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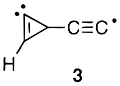

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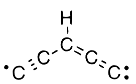

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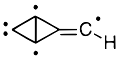

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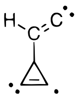

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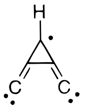

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Charged analogues of C_5H have also received comparatively little attention. Bohme and co-workers have reported a number of ion−molecule reactions of the C_5H cation.[29] Formed from electron impact ionization of 1,4-pentadiyne by a mechanism that is not clear, the C_5H^+ ion observed is assumed to adopt a linear structure (since low-level calculations have suggested this cation to be stable with a linear geometry[14]). Of more interest, however, is related work by the same group that shows that reaction between cationic carbon and neutral diacetylene leads to rapid formation of C_5H^+.[30] This is proposed as a possible synthon for both neutral C_5H and C_5 in the interstellar environment (Scheme 1).

SCHEME 1

experimental: $^{+\bullet}C + HC{\equiv}C{-}C{\equiv}CH \rightarrow$
$^{+}C{=}C{=}C{=}C{=}CH + H^{\bullet}$

proposed: $^{+}C{=}C{=}C{=}C{=}CH \rightarrow$
charge transfer $\rightarrow {}^{\bullet}C{=}C{=}C{=}C{=}CH$

proposed: $^{+}C{=}C{=}C{=}C{=}CH \rightarrow$
proton transfer $\rightarrow :C{=}C{=}C{=}C{=}C:$

We have previously reported a methodology for generating the anion analogue of C_4CH from a suitable precursor in the ion source of a mass spectrometer.[31] Theoretical calculations performed at the time but not reported suggested the stability of the anions $C_2CHC_2^-$, $HC_2C_3^-$, and $C_2C_3H^-$. We have since been able to synthesize $C_2CHC_2^-$ in the gas phase, but suitable precursors for the remaining two stable minima could not be prepared.[32] We report here these calculations, showing both the structures and relative stabilities of the C_5H anions. A number of thermodynamically less favorable yet still stable connectivities are also discussed. The energetics of the relevant neutral species are also discussed, with particular reference to the isomerization pathways available.

Charge reversal (CR)[33−35] and neutralization reionization (NR)[36,37] mass spectrometry have been shown to be good methods for distinguishing isomeric ions. Of particular relevance are a sequence of studies on the related C_nH_2 homologous series. CR and NR techniques have been able to demonstrate the existence of different structural isomers for the ions C_2H_2, C_4H_2, and C_5H_2.[38−40] Further, NR experiments have shown the gas-phase stability of the corresponding neutral species on the microsecond time scale.

The results of NR experiments involving the C_4CH and C_2-CHC_2 anions will be discussed here along with the experimental evidence that these provide for the stability of the corresponding neutrals.

Experimental Section

A. Computational Methods. Geometry optimizations were carried out with the Becke 3LYP method[41,42] initially using the 6-31G basis within the GAUSSIAN 94[43] suite of programs. The larger Dunning aug-cc-pVDZ[44,45] basis was used to further optimize minima on the anion, neutral, and cation surfaces. Stationary points were characterized as either minima (no imaginary frequencies) or transition states (one imaginary frequency) by calculation of the frequencies using analytical gradient procedures. The minima connected by a given transition structure were confirmed by intrinsic reaction coordinate (IRC) calculations. The calculated frequencies were also used to determine the zero-point vibrational energies, which were then scaled by 0.9804[46] and used as a zero-point energy correction for the electronic energies calculated at this and higher levels of theory. We have previously reported the success of the B3LYP method in predicting geometries of unsaturated carbon chain structures. It was demonstrated that this method produced optimized structures, at a low computational cost, which compared favorably with higher level calculations.[40] Similarly, in this study the optimized geometries of the neutrals **1**−**6** (which are available as Supporting Information) showed little deviation from those calculated by Crawford et al. using more rigorous coupled-cluster approaches.[28] The only notable exception was that the B3LYP method predicted a very slightly bent geometry for the neutral C_4CH radical (deviating by less than a degree). With $C_{\infty v}$ symmetry imposed, the resulting stationary point was almost identical in geometry and energy to that of lower symmetry, but a number of imaginary frequencies were observed. In this case the linear geometry is reported, in agreement with higher level optimizations.[17,28] More accurate energies for the B3LYP geometries were determined with the partially restricted open-shell coupled-cluster method, RCCSD(T),[47−52] using the Dunning aug-cc-pVDZ basis set, within the MOLPRO package.[53] The described computational method was tested using *l*-C_3H (**B**), giving a computed adiabatic electron affinity of 1.79 eV compared with the experimentally determined 1.858 ± 0.023 eV.[13] Calculations involving GAUSSIAN 94 geometry optimization were carried out using the Power Challenge supercomputer at the South Australian Super Computing Centre (Adelaide). MOLPRO single-point energy calculations were carried out with the Power Challenge supercomputer at the Australian National University Super Computing Facility (Canberra).

B. Mass Spectrometric Methods. CR and NR spectra were measured using a two-sector reversed geometry VG ZAB 2HF spectrometer. This instrument and the typical experimental conditions of negative ion chemical ionization (NICI) have been described in detail elsewhere.[54] The instrument has been recently upgraded (by inclusion of two collision cells between the magnetic and electric sectors) in order to allow the measurement of NR spectra. Spectra were generated in the following manner. Samples were introduced into the source via a heated septum inlet, producing a measured pressure of 5×10^{-6} Torr inside the source housing. Typical ionization conditions were the following: source temperature, 200 °C; ionizing energy, 70 eV (tungsten filament); accelerating voltage, -7 kV. All slits were fully open in order to minimize mass discrimination effects due to energy resolution.[55,56] The reagent ions HO^- and CH_3O^- were generated respectively from substrates H_2O and CH_3OH (introduced through the heated septum inlet) to give an operating pressure inside the source housing of ca. 5×10^{-5} Torr and thus an estimated pressure inside the ion source of close to 0.1 Torr. Negative ion chemical ionization of the sample either effected (i) deprotonation or dedeuteration as appropriate or (ii) desilylation of a neutral trimethylsilylated substrate, by analogy to the method originally developed by DePuy and co-workers.[57] Collisional activation (CA) spectra were obtained by collision of the incident anions with argon in the first of two collision cells at a pressure typically around 10^{-7} Torr. Neutralization of the anion beam in the first collision cell was achieved by collision with oxygen gas at a typical pressure of 5×10^{-6} Torr. This reduces the main beam to 80% of its initial value, producing essentially single collision conditions in the collision cell.[58] Residual ions were removed using the deflector electrode, with neutrals passing into the second cell where they were reionized to the corresponding cation under identical conditions to those used in the first cell. The spectra were collected by reversing the polarity of the electric sector voltage and scanning the sector voltage. CR spectra were measured under the same conditions as those used for NR spectra except that the deflector electrode is grounded. Although this CR method does increase the likelihood of double collisions, it allows direct comparison between NR and CR spectra.[59−62] All spectra were repeated a minimum of three times in order to establish their reproducibility.

