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Formation of Neutral C_7H_2 Isomers from Four Isomeric C_7H_2 Radical Anion Precursors in the Gas Phase

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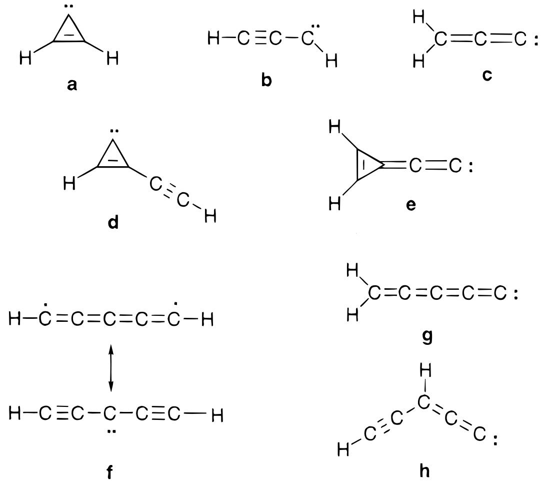
Consideration of theoretical calculations [B3LYP/aug-cc-pVDZ//B3LYP/6-31G(d)] of the structures of ten C_7H_2 neutral isomers and the nine corresponding C_7H_2 radical anions have led us to synthesize four stable C_7H_2 radical anions in the ion source of our ZAB 2HF mass spectrometer, and to convert these to C_7H_2 neutrals. The four radical anion isomers prepared were (i) $[(HC{\equiv}C)_2C{=}C{=}C]^{-\bullet}$ [from the reaction between $(HC{\equiv}C)_3COCH_3$ and HO^-], (ii) $[HC{=}C{=}C{=}C{=}C{=}C{=}CH]^{-\bullet}$ [from the reaction between $HC{\equiv}C{-}C{\equiv}C{-}CD(OH){-}C{\equiv}CH$ and HO^-], (iii) $[C{=}C{=}C{=}C{=}C{=}C{=}CH_2]^{-\bullet}$ [from the reaction between $DC{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}CH_2OCH_2CH_3$ and HO^-], and (iv) $[C{\equiv}C{-}CH_2{-}C{\equiv}C{-}C{\equiv}C]^{-\bullet}$ [from the bis desilylation reaction of $(CH_3)_3Si{-}C{\equiv}C{-}CH_2{-}C{\equiv}C{-}C{\equiv}C{-}Si\ (CH_3)_3$ with $SF_6^{-\bullet}$]. The four anions were further characterized by their collisional activation (negative ion) and charge reversal (CR, positive ion) mass spectra. The anions were converted into their corresponding neutrals by charge stripping, and the correspondence between the charge reversal (CR) and neutralization reionization ($^-NR^+$) mass spectra of each anion is taken as evidence that within the time frame of the $^-NR^+$ experiment (some 10^{-6} s), each neutral is stable and undergoes no major rearrangement or interconversion to a more stable isomer. Theory and experiment are in accord for these systems.

Introduction

Since the discovery of the cyclic carbene C_3H_2 in interstellar and circumstellar environments, interest in the generation of carbenes of the form C_nH_2 has increased.[1,2] The three C_3H_2 isomers **a**−**c** (Scheme 1) have been synthesized[3−7] and studied theoretically.[8,9] Even electron cumulenes C_nH_2 ($n = 2$ and 4) have been studied by mass spectrometric techniques.[10,11] The C_5H_2 isomers **d**−**h** have been studied, of which four (**d**, **f**, **g**, and **h**) have been synthesized.[12−14]

By comparison, less is known experimentally of C_7H_2 structures. No neutral of composition C_7H_2 has been detected in interstellar or circumstellar gas clouds,[15,16] even though models for the chemistry of these regions predict that such species could be present in detectable amounts.[17] However, the C_6CH_2 isomer has been proposed as a prime candidate for astrophysical detection due to its calculated dipole moment of more than 7 D.[13,18] The bond connectivities (and valence bond representations) of 10 C_7H_2 isomers are shown in Scheme 2. The minimum energy structures for seven of these (structures **1**, **2**, **4**, **5**, **6**, **7**, and **8**, Scheme 2) have been computed at the MP2/D95** level of theory. [19] A third C_3 ring structure (**3**) has been proposed to be a stable system; however the energy of this structure has not been determined.[20] Six of the structures computed earlier have the singlet as the lower energy state (**1**, **2**, **4**, and **6**−**8**) while **5** has the triplet as the lower energy structure. The ground states of all seven of these computed structures fall within a range of 22 kcal mol^{-1} (at ACPF/ANO//MP2/D95** level of theory). Structures **1** and **2** are the most stable isomers. Both have $(4n + 2)\pi$ electron occupation of the ring: aromaticity may account for their enhanced stability compared with other isomers. These two structures may be considered as extensions of the aromatic cyclopropenylidene (**a**).[8,9]

SCHEME 1



Three C_7H_2 isomers have been detected in the laboratory, viz. (i) rotational transitions corresponding to cyclic **2** have been detected in a dc electrical discharge in a neon−diacetylene environment: this species is some 15 times less abundant than C_5H_2 isomers generated in the same experiment;[20] (ii) HC_7H (**5**) has been trapped in a low-temperature matrix, and its electronic spectrum provides evidence for the linear triplet ground state predicted by theory;[12] and (iii) a preliminary communication reports the formation of C_6CH_2 (**6**) following neutralization reionization of precursor $[C_6CH_2]^{-\bullet}$ in a mass spectrometer.[21]

We have previously used (i) neutralization of anionic precursors to generate three transient neutral isomers of C_5H_2 and (ii) positive ion mass spectrometry as a probe to characterize the neutrals.[14] An anion with a known bond connectivity is a

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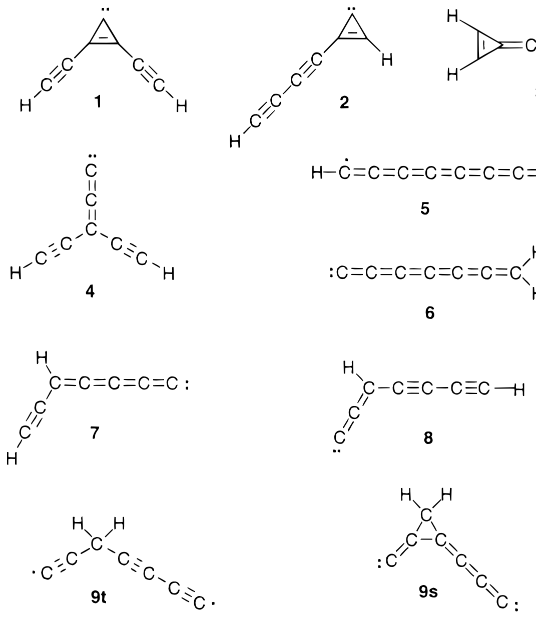
SCHEME 2



particularly reliable precursor for a neutral, because an anion formed by a soft ionization process (like deprotonation or some other appropriate ion−molecule reaction) generally has insufficient excess energy of formation to allow either fragmentation or rearrangement to an anion with a different bond connectivity.[14] In this paper, we use a similar approach to investigate the formation of C_7H_2 isomers from four C_7H_2 radical anion precursors. First, computational chemistry is used to study the structures of anion and neutral C_7H_2 isomers in order to see whether the appropriate anion C_7H_2 isomer is a suitable precursor for the formation of the corresponding neutral. If there is favorable vertical Franck−Condon overlap between anion and neutral potential surfaces, the anion may be a suitable precursor of the neutral. If the synthesis of the appropriate anion is effected, it is then charge stripped in the mass spectrometer to form a neutral. Finally, if there is also favorable Franck−Condon overlap between the neutral and its corresponding cation, we ionize the neutral and investigate the use of the resulting positive ion spectrum as a probe of the bond connectivity of the neutral.

