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Generation of neutrals from ionic precursors in the gas phase. The rearrangement of CCCCCHO to HCCCCCO

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The neutrals HCCCCCO and CCCCCHO have been studied by experiment and by molecular modelling at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory. Neutral HCCCCCO has been made by one-electron reduction of $[HCCCCCO]^+$ in the dual collision cell of a VG ZAB 2HF mass spectrometer. The isomer CCCCCHO is also formed in the dual collision cell, but this time by one-electron oxidation of the anion $[CCCCCHO]^-$. Comparison of the CID and $^+NR^+$ mass spectra of $[HCCCCCO]^+$ indicates that neutral HCCCCCO, when energised, retains its structural integrity. If the excess energy of HCCCCCO is ≥ 170 kJ mol^{-1}, decomposition can occur to give HCCCC and CO (calculations at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory). The situation with the isomer CCCCCHO is different. Comparison of the $^-CR^+$ and $^-NR^+$ spectra of $[CCCCCHO]^-$ shows that both neutral and cationic forms of CCCCCHO partially rearrange to a species which decomposes by loss of CO. The peak corresponding to loss of CO is more pronounced in the $^-NR^+$ spectrum, indicating that the rearrangement is more prevalent for the neutral than the cation. Theoretical calculations suggest that the species losing CO could be CCCCHCO or HCCCCCO, but that HCCCCCO is the more likely. The lowest-energy rearrangement pathway occurs by successive H transfers, namely CCCCCHO ⟶ CCCCHCO ⟶ CCCHCCO ⟶ HCCCCCO. The rearrangement of CCCCCHO to HCCCCCO requires CCCCCHO to have an excess energy of ≥ 94 kJ mol^{-1}. The species HCCCCCO formed by this exothermic sequence (214 kJ mol^{-1}) has a maximum excess energy of 308 kJ mol^{-1}: this is sufficient to effect decomposition to HCCCC and CO.

Introduction

Cumulenes and polycarbon monoxides have been detected in circumstellar envelopes which surround red giant stars and also in dark interstellar molecular clouds.[1–3] Detected cumulenes include a number of C_n (n = 3 and 5), C_nH (n = 2–8) and C_nH_2 (n = 2–4 and 6) molecules.[1–6] In contrast, there has been only limited detection of polycarbon monoxides. The linear species C_2O and C_3O [together with the associated propynal (HC≡C–CHO)] have been detected towards the dark molecular cloud TMC-1,[7,8] while preliminary measurements suggest that C_5O may also be present, but this has yet to be confirmed.[9] Linear C_5O has been synthesised from an anionic precursor.[10] A number of theoretical studies have been devoted to polycarbon monoxides,[11–15] and the photoelectron spectra of C_2O and C_3O have also been determined.[16] The rotational spectra of C_nO (n = 2–9) have been detected in pyrolytic decomposition and pulsed discharge nozzle experiments.[17–19]

It has been suggested that the mechanism of formation of the circumstellar molecules C_3O and propynal may be linked *via* ion molecule chemistry[20] or by photolysis of the cluster $C_3{\cdot}H_2O$,[21–23] and that the reaction $C_3O^{+\bullet} + H_2 \longrightarrow C_3HO^+ + H^\bullet$ may provide a stellar pathway for the consumption of C_3O.[24] We have (i) prepared the stable neutrals C_3O,[25] HCCCO[26] and CCCHO[26] in the gas phase from charged precursors, (ii) shown that energised CCCHO may rearrange to HCCCO, which has sufficient excess energy of formation to effect dissociation to CO and C_2H,[26] and (iii) suggested that HCCCO and CCCHO may co-occur with C_3O and HC≡C–CHO in dark molecular clouds.[26]

Of the many possible cumulenes containing four and five carbon atoms, only C_4H, C_5 and C_5H have been detected in either interstellar dust clouds or circumstellar envelopes.[6] Of these, C_5[26] and some C_5H[27] isomers have been made by neutralisation reionisation processes. Linear and rhombic isomers of C_4[28] and some isomers of C_5H_2 have also been described,[29] but these species have not, as yet, been detected as stellar molecules. Neither have the cumulene oxides CCCCO or HCCCCO, although spectroscopic and/or structural details of CCCCO[16,30–33] and HCCCCO[34,35] have been reported.