C. Synthesis of Precursor Molecules. *Methyl (5-Trimethylsilyl)penta-2,4-diynyl Ether* [$TMSC{\equiv}CC{\equiv}CCH_2OCH_3$]. This preparation has been previously described.[40]

3-Penta-1,4-diynyl Acetate [$HC{\equiv}CCH(OCOCH_3)C{\equiv}CH$]. 1,4-Pentadiyn-3-ol[63,64] (0.5 g) was heated at 120 °C in acetic anhydride (3 cm^3) for 1 h with vigorous stirring. The resultant mixture was quenched with ice (10 g), neutralized with aqueous sodium hydrogen carbonate (saturated, ca. 10 cm^3), extracted with diethyl ether (3×20 cm^3), the ethereal extract separated, washed with water (20 cm^3) and aqueous sodium chloride (saturated, 10 cm^3), and dried ($MgSO_4$). The solvent was removed in vacuo to yield 3-penta-1,4-diynyl acetate (0.76 g, 90%). ^1H NMR (200 MHz, $CDCl_3$): δ 2.09 (s, 3H), 2.54 (d, 2H), 5.98 (t, 1H).

3-[D_1]-3-Penta-1,4-diynyl Acetate [$HC{\equiv}CCD(OCOCH_3)C{\equiv}CH$] was prepared as for the unlabeled species except that [3-D_1]-penta-1,4-diyn-3-ol[40] was used as the starting material. Yield = 88%. D_1 = 98%.

1,5-Bis(trimethylsilyl)-3-penta-1,4-diynyl Acetate [$TMSC{\equiv}CCH(OCOCH_3)C{\equiv}CTMS$]. 1,5-Bis(trimethylsilyl)penta-1,4-diyn-3-ol[65] (0.5 g) was heated at 120 °C in acetic anhydride (3 cm^3) for 1 h, with vigorous stirring. The resultant mixture was quenched with ice (10 g), neutralized with aqueous sodium hydrogen carbonate (saturated, ca. 10 cm^3), extracted with diethyl ether (3×20 cm^3), the ethereal extract separated, washed with water (20 cm^3) and aqueous sodium chloride (saturated, 10 cm^3), and dried ($MgSO_4$). The solvent was removed in vacuo to yield 1,5-bis(trimethylsilyl)-3-penta-1,4-diynyl acetate (0.55 g, 88%). ^1H NMR (200 MHz, $CDCl_3$): δ 0.16 (s, 18H), 2.10 (s, 3H), 6.02 (s, 1H).

TABLE 1: Energies of Various C_5H Isomers on the Anion Potential Surface[a]

isomer	electronic state	electronic energy (hartree)	zero-point energy (hartree)	relative energy (kcal mol^{-1})
(**1**$^-$) C_4CH^-	1A′	−190.409 83	0.02702	6.6
	triplet	−190.413 92	0.02612	3.5
(**2**$^-$) $HC_2C_3^-$	$^1A_1$	−190.410 72	0.02779	6.5
	triplet	*b*		
(**3**$^-$) $C_2C_3H^-$	1A′	−190.421 51	0.02950	0.8
	triplet	−190.345 09	0.02678	47.1
(**4**$^-$) $C_2CHC_2^-$	$^1A_1$	−190.422 72	0.02940	0.0
	$^3B_1$	−190.342 05	0.02633	48.7
(**5**$^-$) HCC_4^-	singlet	*b*		
	triplet	*b*		
(**6**$^-$) *c*-C_3CHC^-	singlet	*b*		
	3A′	−190.326 61	0.02710	58.9
(**7**$^-$) CC_3HC^-	singlet	*b*		
	triplet	*b*		
(**8**$^-$) $C_2CC_2H^-$	1A′	−190.365 94	0.02723	34.3
	triplet	*b*		
(**9**$^-$) *l*-C_3CHC^-	singlet	*b*		
	3A″	−190.339 435 7	0.026059	50.2

[a] Calculated at the RCCSD(T)/aug-cc-pVDZ//B3LYP/aug-cc-pVDZ level of theory. ZPE uncorrected. Relative energy given, including ZPE, corrected by 0.9804.[46] [b] These anions are unstable with respect to isomerization processes.

[1,5-D_2]-3-Penta-1,4-diynyl Acetate [$DC{\equiv}CCH(OCOCH_3)C{\equiv}CD$]. A solution containing 1,5-bis(trimethylsilyl)-3-penta-1,4-diynyl acetate (0.55 g) and 18-crown-6 (0.005 g) in anhydrous tetrahydrofuran (10 cm^3) was added dropwise over 0.5 h to a stirred solution of dry potassium fluoride (1.0 g) in deuterium oxide (1 cm^3) at 0 °C under a nitrogen atmosphere. The solution was then stirred at 25 °C for 12 h and dried ($MgSO_4$), followed by removal of the solvent in vacuo to give [1,5-D_2]-3-penta-1,4-diynyl acetate (0.22 g, 95%, $D_2 > 97\%$).

3-Penta-1,4-diynyl Propionate [$HC{\equiv}CCH(OCOCH_2CH_3)C{\equiv}CH$]. The procedure was adapted from that of Vogel.[66] 1,4-Pentadiyn-3-ol (0.6 g) in anhydrous dichloromethane (20 cm^3) was cooled to 0 °C, and a mixture of propionyl chloride (3.89 cm^3) in anhydrous dichloromethane (30 cm^3) was added dropwise at 0 °C under a nitrogen atmosphere. The mixture was then refluxed for 2 h and cooled to 20 °C. Ice (10 g) was added, and the mixture was extracted with dichloromethane (3×20 cm^3). The combined organic extract was washed with aqueous sodium hydrogen carbonate (saturated, 3×20 cm^3) and dried ($MgSO_4$), and the solvent was removed in vacuo and the product purified on a short silica column (eluted with ethyl acetate/hexane, 30:70) to give 3-penta-1,4-diynyl propionate (0.83 g, 81%). ^1H NMR (200 MHz, $CDCl_3$): δ 1.15 (t, 3H), 2.34 (q, 2H), 2.55 (d, 2H), 6.03 (t, 1H).