Experimental Section

Computational Methods. Geometry optimizations were carried out with the Becke 3LYP method[22,23] utilizing the 6-31G(d) basis set within the GAUSSIAN 94[24]suite of programs. The larger Dunning aug-cc-pVDZ[25,26] basis was used to determine more accurate energies for B3LYP/6−31(d) geometries. 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[27] 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 has been demonstrated that this method produces optimized structures, at a low computational cost, which compare favorably with higher level calculations.[14] The described computational method was tested using l-C_3H_2 (**c**, Scheme 1) giving a computed adiabatic electron affinity of 1.94 eV compared with the experimentally determined 1.794 ± 0.025 eV.[28] Calculations involving GAUSSIAN 94 geometry optimizations at B3LYP/6-31G(d) and single point energy calculations at the B3LYP/aug-cc-pVDZ level were carried out using the Power Challenge Super Computers at the South Australian Super Computing Centre (Adelaide) and the Australian National University Super Computing Facility (Canberra).

Mass Spectrometric Methods. Charge reversal (CR) and neutralization reionization (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.[29] The instrument has been 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 source temperature 200 °C, ionizing energy 70 eV (tungsten filament), and accelerating voltage −7 kV. All slits were fully open in order to minimize mass discrimination effects due to energy resolution.[30,31] The reagent ion HO^- was generated from electron impact on H_2O (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 coworkers[32] and extended by Squires.[33,34]

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.[35] Residual ions were removed using the deflector electrode, with neutrals passing into the second cell where they were reionized to the corresponding cation under conditions identical with 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.[36−39] All spectra were repeated a minimum of three times in order to establish their reproducibility.

Synthesis of Precursor Molecules. *1-Ethoxy-7-deuterio-hepta-2,4,6-triyne* ($DC{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}CH_2{-}OC_2H_5$). 1-Ethoxy-7-trimethylsilylhepta-2,4,6-triyne was prepared by a coupling of 1-lithio-4-trimethylsilylbutadiyne and 1-ethoxy-3-bromopropyne using a reported procedure.[40] To bis(trimethylsilyl)butadiyne (1 g, 5.2 mM) in dry diethyl ether (30 mL) was added ethereal $CH_3Li{\cdot}LiBr$ (5.2 mM) at 20 °C and under nitrogen, the mixture was stirred at 20 °C for 6 h and cooled to 0 °C, and freshly purified CuBr [0.75 g (5.2 mM)] was added. The mixture was allowed to warm to 20 °C and stirred at that temperature for 30 min, the solvent was removed under reduced pressure, and dry pyridine (10 mL) was added followed by 1-ethoxy-3-bromopropyne[41] (0.85 g, 5.2 mM) causing the temperature to rise to 45 °C. The dark brown mixture was stirred at 20 °C for 1 h and poured into aqueous hydrogen chloride (2 M, 50 mL) at 0 °C, the mixture was extracted with diethyl ether (3 × 40 mL), the organic extract was dried ($MgSO_4$) and concentrated under reduced pressure, and the residue was separated by column chromatography over silica eluting with diethyl ether/hexane (1:9) to give 1-ethoxy-7-trimethylsilylhepta-2,4,6-triyne as a light brown oil (0.35 g, 35%). ^1H NMR (200 MHz, $CDCl_3$) 0.15 (s, 9H) 1.23 (t, 3H) 3.5 (q, 2H) 4.15 (s, 2H). $[M - H]^- = 203.08865$ $C_{12}H_{15}OSi$ requires 203.08878.

Desilylation of the above product was carried out with CH_3OD/OD^- (using a procedure described by Ghose[42]) to yield 1-ethoxy-7-deuteriohepta-2,4,6-triyne (in quantitative yield), which decomposes at room temperature within a few hours but is stable for at least a week if stored in the dark at −20 °C.

1,7-Bis(trimethylsilyl)hepta-1,4,6-triyne [$(CH_3)_3Si-C\equiv C-CH_2-C\equiv C-C\equiv C-Si(CH_3)_3$]. An ethereal solution of $CH_3Li \cdot LiBr$ (5.2 mM) was added to bis(trimethylsilyl)butadiyne (1 g, 5.2 mM) in anhydrous tetrahydrofuran (30 mL), the mixture was stirred at 20 °C for 6 h and cooled to 0 °C, and freshly purified CuBr (0.75 g, 5.2 mM) was added. The mixture was stirred at 20 °C for 30 min, 1-trimethylsilyl-3-bromoprop-1-yne (1 g, 5.2 mM) in anhydrous tetrahydrofuran (5 mL) was added, the mixture was heated at reflux for 1 h, then cooled to 20 °C, and extracted with hexane (3 × 40 mL); the organic extract was dried ($MgSO_4$) and concentrated at reduced pressure to obtain the crude product, which was purified by chromatography over silica eluting with hexane to obtain 1,7-bis(trimethylsilyl)hepta-1,4,6-triyne as a colorless oil (0.25 g, 30% yield). ^1H NMR (200 MHz, $CDCl_3$) 0.16 (s, 18H) 3.28 (s, 2H). $M^{+\bullet} = 232.1116$ $C_{13}H_{20}Si_2$ requires 232.1102.

3-Deuterio-3-hydroxyhepta-1,4,6-triyne [$HC\equiv C-CD(OH)-C\equiv C-C\equiv CH$]. An ethereal solution of $CH_3Li \cdot LiBr$ (5.2 mM) was added to bis(trimethylsilyl)butadiyne (1 g, 5.2 mM) in anhydrous tetrahydrofuran (30 mL), the mixture was stirred at 20 °C for 6 h and cooled to 0 °C, freshly prepared magnesium bromide [1.3 equiv (from Mg and 1,2-dibromoethane)] was added, the mixture was allowed to warm to 20 °C, stirred for 1 h, and was cooled to 5 °C; $(CH_3)_3Si-C\equiv C-CDO$[43] (0.65 g, 5.2 mM) in anhydrous tetrahydrofuran (5 mL) was added dropwise, and the mixture was allowed to stir at 20 °C for 16 h. The mixture was cooled to 0 °C, and aqueous ammonium chloride (saturated, 5 mL) was added, followed by extraction with diethyl ether (3 × 40 mL). The organic extract was dried ($MgSO_4$), concentrated under reduced pressure, and chromatographed over silica eluting with diethyl ether/hexane (15:85) to yield 1,7-bis(trimethylsilyl)-3-deuterio-3-hydroxyhepta-1,4,6-triyne as a colorless oil (0.67 g, 52%). ^1H NMR (200 MHz, $CDCl_3$) 0.15 (s, 18H). Desilylation was carried out by a standard method[44] with sodium tetraborate to give 3-deuterio-3-hydroxyhepta-1,4,6-triyne as an reddish brown oil in 65% yield. ^1H NMR (200 MHz, $CDCl_3$) 2.12 (s, 1H), 2.23 (s, 1H).