This study is an extension of our previous work on HC_3O[26] and HC_4O[36] isomers. Both CCCHO and CCCCHO undergo facile H rearrangements to give HCCCO and HCCCCO respectively. The aims of the present investigation are: (i) to make the neutrals HCCCCCO and CCCCCHO from charged precursors in the gas phase, and (ii) to ascertain whether CCCCCHO rearranges to HCCCCCO. Our reason for undertaking this project was that (in comparison with the CCCHO and CCCCHO systems) we anticipated that extending the cumulene chain should make successive H rearrangements along the carbon chain more difficult, whereas, in contrast, it might be easier to bend a longer cumulene to allow direct H transfer from one end of the molecule to the other.

Results and discussion

In previous studies we have preferred to use anions as precursors to neutrals in neutralisation studies.[26–28] This is because the precursor ion has to be energised in order to effect neutralisation, and anions undergo fewer rearrangements than cations when energised. However, in our previous study of C_4HO isomers,[36] we found that the key anion precursor $[CCCCHO]^-$ caused a serious problem because it undergoes facile rearrangement to $[HCCCCO]^-$ when energised.

In order to circumvent such a problem in this study we have first studied the C_5HO anion potential surfaces using theory, to ascertain whether the two key anion precursors $[HCCCCCO]^-$ and $[CCCCCHO]^-$ are stable under the conditions necessary to effect one-electron vertical oxidation to the neutrals HCCCCCO and CCCCCHO. The results are summarised in Figs. 1 and 2, with detailed data on the structures and energies of the various anions listed in Tables 1 and 2.

There are singlet and triplet forms of anions $[HCCCCCO]^-$ and $[CCCCCHO]^-$ and the singlet is the lower energy form of

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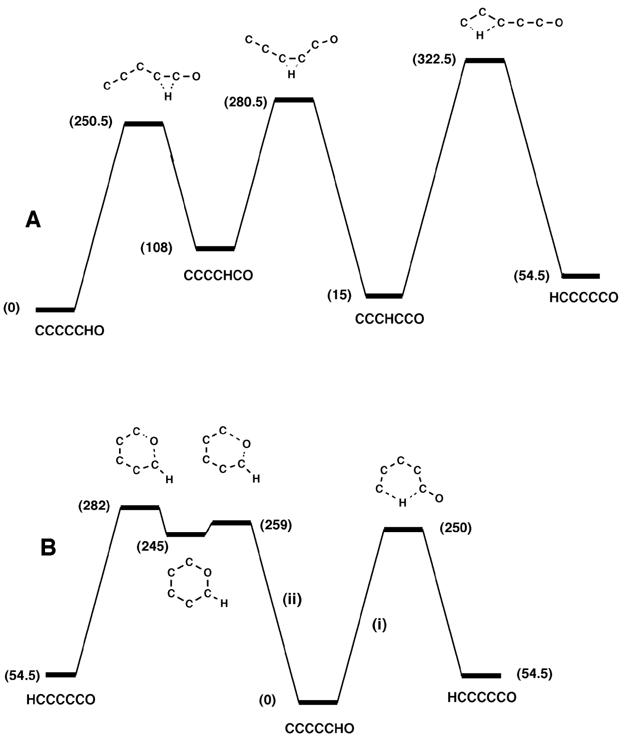
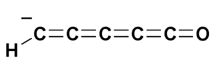
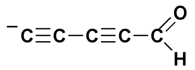


Fig. 1 Rearrangement processes of singlet $[CCCCCHO]^-$. Energies at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory. Structures shown indicate bond connectivities not bond multiplicity. For full details of structures including geometries and energies see Table 1. Relative energies in kJ mol^{-1}. (A) The sequential H transfer mechanism. (B) Six-centre cyclisation processes, (i) the concerted H transfer mechanism, and (ii) the O transfer process.

each anion, by 104.5 and 319 kJ mol^{-1} respectively at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory. The two singlet anions are best represented by the valence bond structures shown below.