3-Penta-1,4-diynyl Formate [$HC{\equiv}CCH(OCOH)C{\equiv}CH$]. The procedure was adapted from that of Carlson et al.[67] 3-Penta-1,4-diynol (0.5 g) was added to a mixture of boron oxide (0.12 g), *p*-toluenesulfonic acid (0.12 g), formic acid (0.33 g), and anhydrous dichloromethane (20 cm^3) at 20 °C and under an atmosphere of nitrogen. The mixture was heated under reflux for 1 h, cooled to 0 °C, and filtered, the filtrate was stirred with potassium carbonate (0.5 g) for 0.25 h and refiltered, and the

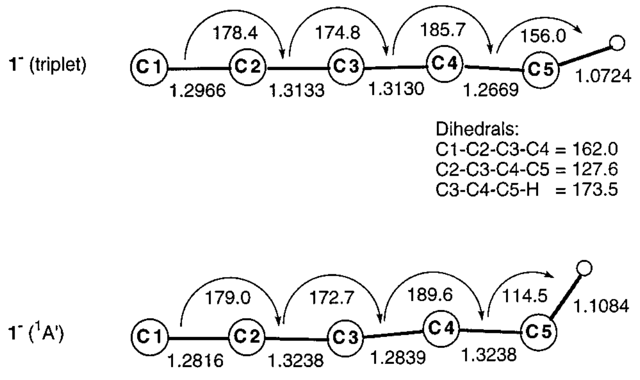


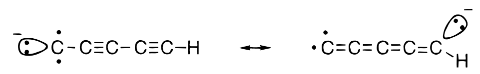
Figure 1. Optimized geometries for the singlet and triplet electronic states of C_4CH^- ($\mathbf{1}^-$). These geometries were calculated at the B3LYP/aug-cc-pVDZ level of theory. All bond lengths are given in angstroms and all angles in degrees.

solvent was removed in vacuo. The residue was purified on a short silica column (eluting with dichloromethane) to give 3-penta-1,4-diynyl formate (0.07 g, 14%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.60 (d, 2H), 6.10 (t, 1H), 8.04 (s, 1H).

Results and Discussion

Theoretical Studies. Of the seven stable C_5H neutral geometries predicted by Crawford et al.,[28] the most stable anions are formed by electron attachment to structures **1**−**4**. The relative energies of the stable anionic species are given in Table 1, and their structures are depicted in Figures 1 and 3−5.

The C_4CH anion shows two closely spaced electronic states: a singlet $^1A'$ state and a nonplanar triplet state that is more stable by 3.1 kcal mol^{-1}. The structure of the singlet state anion is consistent with the valence bond picture of a cumulenic carbenoid, with a formal negative charge on the hydrogen-bearing terminal carbon (Figure 1). For example, the C_3−C_4 and C_4−C_5 bond lengths are 1.28 and 1.32 Å, respectively. The carbon−hydrogen bond length of 1.11 Å and bond angle of 115° are similar to those of a terminal sp^2 system. The slightly bent carbon chain (C_2−C_3−C_4 = 173° and C_3−C_4−C_5 = 170°) is in keeping with theoretical predictions made for the C_3H anion that suggest C−C−C bond angles of around 175°.[23,17] In contrast to the structure of the anion, the neutral ground state has the strictly linear structure of a polyacetylide, with alternating carbon−carbon bond lengths (C_3−C_4 = 1.33 Å and C_4−C_5 = 1.23 Å) and a contracted sp-like carbon hydrogen bond length of 1.07 Å.[68] The geometry of the stable triplet anion (Figure 1) falls somewhere between that of the singlet anion (carbenoid cumulene) and the neutral (polyacetylide) and can be represented, in valence bond terms, as a resonance hybrid of the two:



The geometric differences between both singlet and triplet anions and the radical neutral have significance for the neutralization reionization experiments carried out. The electronic transitions in such an experiment are considered as vertical,[69,70] and in the case of C_4CH, Franck−Condon factors will lead to a vibrationally hot neutral being formed. However, neutral C_4CH lies in a deep potential well on the radical C_5H surface (see Figure 2) and is thus unlikely to rearrange even when the small amount of surplus energy arising from the neutralization process is considered. Rearrangement of C_4CH by cyclization to either HC_2C_3 (**2**) or C_2C_3H (**3**) is a high-energy process requiring some 29 or 50 kcal mol^{-1}, respectively (Figure 2).[71] These values were calculated at the B3LYP/aug-cc-pVDZ//B3LYP/6-31G level of theory and show excellent agreement with those obtained at higher levels by Crawford et al.[28] Rearrangement by hydrogen transfer is also energetically demanding. Formation of C_2CHC_2 (**4**) from C_4CH (**1**) is endothermic by some 48 kcal mol^{-1} and requires a further 22 kcal mol^{-1} to overcome the barrier to this process. Calculations also predict C_4CH cations to be stable (Table 2). The theoretical results suggest that a $^-$NR$^+$ experiment should lead to successful gas-phase generation of the C_4CH radical, which should not isomerize and should be observable by the detection of the analogous cation.

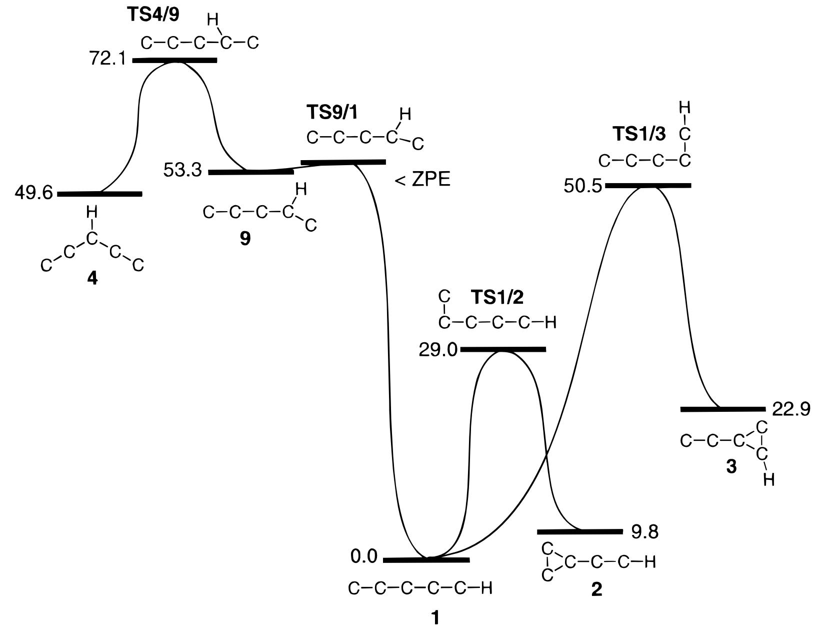


Figure 2. Reaction coordinate diagram for rearrangement processes occurring on the neutral radical C_5H potential surface. The geometries of all stationary points were calculated at the B3LYP/6-31G level of theory; those of the transition structures are available in Supporting Information. The relative energies were calculated using the same theory with the larger basis set, aug-cc-pVDZ, and are given in kcal mol^{-1}, with zero-point energy contributions included.