3-Ethynyl-3-methoxypenta-1,4-diyne [$(HC\equiv C)_3C-OCH_3$] was prepared by a reported procedure.[45]

Results and Discussion

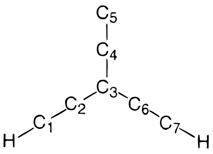
Theoretical Predictions for C_7H_2 Isomers Relative Stability of Isomeric C_7H_2 Neutrals. The neutral C_7H_2 isomers **1**−**9** were optimized at the economical B3LYP level of theory using the 6-31G(d) basis set. The structures determined in this way are in excellent agreement with those (**1**, **2**, and **4**−**8**) calculated at the MP2 level by Aoki and Ikuta using the double ζ D95** basis set.[19] The geometries of neutrals **4**, **5**, **6**, **9s,** and **9t** (those neutrals synthesized in this study) are listed in Table 1, while the geometries of **1**, **2**, **3**, **7**, and **8** are recorded as Supporting Information. The calculated structures are in general accord with the valence bond representations shown in Scheme 2. Isomers **1**−**8** all have stable singlet and triplet electronic states which have similar geometries, and apart from **5**, all have singlet ground states. Optimization of the $C_2CH_2C_4$ connectivity leads to two quite different structures for the singlet and triplet electronic states. The singlet species forms the C3-ring structure **9s**, which is more stable than the open chain triplet structure **9t** by some 20 kcal mol^{-1}. The relative energies, adiabatic electron affinities, and dipole moments of the neutral isomers of C_7H_2 have been determined using the more extensive Dunning, aug-cc-pVDZ basis set at the B3LYP level of theory. Those data are listed in Table 2 for the ground state neutrals of **1**−**8** and for **9s** and **9t.** The energy trend (at the level of theory we have used) of the isomers differs marginally from that reported earlier: our results indicate that, of the 10 isomers, HC_7H (**5**) is the most stable [rather than *c*-HC_4C_3H (**2**)[19]]. As expected, the cyclic structures **1** (*c*-$HC_2C_3C_2H$) and **2** (*c*-HC_4C_3H) are more stable than **3** (*c*-$H_2C_3C_4$) because **1** and **2** have aromatic stabilization in the three-membered ring, which is not possible for **3** where the cyclopropene ring is fully substituted. The triplet **9t** is the least stable of the 10 isomers, being 106.1 kcal mol^{-1} more positive in energy than the global minimum **5**. The isomers have adiabatic electron affinities within the range 1.25−4.08 eV (Table 2). Except for **5** (which has a center of symmetry), all isomers have appreciable dipole moments [3.7−10.9 D (the largest is for **3**); see Table 2]. Should any of these neutrals be present in inter- or circumstellar media, they would be suitable candidates for detection via their rotational spectra because of their substantial dipole moments.

Structures and Relative Stabilities of Isomeric C_7H_2 Radical Anions. The geometries, energies, and dipole moments of the negative ions corresponding to the neutrals are shown in Tables 1 and 3. The level of calculation for the anions is the same as that used (above) for the neutrals. The stability of the neutral C3 ring systems **1** and **2** in comparison to that of **3** has been interpreted in terms of the aromatic ring stabilization of **1** and **2**. Addition of an electron to the singlet structures of **1** or **2** produces the corresponding radical anions which now contain more than $(4n + 2)$ π electrons in the ring, and as a consequence have lost the aromatic stabilization shown by the corresponding neutrals. Thus all three ring anions $\mathbf{1}^{-\bullet}$, $\mathbf{2}^{-\bullet}$, and $\mathbf{3}^{-\bullet}$ are less stable than the majority of the other isomers as a consequence of their unfavorable ring strain (see Table 3). The relative energies of isomers $\mathbf{4}^{-\bullet}$−$\mathbf{8}^{-\bullet}$ all lie within 21 kcal mol^{-1} of each other at the level of theory used, with $C_6CH_2^{-\bullet}$ ($\mathbf{6}^{-\bullet}$) being the lowest energy isomer. Isomer $\mathbf{9}^{-\bullet}$ [($C_2CH_2C_4^{-\bullet}$)], with a relative energy of 57.17 kcal mol^{-1}, is the least stable of all of the isomers listed in Table 3. Isomer $\mathbf{9}^{-\bullet}$, is the precursor of both of the neutrals **9s** and **9t** (Scheme 1 and Tables 1 and 2). The dipole moments of the nine isomeric radical anions fall within the range 1.6−8.8 D, with $\mathbf{3}^{-\bullet}$ having the highest value (Table 3). Should any of the neutrals **1**−**8**, **9s**, and **9t** occur in interstellar or circumstellar environments, there is a significant possibility that their corresponding anions might also be present in view of the high electron affinities of the neutrals (see Table 2).[46] The large dipole moments of these isomeric anions (Table 3) will assist their identification via their rotational spectra.

Comparison of Energies of Anions and Neutrals: Selection of Anions for Synthesis. We now compare the structure of the each radical anion with that of the ground state energy neutral. The geometries of the anion and neutral pair of **4**, **5**, **6**, **9s**, and **9t** are recorded in Table 1, while the corresponding data

TABLE 1: Geometries of Radical Anions, Neutrals, and Cations of 4, 5, 6, and 9 [B3LYP/6-31G(d)]

$HC_2C(C_2)C_2H$ (**4**)



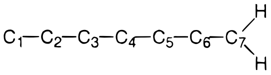
	anion	neutral	cation[a]		anion	neutral	cation[a]
electronic state	$^2B_1$	$^1A_1$	$^2A_1$	C_4-C_5 (Å)	1.271	1.283	1.221
symmetry	C_{2v}	C_{2v}	C_{2v}	$H-C_1-C_2$ (deg)	178.9	179.1	179.8
$H-C_1$ (Å)	1.064	1.068	1.074	$C_1-C_2-C_3$ (deg)	179.6	179.5	179.9
C_1-C_2 (Å)	1.219	1.211	1.218	$C_2-C_3-C_4$ (deg)	121.6	121.4	119.7
C_2-C_3 (Å)	1.424	1.424	1.396	$C_3-C_4-C_5$ (deg)	116.8	117.1	120.6
C_3-C_4 (Å)	1.394	1.355	1.403	$C_4-C_5-C_6$ (deg)	180.0	180.0	180.0

HC_7H (**5**)

$H-C_1-C_2-C_3-C_4-C_5-C_6-C_7-H$

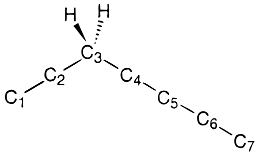
	anion	neutral	cation[a]		anion	neutral	cation[a]
electronic state	$^2A_2$	$^3\Sigma_g$	$^2\Sigma_g$	C_3-C_4 (Å)	1.283	1.277	1.273
symmetry	C_{2v}	$D_{\infty h}$	$D_{\infty h}$	$H-C_1-C_2$ (deg)	143.1		
$H-C_1$ (Å)	1.074	1.066	1.074	$C_1-C_2-C_3$ (deg)	175.0		
C_1-C_2 (Å)	1.258	1.233	1.232	$C_2-C_3-C_4$ (deg)	179.0		
C_2-C_3 (Å)	1.320	1.326	1.318	$C_3-C_4-C_5$ (deg)	179.1		

C_6CH_2 (**6**)



	anion	neutral	cation[a]		anion	neutral	cation[a]
electronic state	$^2B_1$	$^1A_1$	$^2B_2$	C_7-H (Å)	1.090	1.090	1.091
symmetry	C_{2v}	C_{2v}	C_{2v}	$C_1-C_2-C_3$ (deg)	180.0	180.0	180.0
C_1-C_2 (Å)	1.272	1.289	1.227	$C_2-C_3-C_4$ (deg)	180.0	180.0	180.0
C_2-C_3 (Å)	1.334	1.301	1.335	$C_3-C_4-C_5$ (deg)	180.0	180.0	180.0
C_3-C_4 (Å)	1.256	1.270	1.244	$C_4-C_5-C_6$ (deg)	180.0	180.0	180.0
C_4-C_5 (Å)	1.323	1.293	1.314	$C_5-C_6-C_7$ (deg)	180.0	180.0	180.0
C_5-C_6 (Å)	1.261	1.271	1.257	C_6-C_7-H (deg)	122.0	121.6	121.1
C_6-C_7 (Å)	1.345	1.320	1.330	$H-C_7-H$ (deg)	116.0	116.8	117.8