$H\overset{-}{C}=C=C=C=C=O$


$^{-}C\equiv C-C\equiv C-C(=O)H$

Synthetic procedures would be expected to form the singlet anion in each case. Even so, we have considered the potential surfaces of both singlet and triplet anions to investigate possible rearrangement pathways: these are summarised in Figs. 1 and 2. Two different types of rearrangement are considered, namely, those which involve successive H transfers, and cyclisation processes which proceed through six-centred transition states. The singlet anion rearrangements are shown in Fig. 1. The process which involves successive H transfers is shown in Fig. 1A: this involves 1,2, 2,3 and 3,5 H transfers of a type already reported for the analogous rearrangement of $[CCCCHO]^-$ to $[HCCCCO]^-$.[36] The first step in the rearrangement, $[CCCCCHO]^-$ to $[CCCCHCO]^-$, has a barrier of 250.5 kJ mol^{-1}. The first step in the reverse process, *i.e.* $[HCCCCCO]^-$ to $[CCCHCCO]^-$, has a barrier of 268 kJ mol^{-1}. Neither of these anions, on formation, will have sufficient energy to effect these transformations. One of the questions we wished to consider in this context was whether cyclisation reactions involving the cumulene skeleton can compete with the H transfer rearrangements, and data for these processes are shown in Fig. 1B. There are two processes shown in Fig. 1B; the energy requirements for these processes are similar to those shown for the successive H transfer processes (Fig. 1A). Process **(i)** shows concerted H rearrangement through a six-centre transition state with a barrier of 250 kJ mol^{-1}. Process **(ii)** involves C^5–O bond formation through a six-centre state followed by C^1–O bond cleavage to form $[HCCCCCO]^-$ in which O is transferred from C^1 to C^5. For this process to occur, $[CCCCCHO]^-$ must have an excess energy of at least 282 kJ mol^{-1}.

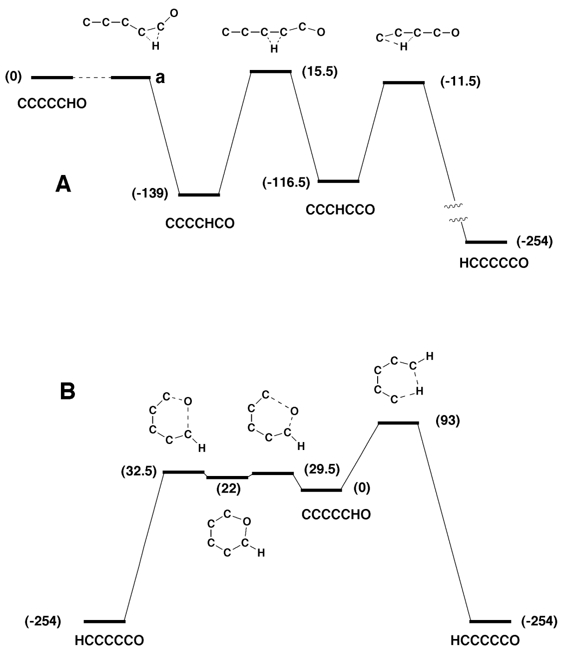


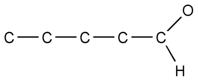
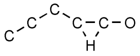
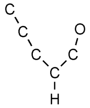
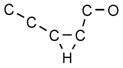
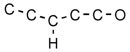
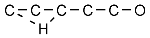
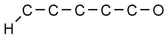
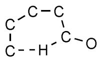
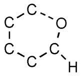
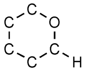
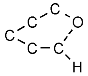
Fig. 2 Rearrangement processes of triplet $[CCCCCHO]^-$. Energies at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory. Structures shown indicate bond connectivities not bond multiplicity. For full details of geometries and energies of structures see Table 2. Relative energies in kJ mol^{-1}. (A) The sequential H transfer mechanism. (B) Six-centre cyclisation processes, (i) the concerted H transfer mechanism, and (ii) the O transfer process. (**a**) This species is a transition state confirmed by IRC calculations. The energy of this transition state with respect to triplet $[CCCCCHO]^-$ is dependent on the level of the calculation and whether zero point energy corrections are made. At the standard level with zero point energy correction it is -13.5 kJ mol^{-1} with respect to triplet $[CCCCCHO]^-$ (see Table 2), which is clearly not practicable. Without the zero point energy difference, the energy difference is $+8.5$ kJ mol^{-1}.

The corresponding data for the triplet anion potential surface are recorded in Fig. 2 and Table 2. In this case the rearrangement of triplet $[CCCCCHO]^-$ to triplet $[HCCCCCO]^-$ by successive H transfers is facile, needing only 15.5 kJ mol^{-1} of excess energy for the process to proceed. The cyclic mechanisms shown in Fig. 2B are energetically unfavourable in comparison.