TABLE 2: Relative Energies of C_5H Cations for Which Stable Anions of the Same Connectivity Have Been Calculated[a]

isomer	electronic state	electronic energy (hartrees)	zero-point energy (hartrees)	relative energy (kcal mol^{-1})
(**1**$^+$) C_4CH^+	1A′	−190.028 22	0.029 07	0.0
(**1**$^+$) C_4CH^+	3Π	−189.966 08	0.026 91	37.6
(**2**$^+$) $HC_2C_3^+$	singlet	*b*		
(**2**$^+$) $HC_2C_3^+$	$^3B_2$	−189.973 03	0.029 47	34.8
(**3**$^+$) $C_2C_3H^+$	singlet	*b*		
(**3**$^+$) $C_2C_3H^+$	3A′	−189.950 31	0.030 38	49.7
(**4**$^+$) $C_2CHC_2^+$	$^1A_1$	−189.898 83	0.027 41	80.1
(**4**$^+$) $C_2CHC_2^+$	3A′	−189.884 52	0.025 36	87.8

[a] Calculated at the RCCSD(T)/aug-cc-pvdz//b3lyp/aug-cc-pVDZ level of theory (the geometries calculated at this level are available in Supporting Information). ZPE uncorrected. Relative energy given, including ZPE, corrected by 0.9804.[46] [b] These cations are unstable with respect to isomerization processes.

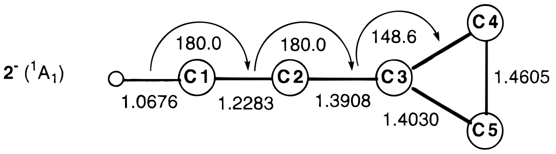
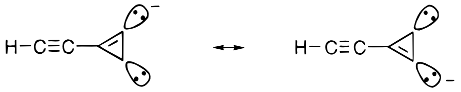


Figure 3. Optimized geometry for the singlet ground state of $HC_2C_3^-$ (**2**$^-$). The geometry was calculated at the B3LYP/aug-cc-pVDZ level of theory. All bond lengths are given in angstroms and all angles in degrees.

The ground-state HC_2C_3 anion was found to be an $^1A_1$ electronic state. No corresponding triplet structure could be found with ring opening leading to formation of triplet C_4CH without barrier. The structure of the stable singlet state shown in Figure 3 is very similar to that of the corresponding neutral radical species.[68] It can be considered as a terminal alkyne bonded to one of the sp^2 carbons of cyclopropene, with the other ring carbons bearing a carbene and the negative charge.



This structure is in keeping with the observed linearity of the $H-C_1-C_2$ moiety and the contracted acetylenic type $H-C_1$ and C_1-C_2 bonds (1.07 and 1.23 Å, respectively). Such a representation provides some insight into the stability of the anion (only some 3 kcal mol^{-1} above the triplet C_4CH ground-state anion), since it possesses the $(4n + 2)$ π electrons ($n = 0$) required for aromatic stabilization. The same rationale has previously been applied to the *c*-C_3H anion.[23,25] In effect,

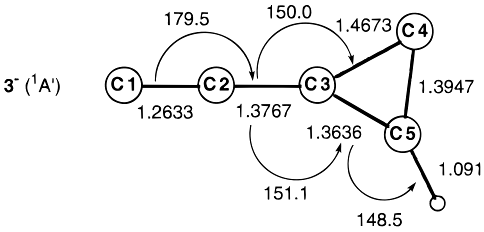
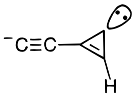


Figure 4. Optimized geometry for the singlet ground state of $C_2C_3H^-$ (**3**$^-$). The geometry was calculated at the B3LYP/aug-cc-pVDZ level of theory. All bond lengths are given in angstroms and all angles in degrees.

$HC_2C_3^-$ may be considered as *c*-C_3H^- with the ring hydrogen replaced by an alkyne moiety. The stability of this anion suggests that it is a good candidate for formation in the gas phase if a suitable precursor can be found. The structural similarity between anion and neutral points to favorable overlap of the potential surfaces and hence a good probability of forming the neutral radical from the anion in either a collision-based or spectroscopic neutralization event.

The C_4CH structure is not the most stable arrangement on the anion potential surface. While the C_4CH neutral radical is 21 kcal mol^{-1} more stable than C_2C_3H, the trend is reversed for the anions (Tables 1 and 3). The ground state of $C_2C_3H^-$ is more stable than the triplet C_4CH anion by approximately 2 kcal mol^{-1}. The ground-state C_2C_3H anion (Figure 4 and Table 1) is a singlet $^1A'$, with an excited nonplanar triplet state calculated to be 46 kcal mol^{-1} less stable (Tables 1 and 4). Once again it is reasonable to consider the structure of the C_2C_3H ground-state anion based on the valence picture of the *c*-C_3H anion. If, in this instance, the negative charge of *c*-C_3H^- is replaced with an acetylide moiety, the resulting structure agrees with calculated parameters. These structural characteristics are best highlighted by the shortened acetylenic C_1-C_2 bond length (1.26 Å) and the two long sides ($C_3-C_4 = 1.47$ Å and $C_4-C_5 = 1.39$ Å) and the one short side ($C_3-C_5 = 1.36$ Å) of the three-membered carbon ring.



The ground-state C_2C_3H anion may be thought of as possessing a carbon−carbon double bond bonded directly to the acetylide anion. This represents a contrast to the situation for the neutral. The neutral radical has less alternation in the bond lengths C_1-C_2 and C_2-C_3 (1.29 and 1.33 Å, respectively).[68] The alkene-like bond C_4-C_5 in the three-membered ring is 1.35 Å compared with C_3-C_4 and C_3-C_5 (1.46 and 1.42, Å respectively). This

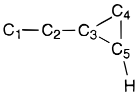
TABLE 3: Energies of Various C_5H Isomers on the Neutral Potential Surface[a]

isomer	state	electronic energy (hartrees)	zero-point energy (hartrees)	relative energy (kcal mol^{-1})	previous study[b] (kcal mol^{-1})	electron affinity (eV)
(**1**) C_4CH	2Π	−190.328 71	0.02622	0.0	0.0	2.44
(**2**) HC_2C_3	$^2B_2$	−190.323 31	0.02814	4.6	4.9	2.39
(**3**) C_2C_3H	2A′	−190.297 98	0.02885	20.9	22.0	3.34
(**4**) C_2CHC_2	$^2B_2$	−190.254 27	0.02773	47.6	49.7[c]	4.54
(**5**) HCC_4	2A′	−190.276 70	0.02781	33.6	32.5	*d*
(**6**) *c*-C_3CHC	2A′	−190.250 50	0.02693	49.5	49.1	*d*
(**7**) CC_3HC		*e*			67.0	

[a] Calculated at the RCCSD(T)/aug-cc-pvdz//b3lyp/aug-cc-pVDZ level of theory (the geometries calculated at this level are available in Supporting Information). ZPE uncorrected. Relative energy given, including ZPE, corrected by 0.9804.[46] Adiabatic electron affinity estimated from indicated neutral and the corresponding ground-state anion (Table 1). [b] CCSD(T)/DZP//CCSD(T)/DZP level of theory.[28] [c] Estimated from EOMIP-CCSD*/DZP//EOMIP-CCSD/DZP calculations. [d] Electron affinities are not available at this level of theory because the corresponding minima on the anion surface are not stable for these geometries. [e] A minimum corresponding to geometry **7** could not be located at this level of theory.