$C_2CH_2C_4$[b] (**9**)



	anion	neutral **9s**	neutral **9t**	cation[a]		anion	neutral 9s	neutral 9t	cation[a]
electronic state	$^2A''$	$^1A'$	$^3A''$	$^2A'$	$C_2-C_4-C_5$ (deg)		146.2		
symmetry	C_s	C_s	C_s	C_s	$C_3-C_4-C_5$ (deg)	176.3		177.7	183.2
C_1-C_2	1.263	1.300	1.240	1.211	$C_4-C_5-C_6$ (deg)	177.5	179.4	181.1	178.9
C_2-C_3 (Å)	1.472	1.541	1.474	1.466	$C_5-C_6-C_7$ (deg)	178.9	179.7	180.1	184.6
C_2-C_4 (Å)	2.288	1.430	2.416	2.364	C_2-C_3-H (deg)	112.5	116.5	110.9	112.0
C_3-C_4 (Å)	1.460	1.474	1.456	1.446	$H-C_1-C_2-C_3$ (deg)	−60.2	−71.8		
C_4-C_5 (Å)	1.237	1.297	1.236	1.260	$C_1-C_2-C_3-C_4$ (deg)	180.0	180.0	180.0	180.0
C_5-C_6 (Å)	1.343	1.290	1.329	1.298	$C_2-C_3-C_4-C_5$ (deg)	0.0	180.0	0.0	0.0
C_6-C_7 (Å)	1.272	1.293	1.293	1.335	$C_2-C_4-C_5-C_6$ (deg)		180.0		
C_3-H (Å)	1.103	1.089	1.101	1.106	$C_3-C_4-C_5-C_6$ (deg)	180.0		180.0	180.0
$C_1-C_2-C_3$ (deg)	176.3	137.0	164.0	181.5	$C_4-C_5-C_6-C_7$ (deg)	0.0	0.0	0.0	0.0
$C_1-C_2-C_4$ (deg)		163.6			$C_1-C_2-C_3-H$ (deg)	60.2	71.8	58.6	53.0
$C_2-C_3-C_4$ (deg)	102.6	56.6	111.1	108.6					

[a] Cation energies [B3LYP/aug-cc-pVDZ//B3LYP/6-31G(d)] in hartrees (zero point energy corrected): $\mathbf{4}^{+\bullet}$, −267.29716, $\mathbf{5}^{+\bullet}$, −267.36841, $\mathbf{6}^{+\bullet}$, −267.26180; and $\mathbf{9}^{+\bullet}$, −267.14728. [b] The anion $\mathbf{9}^{-\bullet}$, triplet neutral **9t**, and cation $\mathbf{9}^{+\bullet}$ have structures based on the bond connectivity shown above. Singlet **9s**, in contrast, contains a single bond (1.430 Å) between C_2 and C_4 (see Scheme 2 for a representation of the structure of **9s**).

for **1**−**3**, **7**, and **8** are provided as Supporting Information. Comparison of these data show that the geometries of all structural pairs $\mathbf{1}/\mathbf{1}^{-\bullet}$ to (and including) $\mathbf{8}/\mathbf{8}^{-\bullet}$ are very similar. This suggests that neutrals **1**−**8** should be accessible via the anions $\mathbf{1}^{-\bullet}$−$\mathbf{8}^{-\bullet}$ because of favorable vertical Franck−Condon overlap between the anion and neutral potential surfaces. In

TABLE 2: Energies, Electron Affinities, and Dipole Moments of Neutrals 1−9 [B3LYP/aug-cc-pVDZ//B3LYP/6-31G(d)]

isomer	electronic state (point group)	electronic energy[a] (hartrees)	zero-point energy (hartrees)	relative energy[b] (kcal mol^{-1})	adiabatic electron affinity (eV)	dipole moment (D)
1 c-$HC_2C_3C_2H$	$^1A'$ (C_s)	−267.691 51	0.052 61	17.51	1.25	3.74
2 c-HC_4C_3H	$^1A'$ (C_s)	−267.691 51	0.052 61	13.65	1.43	3.63
3 c-$H_2C_3C_4$	$^1A'$ (C_{2v})	−267.659 71	0.053 22	33.99	1.75	10.88
4 $HC_2C(C_2)C_2H$	$^1A_1$ (C_{2v})	−267.655 90	0.051 15	35.11	2.74	5.58
5 HC_7H	$^3\Sigma_g$ ($D_{\infty h}$)	−267.710 51	0.049 77	0.0	1.86	0
6 C_6CH_2	$^1A_1$ (C_{2v})	−267.678 25	0.052 93	22.17	3.09	7.33
7 HC_2CHC_4	$^1A'$ (C_s)	−267.670 97	0.052 30	26.36	2.94	6.69
8 C_2CHC_4H	$^1A'$ (C_s)	−267.670 72	0.052 52	26.65	2.73	5.93
9t $C_2CH_2C_4$	$^3A''$ (C_s)	−267.542 84	0.049 36	106.13		4.08
9s $C(c$-$CCH_2C)C_3$	$^1A'$ (C_s)	−267.575 10	0.051 28	85.89	3.38	3.88

[a] ZPE uncorrected. [b] Relative energy includes ZPE corrected by 0.9804.

TABLE 3: Energies and Dipole Moments of Radical Anions of 1−9 [B3LYP/aug-cc-pVDZ//B3LYP/6-31G(d)]

isomer	electronic state (point group)	electronic energy[a] (hartrees)	zero-point energy (hartrees)	relative energy[b] (kcal mol^{-1})	dipole moment (D)
$\mathbf{1}^{-\bullet}$ c-$HC_2C_3C_2H$	(C_1)	−267.726 06	0.047 30	37.85	3.04
$\mathbf{2}^{-\bullet}$ c-HC_4C_3H	(C_1)	−267.740 78	0.049 34	29.87	2.68
$\mathbf{3}^{-\bullet}$ c-$H_2CC_3C_4$	(C_1)	−267.721 91	0.051 03	42.75	8.75
$\mathbf{4}^{-\bullet}$ $H_2C(C_2)C_2H$	$^2B_1$ (C_{2v})	−267.753 64	0.048 27	21.14	7.07
$\mathbf{5}^{-\bullet}$ HC_7H	$^2B_1$ (C_{2v})	−267.777 81	0.048 86	6.34	1.63
$\mathbf{6}^{-\bullet}$ C_6CH_2	$^2B_1$ (C_{2v})	−267.776 85	0.052 11	0.00	8.09
$\mathbf{7}^{-\bullet}$ HC_2CHC_4	$^2A''$ (C_s)	−267.776 85	0.050 25	7.79	8.71
$\mathbf{8}^{-}$ C_2CHC_4H	(C_1)	−267.769 03	0.050 45	12.82	8.57
$\mathbf{9}^{-\bullet}$ $C_2CH_2C_4$	$^2A'$ (C_s)	−267.699 90	0.052 02	57.17	5.98

[a] ZPE uncorrected. [b] Relative energy includes ZPE corrected by 0.9804.

contrast, the situation for $\mathbf{9}^{-\bullet}$ [$(C_2CH_2C_4)^{-\bullet}$] is more complex. In this case the structure of the anion is similar to that of the higher energy triplet **9t**, but significantly different from that of the lower energy singlet neutral **9s**, suggesting that **9t** is likely to be the major product following vertical Franck−Condon charge stripping of $\mathbf{9}^{-\bullet}$.