We infer from these data that both singlet and triplet $[HCCCCCO]^-$ are stable to rearrangement under conditions required to effect one-electron vertical oxidation to the doublet neutral HCCCCCO. Similarly, singlet anion $[CCCCCHO]^-$ should not rearrange under conditions of collision activation, but triplet $[CCCCCHO]^-$ will undergo facile rearrangement to $[HCCCCCO]^-$. However, the triplet form of $[CCCCCHO]^-$ is unlikely to be formed by a synthetic procedure because it lies 319 kJ mol^{-1} above the ground state singlet anion. So far, the theoretical data suggest that $[HCCCCCO]^-$ and $[CCCCCHO]^-$ should be appropriate precursors for the formation of the analogous neutrals.

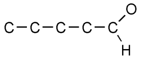
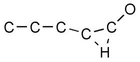
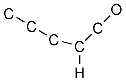
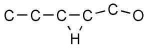
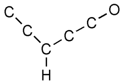
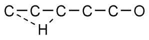
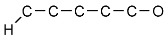
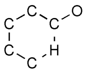
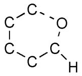
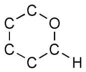
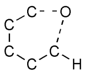
The next question to be addressed is whether the two species $[HCCCCCO]^-$ and $[CCCCCHO]^-$ are stable to decomposition under the collisional conditions required to charge strip them to the required neutrals. The major fragmentations of $[HCCCCCO]^-$ and $[CCCCCHO]^-$ involve losses of CO and $CHO^{\bullet}$ respectively. The data shown in Table 3 show that whereas decompositions of both singlet and triplet $[CCCCCHO]^-$ are unfavourable, the loss of CO from singlet $[HCCCCCO]^-$ is exothermic by 30.5 kJ mol^{-1}. The latter process must have (at least) a small endothermic barrier, because the theoretical calculations show that singlet $[HCCCCCO]^-$ is "stable", *i.e.* it occupies a minimum on the potential surface.

Table 1 Singlet anion potential surface

											
State	^{1}A′	^{1}A′	^{1}A′	^{1}A′	^{1}A′	^{1}A′	^{1}A′		^{1}A′	^{1}A′	^{1}A′
Symmetry	C_s	C_s	C_s	C_s	C_s	C_s	C_s	C_1	C_s	C_s	C_s
Energy/Hartree[a]	−265.53928	−265.44379	−265.49811	−265.43250	−265.53353	−265.41646	−265.51858	−265.44418	−265.44032	−265.44613	−265.43186
Dipole/debye[b]	5.79	6.68	5.88	4.20	5.21	4.59	2.46	2.14	2.61	3.43	2.46
Bond length/Å[b] or angle/°[b]											
C1C2	1.408	1.302	1.429	1.410	1.268	1.274	1.266	1.457	1.418	1.371	1.285
C2C3	1.24	1.353	1.368	1.349	1.37	1.314	1.315	1.295	1.317	1.339	1.592
C3C4	1.345	1.347	1.34	1.351	1.384	1.379	1.281	1.329	1.304	1.229	1.328
C4C5	1.264	1.278	1.275	1.283	1.265	1.308	1.323	1.289	1.413	1.541	1.455
C1O	1.236	1.204	1.191	1.207	1.207	1.212	1.213	1.200	1.311	1.395	1.93
C5O									1.693	1.377	1.272
C1H	1.118	1.457						1.632	1.104	1.094	1.076
C2H		1.364	1.085	1.242							
C3H				1.400	1.104	1.455					
C5H						2.164	1.110	1.478			
C1C2C3	175.3	160.5	111.9	147.8	156.1	168.4	178.9	116.6	98.3	101.3	160.7
C2C3C4	179.9	132.9	136.7	155.7	128.6	160.4	178.0	126.9	157.8	156.7	60.9
C3C4C5	179.7	175.4	177.0	175.1	176.5	171.7	172.5	146.9	106.6	97.4	176.1
OC1C2	127.8	174.8	143.0	141.1	173.0	174.0	179.1	138.2	125.4	121.1	108.8
HC1C2	113.7	58.9							121.9	129.0	
HC2C3			127.9	65.3							
HC3C4					115.1	49.7					
HC5C4							113.5	80.7			
C1C2C3C4	0.0	180.0	0.0	0.0	180.0	180.0	180.0	0.0	0.0	0.0	0.0
C2C3C4C5	0.0	180.0	180.0	180.0	180.0	180.0	180.0	0.2	0.0	0.0	180.0
OC1C2C3	180.0	0.0	0.0	180.0	180.0	180.0	180.0	180.0	0.0	0.0	0.0
HC1C2C3	0.0	180.0						0.0	180.0	180.0	180.0
HC2C3C4			180.0	180.0							
HC5C4C3					0.0	180.0	180.0				