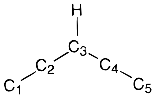
TABLE 4: Geometries of Excited Electronic States and Less Stable C_5H Anion Minima (Ground States for 1−4 Are Given in Figures 1 and 3−5)[a]

3^- (C_1) triplet



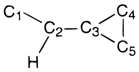
bond length	C_1-C_2	1.2760
	C_2-C_3	1.3488
	C_3-C_4	1.3554
	C_3-C_5	1.6260
	C_4-C_5	1.4025
	C_5-H	1.1019
angle	$C_1-C_2-C_3$	177.5
	$C_2-C_3-C_4$	166.7
	$C_3-C_4-C_5$	138.0
	C_3-C_5-H	122.8
dihedral angle	$C_1-C_2-C_3-C_4$	147.3
	$C_2-C_3-C_4-C_5$	−26.7
	$C_3-C_4-C_5$-H	57.2

4^- (C_{2v}) $^3B_1$



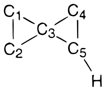
bond length	C_1-C_2	1.2855
	C_2-C_3	1.3809
	C_3-C_4	1.3809
	C_4-C_5	1.2855
	C_5-H	1.1121
angle	$C_1-C_2-C_3$	180.1
	$C_2-C_3-C_4$	140.4
	$C_3-C_4-C_5$	180.1
	$H-C_3-C_2$	109.8

6^- (C_s) $^3A'$



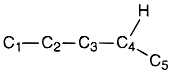
bond length	C_1-C_2	1.3751
	C_2-H	1.1109
	C_2-C_3	1.4146
	C_3-C_4	1.3927
	C_3-C_5	1.4579
	C_4-C_5	1.3576
angle	$C_1-C_2-C_3$	125.5
	$H-C_2-C_3$	113.5
	$C_2-C_3-C_4$	156.5
	$C_2-C_3-C_5$	146.7

8^- (C_s) $^1A'$



bond length	C_1-C_2	1.3234
	C_1-C_3	1.5193
	C_2-C_3	1.5952
	C_3-C_4	1.5437
	C_3-C_5	1.3948
	C_4-C_5	1.3543
	C_5-H	1.0909
angle	$C_1-C_2-C_3$	61.9
	$C_2-C_3-C_4$	178.6
	$C_3-C_4-C_5$	57.1
	$H-C_5-C_4$	151.3
dihedral angle	$C_1-C_2-C_3-C_4$	180.0
	$C_2-C_3-C_4-C_5$	0.0
	$H-C_5-C_4-C_3$	180.0

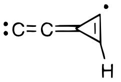
9^- (C_s) $^3A''$



bond length	C_1-C_2	1.3047
	C_2-C_3	1.3003
	C_3-C_4	1.3886
	C_4-C_5	1.3599
	$H-C_4$	1.1030
angle	$C_1-C_2-C_3$	174.6
	$C_2-C_3-C_4$	171.4
	$C_3-C_4-C_5$	106.9
	$H-C_4-C_3$	124.7
dihedral angle	$C_1-C_2-C_3-C_4$	180.0
	$C_2-C_3-C_4-C_5$	0.0
	$H-C_4-C_3-C_2$	180.0

[a] Calculated at the B3LYP/aug-cc-pvdz level of theory. All bond lengths are given in angstroms and all angles in degrees.

structure is more in keeping with an allenic carbene fused to a dehydrocyclopropene.



Some insight can be gained as to the relative stability of the anionic and radical species on their respective surfaces by contrasting these two valence structures. While the anion may be considered aromatic with 2π electrons, the corresponding neutral has less aromatic stabilization with a π-electron population of >2 because of the greater π-overlap of carbons C_1, C_2, and C_3.

At the level of theory used in this investigation, C_2CHC_2 (**6**) proves to be the most stable anion (Table 1). However, the ground-state anions derived from **1**−**4** have energies within a 10 kcal mol^{-1} range. The stability of $C_2CHC_2^-$ is surprising, since the corresponding neutral radical is almost 50 kcal mol^{-1} less stable than C_4CH, the global minima on the neutral surface (Table 3). Both singlet and triplet states have been calculated for $C_2CHC_2^-$ with the $^1A_1$ ground state being some 49 kcal mol^{-1} more stable than the $^3B_1$ state. The structures of these anions are given in Figure 5 and Table 4, respectively.

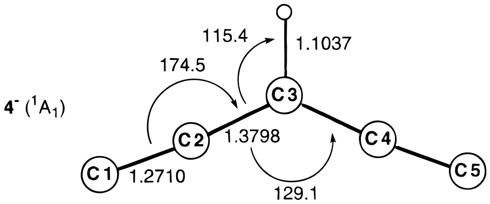
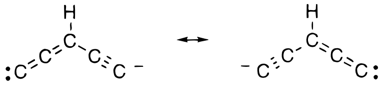


Figure 5. Optimized geometry for the singlet ground state of $C_2CHC_2^-$ (4^-). The geometry was calculated at the B3LYP/aug-cc-pVDZ level of theory. All bond lengths are given in angstroms and all angles in degrees.

The ground-state anion structure is best represented as an allene carbenoid substituted with hydrogen and an acetylide ion.