Which precursor anions should we choose for synthesis? Those containing C3 rings ($\mathbf{1}^{-\bullet}$−$\mathbf{3}^{-\bullet}$) are not good choices, since (i) all three radical anions have relatively high energies (Table 3) and (ii) unequivocal syntheses of these three anions would be very difficult. In principle, anions $\mathbf{4}^{-\bullet}$−$\mathbf{8}^{-\bullet}$ are all appropriate, since all have relative energies within 21 kcal mol^{-1} of the global minimum ($\mathbf{6}^{-\bullet}$). Of these, we have chosen to synthesize $\mathbf{4}^{-\bullet}$, $\mathbf{5}^{-\bullet}$, and $\mathbf{6}^{-\bullet}$. We have not attempted the synthesis of $\mathbf{7}^{-\bullet}$ and $\mathbf{8}^{-\bullet}$ because these syntheses are particularly challenging. Finally, isomer [$(C_2CH_2C_4{}^{-\bullet})$] ($\mathbf{9}^{-\bullet}$) is interesting since (i) $\mathbf{9}^{-\bullet}$ is the least stable of the nine anionic isomers (by some 57 kcal mol^{-1}) and on formation may well rearrange to a more stable anion, (ii) if **9s** is formed, it has significant excess energy and may rearrange, and (iii) **9t** may be formed in preference to **9s** because of the more favorable vertical Franck−Condon overlap. Thus there is some possibility of rearrangement of anion and/or neutral, and for precisely this reason, we have decided to investigate system $\mathbf{9}^{-\bullet}$ experimentally.

Let us now consider the four anion systems we have chosen in more detail, viz., [$H_2C(C_2)C_2H^{-\bullet}$] ($\mathbf{4}^{-\bullet}$), [$HC_7H^{-\bullet}$] ($\mathbf{5}^{-\bullet}$), [$C_6CH_2{}^{-\bullet}$] ($\mathbf{6}^{-\bullet}$), and [$C_2CH_2C_4{}^{-\bullet}$] ($\mathbf{9}^{-\bullet}$). First, we need to know the minimum excess energy contained by each neutral following formation from the anion. This should give some insight into whether the neutral is likely to be stable under the conditions of the planned NR experiment. This excess energy is the difference in energy between that of the neutral minimum and that of the anion geometry on the ground state neutral surface. These results are listed in Table 4. It should be stressed that these values do not include any excess energy that the precursor anions may have on formation.[47]

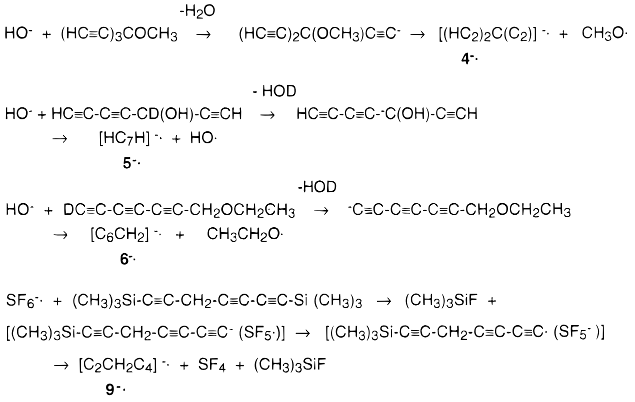
Second, we need to have a method to probe the structure of the neutral once it has been formed, and in previous studies we have used the positive ion spectrum of the neutral (i.e., the $^-NR^+$ method) for this purpose.[14] Therefore, assuming the correct neutral is formed (by electron loss from the anion), we need to know the minimum excess energy contained by the radical cation formed by ionization of the neutral. The method is qualitative only (i.e., we assume the neutral initially has no excess energy), and is similar to that outlined above for the anion/neutral process: The geometries of the particular product cations formed in these reactions are shown in Table 1, and the minimum excess energy contained by the cation following charge stripping of the neutral is listed in Table 4. The data shown in Table 4 indicate that the situation for neutrals **4**, **5**, and **6** is straightforward. Each of these neutrals should be formed from the anions with a minimum of additional excess energy: this excess energy should not, by itself, be enough to effect rearrangement of the neutrals. Also, cations **4**, **5**, and **6** should also be formed from the neutrals with minimal excess energy: in these cases, major rearrangement of the parent cation seems unlikely.

TABLE 4: Excess Energies of Species Formed by the Processes Shown (Precursors Assumed To Have No Excess Energy) [B3LYP/aug-cc-pVDZ//B3LYP/6-31G(d)]

	kcal mol^{-1}		kcal mol^{-1}
$\mathbf{4}^{-\bullet} \rightarrow \mathbf{4}$ (singlet)	0.94	$\mathbf{4}$ (singlet) $\rightarrow \mathbf{4}^{+\bullet}$	5.19
$\mathbf{5}^{-\bullet} \rightarrow \mathbf{5}$ (triplet)	8.37	$\mathbf{5}$ (triplet) $\rightarrow \mathbf{5}^{+\bullet}$	0.48
$\mathbf{6}^{-\bullet} \rightarrow \mathbf{6}$ (singlet)	4.58	$\mathbf{6}$ (singlet) $\rightarrow \mathbf{6}^{+\bullet}$	8.95
$\mathbf{9}^{-\bullet} \rightarrow \mathbf{9s}$ (singlet)	34.47	$\mathbf{9s}$ (singlet) $\rightarrow \mathbf{9}^{+\bullet}$	27.95
$\mathbf{9}^{-\bullet} \rightarrow \mathbf{9t}$ (triplet)	2.12	$\mathbf{9t}$ (triplet) $\rightarrow \mathbf{9}^{+\bullet}$	3.15

The situation concerning the $^-NR^+$ experiment with [$C_2CH_2C_4$]$^{-\bullet}$ ($\mathbf{9}^{-\bullet}$) is more complex. If the lower energy neutral **9s** is formed from radical anion $\mathbf{9}^{-\bullet}$, then the neutral will contain significant excess energy, perhaps enough to allow rearrangement to a more stable isomer. In addition, charge stripping of neutral **9s** yields a cation $\mathbf{9}^{+\cdot}$ which itself is significantly excited, suggesting that ionization of **9s** may induce rearrangement of $\mathbf{9}^{+\cdot}$. Perhaps charge stripping of $\mathbf{9}^{-\bullet}$ will preferentially form the higher energy neutral **9t**? The potential surfaces of $\mathbf{9}^{-\bullet}$, **9t**, and $\mathbf{9}^{+\cdot}$ all show favorable vertical Franck−Condon overlap (see

SCHEME 3



Tables 1 and 4): perhaps the $^-NR^+$ experiment might be meaningful if one-electron oxidation of $\mathbf{9}^{-\bullet}$ preferentially forms **9t**?

In summary, we anticipate that it will be feasible to form stable neutrals **4**, **5**, and **6** from the precursor anions, and that the $^-NR^+$ technique should provide a fingerprint for the structure of each of these neutrals. In contrast, from the theoretical data provided, it seems likely that charge stripping of $[C_2CH_2C_4]^{-\bullet}$ ($\mathbf{9}^{-\bullet}$) may be complex, and the $^-NR^+$ data for $\mathbf{9}^{-\bullet}$ may be difficult to interpret.