This structure is consistent with (i) the contracted C_1-C_2 and C_4-C_5 bond lengths of 1.27 Å, (ii) the C_2-C_3 and C_3-C_4 bond lengths of 1.38 Å (representative of carbon−carbon bonds between single and double bond character), and (iii) the C_2-C_3-H bond angle of 115° (close to the 120° expected for an sp^2-hybridized carbon). This structure differs somewhat from that calculated for the corresponding neutral. While the relative bond lengths remain almost the same, the $C_2-C_3-C_4$ bond angle is reduced from 129.1° in the anion to 112° in the neutral.[72] As with C_4CH, this geometric difference between the minimum energy geometries on the anion and neutral surfaces becomes significant in neutralization reionization experiments. In this case a vertical neutralization process will yield a vibrationally hot C_2CHC_2, particularly with respect to the $C_2-C_3-C_4$ scissor mode. Calculation of the energy of the anion geometry on the neutral surface gives an indication of the excess energy that may be attained. At the B3LYP/aug-cc-pVDZ//B3LYP/6-31G level of theory the anion geometry on the neutral surface was found to be 4.5 kcal mol^{-1} above the radical minima (not including zero-point energy contributions). Transition-state calculations for the neutral surface suggest that C_2CHC_2 is stable with respect to isomerization processes even when generated with 4.5 kcal mol^{-1} of excess internal energy. Only one isomerization pathway has been found leading from the C_2CHC_2 minimum (Figure 2). This is a 1,2-hydrogen shift via **TS4/9**, which produces noncyclic *l*-C_3CHC (**9**). Structure **9** is essentially unstable, with the barrier to a further 1,2-hydrogen shift below the zero-point energy of the minimum. Thus, further rearrangement via **TS9/1** yields C_4CH. **TS4/9** lies some 22 kcal mol^{-1} above C_2CHC_2; this is therefore the barrier for isomerization to C_4CH. Isomerization pathways of **4**, via cyclization processes, were not found. The energies of cationic C_2CHC_2 species have also been calculated (Table 2). Stable singlet and triplet electronic states were calculated, and it is therefore expected that these cations would be observed in vertical electron transfers from either anion or neutral charged states. We conclude from these data that (i) $C_2CHC_2^-$ is stable and a good candidate for synthesis in the gas phase and (ii) we would predict this anion should be a suitable precursor to laboratory generation of the C_2CHC_2 radical by vertical neutralization.

Several other stable anion connectivities have been established by this computational approach. These species are dramatically less stable than the ground-state anions discussed so far (for energies and structures see Tables 1 and 4, respectively). The neutral *c*-C_3CHC is stable, although nearly 50 kcal mol^{-1} more energetic than C_4CH. Electron attachment to this radical produces a $^3A'$ species almost 60 kcal mol^{-1} above the anionic global minima; the corresponding singlet is unstable and rearranges by ring closure to form a 3,3-bicyclic species, which is referred to here as $C_2CC_2H^-$ (**8**). $C_2CC_2H^-$ is only 34 kcal mol^{-1} above $C_2CHC_2^-$. The remaining stable anion connectivity is *l*-C_3CHC (**9**). This has a $^3A''$ state and is 50 kcal mol^{-1} above the global minima. This structure is essentially a ring-opened form of *c*-C_3CHC and is only stable on the anion surface. The corresponding neutral undergoes a barrierless 1,2-hydrogen transfer to give C_4CH in the manner previously discussed (Figure 2).

To summarize the theoretical results, (i) the radicals C_4CH (**1**), HC_2C_3 (**2**), C_2C_3H (**3**) are the most stable neutral isomers. Electron attachment to each of these species is a highly exothermic process with adiabatic electron affinities estimated at 2.44, 2.39, and 3.34 eV, respectively. Consequently, the corresponding anions would seem to be logical precursors for the neutral radicals in the gas phase, via an electron detachment process. (ii) The most stable C_5H anion structure is found to be C_2CHC_2, which represents the global minimum on the anion potential surface. The C_2CHC_2 anion would therefore be a logical starting point in attempts to generate the neutral C_2CHC_2 radical (and hence the first nonlinear C_5H species) in the laboratory.

Synthesis of Two Isomeric C_5H Anions and Neutrals. Experimental Confirmation of Structure. Previous studies have established the negative ion decomposition behavior of $^-C{\equiv}CCH_2-OCH_3$.[22] Collisional activation of this ion induced loss of methanol, forming *l*-C_3H^- as one of the major product ions. This process is rationalized as shown in Scheme 2.

SCHEME 2

$$^-C{\equiv}CCH_2{-}OCH_3 \rightarrow [(:C{=}C{=}CH_2)^-OCH_3] \rightarrow :C{=}C{=}CH^- + HOCH_3$$

A simple extension of this procedure to the corresponding diacetylide precursor resulted in observation of C_4CH^-.[31] The ion $^-C{\equiv}CC{\equiv}CCH_2-OCH_3$ can be formed by deuterium abstraction from $DC{\equiv}CC{\equiv}CCH_2-OCH_3$ or by desilylation of $TMSC{\equiv}CC{\equiv}CCH_2-OCH_3$ by hydroxide ions under the same chemical ionization conditions. The latter method is analogous to that originally developed by DePuy and co-workers.[57] Collisional activation of $^-C{\equiv}CC{\equiv}CCH_2OCH_3$ leads to losses of methanol, the methoxide radical, and formaldehyde corresponding to the anions of C_5H, C_5H_2 and C_5H_3, respectively (Table 5). The $C_5H_3^-$ species should have the structure $C_4CH_3^-$ given that hydride donation from the methoxide ion occurs at the same terminus from which it was eliminated.[22] The ion C_5H_2 has been shown previously by deuterium labeling to be C_4CH_2,[40] while the loss of methanol from $^-C{\equiv}CC{\equiv}CCH_2-OCH_3$ can only generate the C_4CH anion. These processes can also occur in the ion source of the mass spectrometer. The C_4CH anion can therefore be mass-selected and subjected to $^-CR^+$ and $^-NR^+$ experiments.

Theoretical predictions of the stability of the symmetrical C_2CHC_2 anion lead us to investigate ways to generate this ion in the gas phase. Initially, it was proposed that an analogous chemistry could be used for this system as for C_4CH described, i.e., loss of methanol from a 3-substituted pentadiyne precursor. Methanol is lost from the precursor ion $^-C{\equiv}CCH(OCH_3)C{\equiv}CD$ under collisional activation; however, deuterium labeling at the acetylenic positions shows exclusive loss of CH_3OH to form C_4CD^- (Scheme 3).

SCHEME 3

$$^-C{\equiv}CCH(OCH_3)C{\equiv}CD \rightarrow [(:C{=}C{=}CHC{\equiv}CD)^-OCH_3] \rightarrow C_4CD^- + HOCH_3$$

The methoxide ion shows preference for removing the proton from the 3-position over migration to the end of the carbon chain and removal of the more acidic acetylenic deuterium. A new approach was therefore required in order to synthesize $C_2CHC_2^-$ in the gas phase. The acetylide anion, $^-C{\equiv}CCH(OCOCH_3)C{\equiv}CH$, was formed by deprotonation of 3-penta-1,4-diynyl acetate under typical negative ion chemical ionization conditions. The collisional activation spectrum of this ion

TABLE 5: CA-MIKE Spectra for C_4CH and C_2CHC_2 Anion Precursors

precursor ion (*m*/*z*)	product ions [*m*/*z*, (loss or formation), relative abundance]
$[TMSC{\equiv}CC{\equiv}CCH_2OCH_3 - TMS^+]^-$ (*m*/*z* 93)	78 ($CH_3^\bullet$) 43, 77 (CH_4) 54, 63 (CH_2O) 47, 62 ($CH_3O^\bullet$) 42, 61 (CH_3OH) 100
$[HC{\equiv}CCH(OCOCH_3)C{\equiv}CH - H^+]^-$ (*m*/*z* 121)	120 ($H^\bullet$) 46, 95 (C_2H_2) 100, 93 (CO) 45, 79 (H_2C_2O) 44, 77 (CO_2) 39, 61 (C_5H^-) 43, 59 ($CH_3CO_2^-$) 37
$[HC{\equiv}CCD(OCOCH_3)C{\equiv}CH - H^+]^-$ (*m*/*z* 122)	121 ($H^\bullet$) 66, 96 (C_2H_2) 95, 95 (C_2HD) 100, 80 (H_2C_2O) 49, 78 (CO_2) 36, 62 (C_5D^-) 29, 59 ($CH_3CO_2^-$) 14
$[DC{\equiv}CCH(OCOCH_3)C{\equiv}CD - D^+]^-$ (*m*/*z* 122)	121 ($H^\bullet$) 66, 95 (C_2HD) 100, 80 (H_2C_2O) 41, 78 (CO_2) 24, 61 (C_5H^-) 41, 59 ($CH_3CO_2^-$) 30
$[HC{\equiv}CCH(OCOH)C{\equiv}CH - H^+]^-$ (*m*/*z* 107)	106 ($H^\bullet$) 53, 81 (C_2H_2) 16, 79 (CO) 40, 77 (H_2CO) 5, 63 ($C_5H_3^-$) 100, 61 (C_5H^-) 16, 51 ($C_4H_3^-$) 5, 49 (C_4H^-) 5, 45 (HCO_2^-) 9
$[HC{\equiv}CCH(OCOCH_2CH_3)C{\equiv}CH - H^+]^-$ (*m*/*z* 135)	134 ($H^\bullet$) 60, 120 ($CH_3^\bullet$) 21, 109 (C_2H_2) 100, 107 (CO) 67, 91 (CO_2) 26, 73 ($CH_3CH_2CO_2^-$) 27, 61 (C_5H^-) 11

showed formation of C_5H^- at *m*/*z* 61 (Table 5). Deuterium labeling at all positions assisted with structure determination of this product ion. The ion $[HC{\equiv}CCD(OCOCH_3)C{\equiv}CH - H^+]^-$, yields only *m*/*z* 62, while $[DC{\equiv}CCH(OCOCH_3)C{\equiv}CD - D^+]^-$ gives exclusively *m*/*z* 61 (Table 5). The products are thus $C_2CDC_2^-$ and $C_2CHC_2^-$, respectively. The mechanism of this reaction has been probed by examination of the labeling data and by investigation of the behavior of some related esters. The CA-MIKE (collisional activation mass-analyzed ion kinetic energy) spectrum of $[DC{\equiv}CCH(OCOCH_3)C{\equiv}CD - D^+]^-$ shows formation of $C_2CHC_2^-$, suggesting that the precursor ion is an acetylide rather than an enolate anion. This points to either elimination of acetic acid or loss of carbon dioxide and methane as two possible reaction pathways (Scheme 4).

SCHEME 4

$$^-C{\equiv}CCH(OCOCH_3)C{\equiv}CH \rightarrow C_2CHC_2^- + HO_2CCH_3$$

$$^-C{\equiv}CCH(OCOCH_3)C{\equiv}CH \rightarrow C_2CHC_2^- + CO_2 + CH_4$$

The corresponding formate and propionate esters have also been synthesized. The $[M-H]^-$ ions of both of these precursors show *m*/*z* 61 in their respective CA mass spectra.[73] Source-formed C_5H anions from all these ester precursors gave identical $^-CR^+$ spectra, confirming the proposal of the same connectivity in each case.

Further support for the structures of the two C_5H anions can be gained by examining their spectra. The conventional CA mass spectra of the respective ions yield virtually no structural information, since both species show only loss of a hydrogen radical with formation of $C_5^{\bullet-}$. In comparison, the $^-CR^+$ spectra show extensive fragmentation, with the decomposition of the carbon chain giving fragments C_nH^+ and $C_n^{\bullet+}$ ($n = 2-5$). The charge reversal spectra of both isomers show the formation of common fragments, but the abundances of peaks are dramatically different (Figure 6). Consideration of the charge-reversed parent ion C_5H^+ in each spectrum serves to illustrate this difference. The ion corresponding to C_4CH^+ is the base peak in the $^-CR^+$ spectrum of C_4CH^-, suggesting this cation is a very stable species with respect to decomposition processes. The major fragmentation observed is loss of a hydrogen radical (79% of the base peak), while further decompositions are minor processes with the largest of these being the formation of $C_4^{\bullet+}$ at *m*/*z* 48 (9%). This is in contrast to the situation for the isomeric C_2CHC_2 anion. The $^-CR^+$ spectrum of this species shows not the charge-reversed parent ion but a fragment ion, namely, $C_5^{\bullet+}$, as the base peak of the spectrum. Further fragmentations to lower mass product ions are also much more pronounced, with $C_4^{\bullet+}$ (37%) of comparable intensity with the parent cation (49%). This result suggests a much lower stability of the cation produced in the latter charge reversal experiment over that generated in the former. This is in line with the trend predicted for connectivities C_4CH and C_2CHC_2 by the molecular orbital calculations previously described. That is, while the anions of these geometries are of comparable energy, their corresponding cations (formed here by vertical two-electron transfer in the charge reversal process[35,74]) differ significantly in stability. Ground-state C_4CH^+ is some 80 kcal mol^{-1} lower in energy than singlet $C_2CHC_2^+$ (Table 4) and as such is significantly more stable with respect to decomposition processes. These charge reversal spectra clearly distinguish the structures of the two C_5H^- anions by the differing abundances of each fragmentation from their corresponding cations. This established, it would seem that these anions are suitable precursors for the formation of the corresponding neutrals by neutralization reionization mass spectrometry.