Syntheses of the Four C_7H_2 Radical Anions. The procedures used for the syntheses of the precursor anions $\mathbf{4}^{-\bullet}$, $\mathbf{5}^{-\bullet}$, $\mathbf{6}^{-\bullet}$, and $\mathbf{9}^{-\bullet}$ are summarized in Scheme 3. The branched radical anion $[H_2C_2C(C_2)C_2H]^{-\bullet}$ ($\mathbf{4}^{-\bullet}$) was made by deprotonation of 3-methoxy-3-ethynylpenta-1,4-diyne with HO^- in the ion source of the mass spectrometer. The deprotonated species so formed then loses $CH_3O^\bullet$ to produce $\mathbf{4}^{-\bullet}$ in the ion source. Anion $[HC_7H]^{-\bullet}$ ($\mathbf{5}^{-\bullet}$) was prepared by a procedure used previously for the formation of anion $[HC_5H]^{-\bullet}$,[14] i.e., in the current case by loss of $HO^\bullet$ from the $[M - D]^-$ ion of $HC{\equiv}C{-}C{\equiv}C{-}CD(OH){-}C{\equiv}CH$ (see Scheme 3). The isomer $[C_6CH_2]^{-\bullet}$ ($\mathbf{6}^{-\bullet}$) was prepared by a standard route[14] from $DC{\equiv}C{-}C{\equiv}C{-}C{\equiv}CCH_2OCH_3$: this synthesis has been reported previously.[21] Finally, $[C_2CH_2C_4]^{-\bullet}$ ($\mathbf{9}^{-\bullet}$) was prepared by the reaction between the bis(trimethylsilyl) (TMS) species $TMSC{\equiv}CCH_2C{\equiv}C{-}C{\equiv}CTMS$ and $SF_6^{-\bullet}$, a process similar to a bis-desilylation process first introduced by Squires.[33,34]

Characterization of the Anions by CA and CR Spectroscopy. The collisional activation (CA), charge reversal (CR), and neutralization reionization ($^-NR^+$) mass spectra of the four C_7H_2 radical anions are listed in Table 5. The CR spectra are also shown in Figure 1 for ease of comparison. In a previous study, the CA (negative ion) spectra of C_5H_2 radical anions were uninformative, showing peaks corresponding only to losses of $H^\bullet$ and $2H^\bullet$ from the parent anion. In contrast, the CA spectra of the four C_7H_2 radical anions show losses of $H^\bullet$ and $2H^\bullet$ together with the formation of fragment anions arising from cleavage of the carbon skeleton. Apart from loss of C and C_2 [processes only seen in the spectrum of $[C_2CH_2C_4]^{-\bullet}$ ($\mathbf{9}^{-\bullet}$)], all spectra exhibit peaks with the same *m*/*z* values. These spectra are reproducible and are significantly different as far as relative abundances of peaks are concerned.

The four CR (positive ion) spectra are shown in Figure 1. These spectra are all reproducible and show quite significant differences. Some of the more obvious differences between the spectra reflect the bond connectivity of the particular anion, and are as follows: the CR spectrum of (i) $[(HC{\equiv}C)_2CC_2]^{-\bullet}$ ($\mathbf{4}^{-\bullet}$) shows major losses of C and C_2, (ii) $[HC_7H]^{-\bullet}$ ($\mathbf{6}^{-\bullet}$) shows major losses of $CH^\bullet$ and $C_2H^\bullet$, and (iii) $[C_2CH_2C_4]^{-\bullet}$ ($\mathbf{9}^{-\bullet}$) is the only one showing pronounced losses of C, C_2, C_3, and C_4. The theoretical calculations indicate that isomers $\mathbf{4}^{-\bullet}$, $\mathbf{5}^{-\bullet}$, and $\mathbf{6}^{-\bullet}$ are stable species: this is supported by the CA and CR spectra of these three isomers. However the ab initio calculations also show that $\mathbf{9}^{-\bullet}$ is the least stable of the nine isomers, and the possibility that this species, once formed, might isomerize to a more stable isomer needs to be considered. The spectroscopic data for this isomer do not support such a scenario; indeed, the CR spectrum of $[C_2CH_2C_4]^{-\bullet}$ is the most diagnostic of structure of the four CR spectra.

It is of interest that $[C_2CH_2C_4]^{-\bullet}$ ($\mathbf{9}^{-\bullet}$) appears not to isomerize on formation (cf. Scheme 3) or following collisional activation. We have calculated the barrier for what seems a likely pathway for rearrangement of this anion, i.e., the 1,3-proton transfer of $[C_2CH_2C_4]^{-\bullet}$ ($\mathbf{9}^{-\bullet}$) to yield $[HC_2CHC_4]^{-\bullet}$ ($\mathbf{7}^{-\bullet}$). This

TABLE 5: Collisional Activation (CA), Charge Reversal (CR), and Neutralization Reionization ($^-NR^+$) Spectra of the $C_7H_2^{-\bullet}$ Isomers

precursor and C_7H_2 isomer	fragmentations: *m*/*z* (intensity relative to base peak)[a]
m/*z* 86 from $(HC{\equiv}C)_3COH$; $4^{-\bullet}$, $HC_2C(C_2)C_2H^{-\bullet}$	CA: 86, 85 (100), 84 (56), 73 (63), 72 (67), 61 (48), 60 (44), 49 (28)
	CR: 86 (44), 85 (100), 84 (84), 74 (13), 73 (22), 72 (9), 62 (22), 61 (78), 60 (47), 50 (4), 49 (9), 48 (7), 37 (13), 36 (9), 25 (2), 24 (1.5)
	NR:[b] 86 (56), 85 (90), 84 (100), 74 (23), 73 (37), 72 (12), 62 (20), 61 (77), 60 (76), 50 (21), 49 (43), 48 (32), 37 (22), 36 (21)
m/*z* 86 from $HC{\equiv}CCD(OH)C{\equiv}CC{\equiv}CH$; $5^{-\bullet}$, $HC_7H^{-\bullet}$	CA: 86, 85 (100), 84 (2), 73 (0.4), 72 (0.3), 61 (0.3), 60 (0.5), 49 (0.2), 48 (0.1)
	CR: 86 (89), 85 (100), 84 (32), 74 (2), 73 (15), 61 (18), 60 (12), 50 (2), 49 (6), 48 (3), 37 (3), 25 (2)
	NR:[b] 86 (90), 85 (100), 84 (48), 74 (<5), 73 (22), 61 (52), 60 (45), 49 (24), 48 (12), 37 (12), 25 (3)
m/*z* 86 from $DC{\equiv}CC{\equiv}CC{\equiv}CCH_2OCH_2CH_3$; $6^{-\bullet}$, $C_6CH_2^{-\bullet}$	CA: 86, 85 (100), 84 (37), 73 (85), 72 (55), 61 (71), 60 (27), 49 (21)
	CR: 86 (49), 85 (88), 84 (100), 74 (4), 73 (57), 72 (13), 61 (43), 60 (29), 50 (3), 49 (19), 48 (9), 37 (15), 36 (9), 25 (1), 24 (0.5)
	NR: 86 (67), 85 (93), 84 (100), 74 (8), 73 (58), 72 (22), 61 (44), 60 (45), 50 (10), 49 (21), 48 (15), 37 (15), 36 (15), 25 (2), 24 (2)
m/*z* 86 from $TMSC{\equiv}CCH_2C{\equiv}CC{\equiv}CTMS$; $9^{-\bullet}$, $C_2CH_2C_4^{-\bullet}$	CA: 86, 85 (100), 84 (39), 74 (11), 73 (25), 72 (19), 62 (8), 60 (47), 38 (16), 36 (5)
	CR: 86 (47), 85 (100), 84 (40), 74 (9), 73 (10), 72 (11), 62 (5), 61 (14), 60 (13), 50 (3), 49 (4), 48 (5), 38 (3), 37 (4), 36 (5), 26 (0.3), 25 (0.3), 24 (0.6)
	NR: 86 (63), 85 (100), 84 (54), 74 (5), 73 (7), 72 (9), 62 (4), 61 (13), 60 (4), 50 (5), 49 (8), 48 (8), 36 (2), 37 (5), 36 (8), 26 (1), 25 (1), 24 (2)

[a] For CA spectra the parent signal is excluded and the most abundant fragment peak is used to calculate relative intensity. [b] This spectrum is quite weak with a low signal-to-noise ratio.

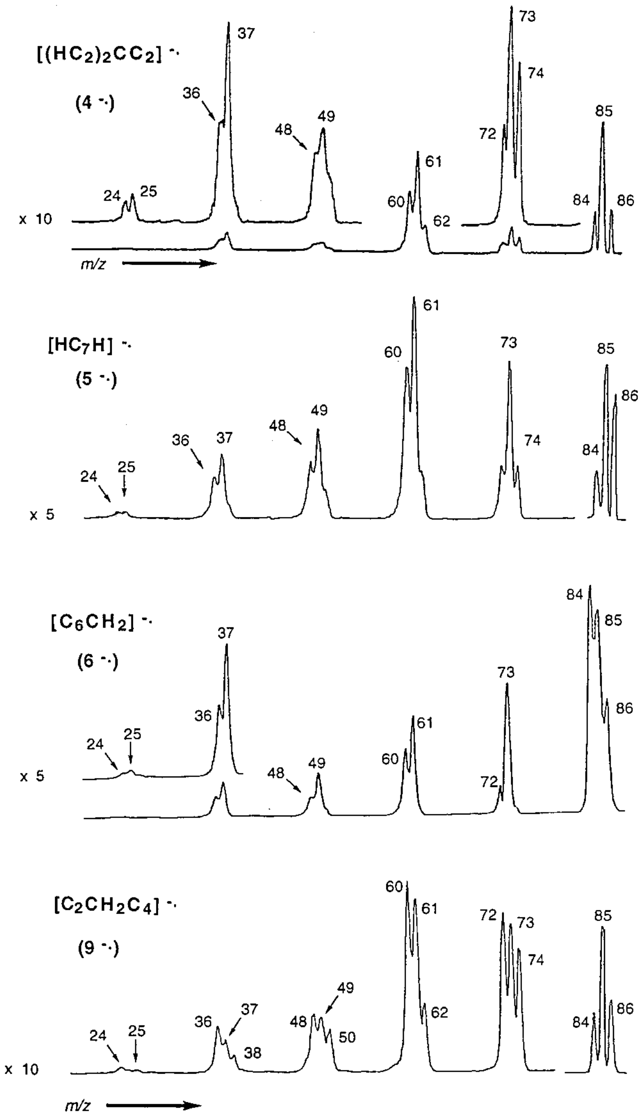


Figure 1. Charge reversal mass spectra of (a) $[(HC_2)_2CC_2]^{-\bullet}$ ($\mathbf{4}^{-\bullet}$), (b) $[HC_7H]^{-\bullet}$ ($\mathbf{5}^{-\bullet}$), (c) $[C_6CH_2]^{-\bullet}$ ($\mathbf{6}^{-\bullet}$), and (d) $[C_2CH_2C_4]^{-\bullet}$ ($\mathbf{9}^{-\bullet}$). VG ZAB 2HF instrument; for experimental conditions see Experimental Section.

process is summarized in Figure 2. The transition state, some 40 kcal mol^{-1} above $\mathbf{9}^{-\bullet}$, presents a substantial barrier to isomerization, and it would be expected that other rearrangement pathways would have at least comparable barriers. This supports the experimental evidence that, once formed, $\mathbf{9}^{-\bullet}$ does not undergo extensive rearrangement.

There is another possibility for anion rearrangement that needs to be considered. Three of the anions, viz., $\mathbf{4}^{-\bullet}$, $\mathbf{5}^{-\bullet}$, and $\mathbf{6}^{-\bullet}$, are formed following deprotonation of precursor neutrals with HO^- (from H_2O). Perhaps an intermolecular base catalyzed proton transfer might occur in the ion source of the mass spectrometer concomitant with the formation of these anions. An example is the interconversion of $\mathbf{6}^{-\bullet}$ and $\mathbf{5}^{-\bullet}$ by the following equilibrium process

$$[C_6CH_2]^{-\bullet} + H_2O \rightleftarrows [(HCC_5CH_2)\cdot HO^-] \rightleftarrows [HC_7H]^{-\bullet} + H_2O$$

This possibility is excluded by the experimental observation that there is no incorporation of deuterium into any $C_7H_2^{-\bullet}$ isomer when D_2O replaces H_2O as the reagent gas.

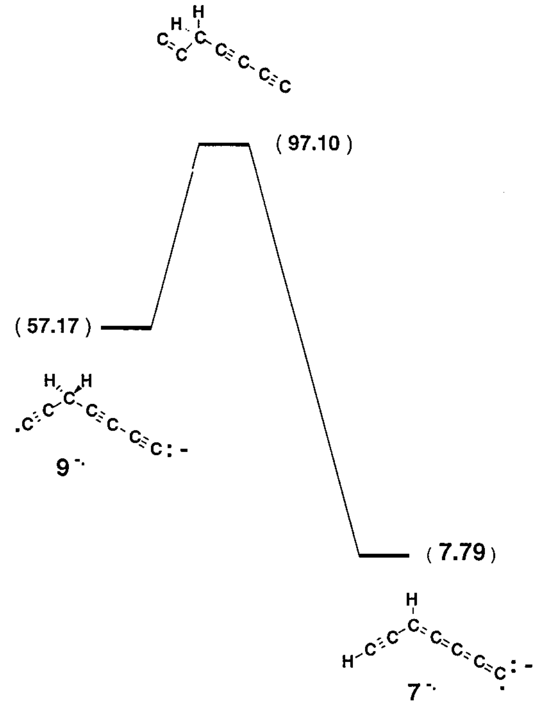


Figure 2. Data for the 3,1-H rearrangement of $[C_2CH_2C_4]^{-\bullet}$ ($\mathbf{9}^{-\bullet}$) to $[HCCCHC_4]^{-\bullet}$ ($\mathbf{7}^{-\bullet}$). Calculations at the B3LYP/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory. Energies shown in kcal mol^{-1} with reference to the global minimum on the potential surface [$(C_6CH_2)^{-\bullet}$ ($\mathbf{6}^{-\bullet}$); see Table 3]. For structural details of transition state see Supporting Information.

TABLE 6: Relative Energies of Singlet and Triplet Neutrals of 4, 5, 6, and 9 [B3LYP/aug-cc-pVDZ//B3LYP/6-31G(d)]

neutral	singlet energy (hartrees)	triplet energy (hartrees)	energy difference (kcal mol^{-1})
4	−267.605 75	−267.562 99	26.83
5	−267.634 97	−267.661 70	16.76
6	−267.626 36	−267.609 24	10.74
9s, **9t**	−267.524 83	−267.494 45	19.05

From a consideration of the theoretical and experimental data to date, our conclusions are that (i) we have successfully prepared anions $\mathbf{4}^{-\bullet}$, $\mathbf{5}^{-\bullet}$, $\mathbf{6}^{-\bullet}$, and $\mathbf{9}^{-\bullet}$ and (ii) there is no evidence for any major rearrangement of any one of the anion isomers to a more stable structure.

Gas-Phase Syntheses of Isomeric C_7H_2 Neutrals. The theoretical results discussed previously suggest that the ground state species singlet **4**, triplet **5**, and singlet **6** exist as discrete species on the C_7H_2 potential surface, and that they are the most likely products of the oxidation of the corresponding radical anions in NR experiments. However, the excited state species triplet **4**, singlet **5** and triplet **6** may, in principle, also be accessible in each neutralization experiment. Hopefully, the NR experiment will allow us to probe the bond connectivity of the neutral: the method will however not allow the experimental differentiation of singlet and triplet structures and it is likely that some mixture of both will be formed. The energies of the ground and excited states of each of the neutrals **4**, **5**, and **6** are listed in Table 6, while the geometries of each higher energy neutral are available as Supporting Information to this paper. In addition, we have already mentioned that neutralization of $[C_2CH_2C_4]^{-\bullet}$ ($\mathbf{9}^{-\bullet}$) may produce the higher energy triplet neutral **9t** (which has minimal energy of formation from $\mathbf{9}^{-\bullet}$) in preference to the lower energy singlet neutral **9s** [which is formed with significant excess energy following the vertical Franck−Condon oxidation (see Table 4)].