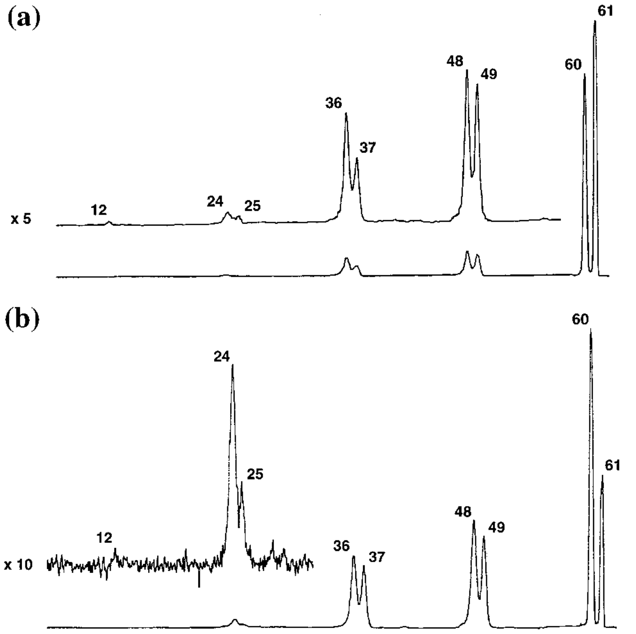


Figure 6. $^-CR^+$ (O_2, 80% T; O_2, 80% T) spectra of *m*/*z* 61 from (a) $TMSC{\equiv}CC{\equiv}CCH_2OCH_3$, giving C_4CH^-, and (b) $HC{\equiv}CCH(OCOCH_2CH_3)C{\equiv}CH$, giving $C_2CHC_2^-$. These spectra both show fragments of the forms C_nH^+ and $C_n^{\bullet+}$.

The $^-NR^+$ spectra of both C_4CH^- and $C_2CHC_2^-$ are shown in Figure 7. As with the charge reversal spectra, the peaks observed in these spectra are of masses corresponding to the ions C_nH^+ and $C_n^{\bullet+}$ ($n = 2-5$). Significantly, survivor ions (ions of *m*/*z* 61, corresponding to C_5H^+ species) are detected in the $^-NR^+$ spectra of C_4CH^- and $C_2CHC_2^-$. This can only occur if some stable neutral C_5H is accessed in the neutralization reionization process. From the molecular orbital calculations previously outlined, it has been shown that both C_4CH and C_2CHC_2 have stable anions, neutrals, and cations, and as such, it

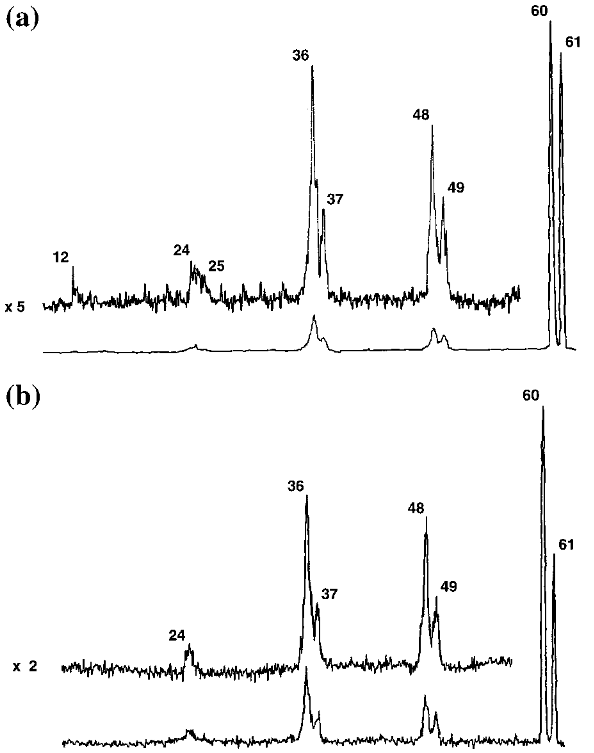


Figure 7. $^{-}NR^{+}$ (O_2, 80% T; O_2, 80% T) spectra of *m/z* 61 from (a) TMSC≡CC≡CCH_2OCH_3, giving C_4CH^-, and (b) HC≡CCH($OCOCH_2$-CH_3)C≡CH, giving $C_2CHC_2^-$. These spectra both show fragments of the forms C_nH^+ and $C_n^{\bullet+}$.

is expected that the neutral produced in this experiment is of the same connectivity as the anion. Experimentally, should isomerization of the neutral occur, it would be expected that there should be major discrepancies between the corresponding $^{-}CR^{+}$ and $^{-}NR^{+}$ spectra. The cations resulting from both processes should have different geometries and energies and should display different fragmentations (cf., refs 59, 60, and 62). Comparison of the charge reversal and neutralization reionization spectra of C_2CHC_2 [Figures 6b and 7b] reveal a consistency between the fragmentations observed. Most noticeably, the parent cation (*m/z* 61) remains at about the same intensity with respect to the C_5^+ fragment (56%). The similarities between these spectra point to (i) structural continuity between the incident C_2CHC_2 anion and the neutral and cation formed in this experiment and (ii) favorable Franck−Condon overlap of the three surfaces.[68,69] It can be concluded that the neutral C_2CHC_2 radical has been generated in this experiment.

A similar inspection of the C_4CH^- spectra [Figures 6a and 7a] reveals some subtle variation, most notably in the region of the parent cation. While *m/z* 61 is the base peak in the $^{-}CR^{+}$ spectrum, it is slightly less intense than the C_5^+ signal (92%) in the $^{-}NR^{+}$ spectrum. This is most likely due to some fragmentation of the neutral. In their theoretical work, Crawford et al. discovered that along with the stable $^2\Pi$ ground state of neutral C_4CH there exists a dissociative $^2\Sigma^+$ surface that leads to production of C_2H and C_3.[28] This surface could be accessible by vertical excitation of the C_4CH anion by collision, producing neutral fragments concomitant with the generation of the stable C_4CH neutral $^2\Pi$ state. This rationale is proposed to account for the different abundances of *m/z* 61 in CR and NR experiments. Such a process is more probable than isomerization of neutral C_4CH (see earlier). The recovery signal observed in the $^{-}NR^{+}$ spectrum of C_4CH^- is thus attributed to the neutral $^2\Pi$ C_4CH species.

Conclusions

Theoretical studies have shown the stability of a range of anions of the form C_5H. This has prompted attempts to use these charged species as gas-phase precursors of the corresponding neutrals by neutralization reionization mass spectrometry. Anions and neutrals with the connectivities C_4CH and C_2CHC_2 have been synthesized in the gas phase with the neutrals shown to be stable on the time scale of the NR experiment (ca. 10^{-6} s). This is the first report of the observation of a nonlinear C_nH isomer (where $n > 3$). The stability of this molecule in the laboratory lends support to its candidacy as a possible interstellar species. Further, the large electron affinities of the radicals C_4-CH and C_2CHC_2 (2.44 and 4.54 eV) suggest the anions too may be present in these galactic environments.[75]

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Supporting Information Available: The geometries of (i) C_5H neutrals **1**−**6** calculated at the B3LYP/aug-cc-pVDZ levels, (ii) the transition structures and intermediates **TS4/9**, **9**, **TS9/1**, **TS1/2**, and **TS1/3** calculated at the B3LYP/6-31G level, (iii) geometries for the C_5H cations listed in Table 2 calculated at the B3LYP/aug-cc-pVDZ level, and (iv) dipole moments, rotational constants, harmonic frequencies, and intensities for the four stable ground-state anions are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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