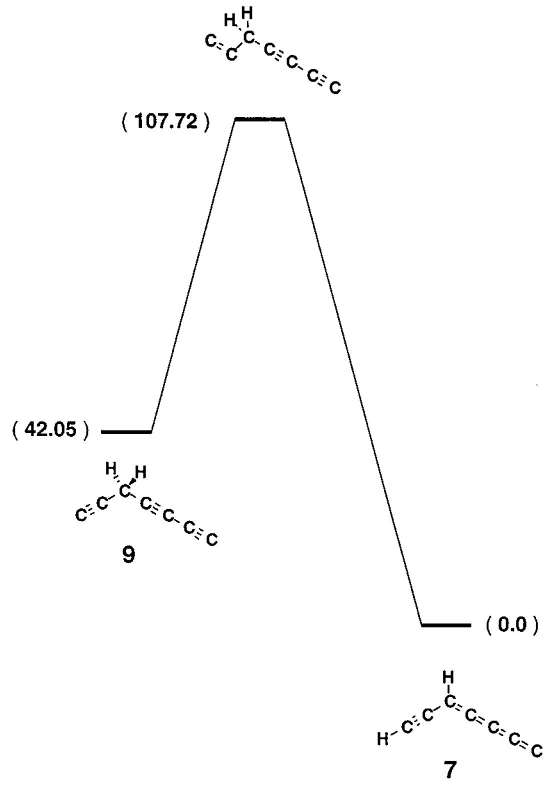


Figure 3. Data for the 3,1-H rearrangement of triplet neutral $C_2CH_2C_4$ (**9**) to triplet $HCCCHC_4$ (**7**). Calculations at the B3LYP/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory. Energies (kcal mol^{-1}) relative to the more stable triplet structure **7**. For structural details of transition state and product see Supporting Information.

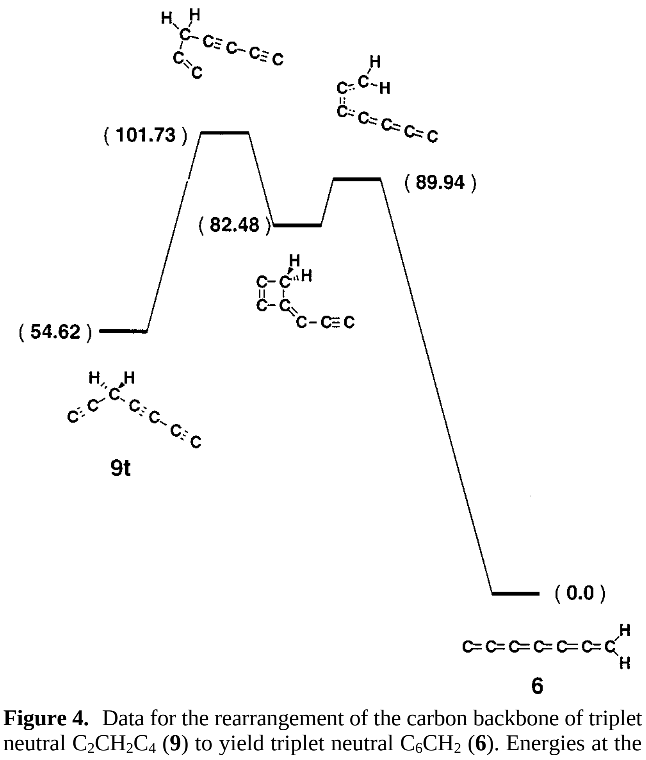


Figure 4. Data for the rearrangement of the carbon backbone of triplet neutral $C_2CH_2C_4$ (**9**) to yield triplet neutral C_6CH_2 (**6**). Energies at the B3LYP/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory. Energies (kcal mol^{-1}) relative to the more stable triplet structure **6**. For structural details of the reactive intermediate and transition states see Supporting Information.

The neutralization reionization spectra of each of the four C_7H_2 radical anion isomers under study are listed in Table 1. Each $^-NR^+$ spectrum shows a strong recovery signal at *m*/*z* 86 indicative of C_7H_2 neutrals surviving during each neutralization process; i.e., each species survives at least during the time frame of the $^-NR^+$ experiment (ca. 10^{-6} s). Theoretical calculations indicate that the ground state neutrals of **4**, **5**, and **6** have little excess energy following the anion−neutral electronic transition, hence rearrangement on the neutral surface is unlikely in these NR experiments. This is supported by the close similarity between the $^-NR^+$ and CR spectra for each of these three isomers (see Table 1). Any rearrangement of a neutral during the $^-NR^+$ experiment should result in the formation of a cation different from that resulting from the CR procedure. As a consequence, differences should be observed between the $^-NR^+$ and CR spectra.[37−39,48] It appears therefore that neutral isomers **4**, **5**, and **6** are stable species. There is no evidence of major rearrangement of these species on the mass spectrometry time scale.

The CR and $^-NR^+$ spectra of $[C_2CH_2C_4]^{-\bullet}$ (**9**$^{-\bullet}$) are also very similar: both show the characteristic losses of C, C_2, C_3, and C_4 . These data suggest that the bond connectivities of **9**$^{-\bullet}$, the neutral(s) formed from **9**$^{-\bullet}$, and the product cation **9**$^{+\cdot}$ are the same, which must mean that there is no major rearrangement of the neutral(s) from **9**$^{-\bullet}$ during or following the neutralization process. This is an interesting result when the previous theoretical data for this system are taken into consideration. An explanation which would account for both the experimental and theoretical data is that **9**$^{-\bullet}$, on charge stripping, is forming **9t** rather than **9s**.

To place this experimental result in context, we have carried out theoretical calculations on two neutral rearrangements that we consider are likely for this system. We have chosen triplet **9t** for these calculations since the available data suggest that **9t** is the more likely product from **9**$^{-\bullet}$. The two triplet rearrangements we have chosen to study are (i) 1,3-H transfer within $C_2CH_2C_4$ to yield $HCCCHC_4$ (**7**) and (ii) the rearrangement of the carbon backbone of $C_2CH_2C_4$ to form C_6CH_2 (**6**). These two processes are illustrated in Figures 3 and 4. The geometries of all transition states and of the reactive intermediate (of Figure 4) are available as Supporting Information to this paper. The two rearrangement processes have significant barriers: the conversion of triplet $C_2CH_2C_4$ to triplet $HCCCHC_4$ has a barrier of nearly 65 kcal mol^{-1} while the conversion of triplet $C_2CH_2C_4$ to triplet C_6CH_2 involves a barrier of some 46 kcal mol^{-1} at the B3LYP/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory. Major neutral rearrangements of this type thus seem unlikely under the experimental conditions.

We conclude that four isomeric C_7H_2 neutrals have been made from their precursor anions. In three cases the major products are most likely the neutral ground states, singlet $(HC_2)_2CC_2$ (**4**), triplet HC_7H (**5**), and singlet C_6CH_2 (**6**); however the experimental data do not preclude the formation of some excited neutrals in each case. Neutralization of $[C_2CH_2C_4]^{-\bullet}$ (**9**$^{-\bullet}$) seems likely to give triplet **9t** as a major product which although predicted to be relatively high in energy is nevertheless bound with respect to isomerization processes. In fact there is no evidence to suggest major rearrangement of any of the studied neutrals to produce a more stable connectivity.

Supporting Information Available: Tables 7−11 listing geometries of each higher energy neutral. This material is available free of charge via the Internet at http://pubs.acs.org.

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(46) See, for example: McCarthy, M. C.; Travers, M. J.; Korvacs, A.; Chem, W.; Novick, S. E.; Gottlieb, C. A.; Thaddeus, P. *Science* **1997**, *275*, 518.

(47) In general, anions produced by “soft” ionization processes such as this do not have appreciable excess energy. Indeed, anions often have to be collisionally activated in order for the anions to undergo fragmentation. This is the situation with these anions: no fragmentations of the negative ions occur unless they are collisionally activated. For the collision-induced spectra of the four isomeric C_7H_2 isomers, see Table 5.

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