[a] CCSD(T)/aug-cc-pVDZ level of theory including zero point energy (calculated from vibrational frequencies at the B3LYP/6-31G(d) level of theory and scaled by 0.9804). [b] B3LYP/6-31G(d) level of theory.

Table 2 Triplet anion potential surface

											
State	$^3A''$		$^3A''$	$^3A''$	$^3A''$	$^3A''$	$^3A''$		$^3A'$	$^3A'$	
Symmetry	C_s	C_1	C_s	C_s	C_s	C_s	C_s	C_1	C_s	C_s	C_1
Energy/Hartree[a]	−265.41771	−265.42285	−265.47064	−265.41180	−265.46222	−265.42116	−265.51465	−265.38240	−265.39686	−265.40925	−265.40522
Dipole/debye[b]	1.97	5.10	7.96	5.37	4.92	3.9722	0.78	7.94	3.01	2.82	8.02
Bond length/Å[b] or angle/°[b]											
C1C2	1.384	1.312	1.341	1.293	1.267	1.266	1.268	1.394	1.391	1.354	1.301
C2C3	1.281	1.322	1.431	1.350	1.394	1.317	1.313	1.353	1.361	1.394	1.381
C3C4	1.315	1.304	1.304	1.319	1.394	1.338	1.229	1.421	1.380	1.369	1.38
C4C5	1.306	1.301	1.307	1.289	1.280	1.332	1.280	1.294	1.331	1.383	1.364
C1O	1.273	1.225	1.194	1.221	1.217	1.214	1.219	1.217	1.294	1.398	1.736
C5O									1.82	1.372	1.278
C1H	1.115	1.351						1.393	1.106	1.092	1.080
C2H		1.419	1.095	1.274							
C3H				1.365	1.091	1.366					
C5H						2.263	1.076	1.480			
C1C2C3	179.2	164.0	120.4	169.9	171.4	178.1	179.7	122.6	121.2	115.7	123.5
C2C3C4	178.6	171.5	155.5	179.3	113.7	178.3	179.7	128.8	115.2	120.3	121.9
C3C4C5	179.5	178.8	175.1	179.2	178.4	176.9	174.7	114.9	139.5	124.9	110.2
OC1C2	124.7	164.0	174.8	167.1	176.7	179.5	180.0	142.8	125.9	123.4	111.9
HC1C2	114.4	64.4							120.6	128.3	142.3
HC2C3			122.1	62.6							
HC3C4					123.8	56.4					
HC5C4							142.9	107.3			
C1C2C3C4	180.0	−151.1	0.0	0.0	0.0	180.0	0.0	−10.7	0.0	0.0	−28.9
C2C3C4C5	0.0	−170.1	180.0	180.0	180.0	0.0	180.0	23.8	0.0	0.0	36.8
OC1C2C3	0.0	130.3	0.0	180.0	180.0	180.0	180.0	178.9	0.0	0.0	4.5
HC1C2C3	0.0	−162.6						−6.7	180.0	180.0	171.8
HC2C3C4			180.0	180.0							
HC5C4C3					0.0	180.0	180.0				

[a] CCSD(T)/aug-cc-pVDZ level of theory including zero point energy (calculated from vibrational frequencies at the B3LYP/6-31G(d) level of theory and scaled by 0.9804). [b] B3LYP/6-31G(d) level of theory.

Table 3 Decomposition pathways for anions and cations [CCSDT/aug-cc-pVDZ//B3LYP-6-31G(d) level of theory][a]

$^1HCCCCCO^- \longrightarrow {}^1HCCCC^- + {}^1CO$	−30.5 kJ mol^{-1}
$^3HCCCCCO^- \longrightarrow {}^1HCCCC^- + {}^3CO$	528.5
$^3HCCCCCO^- \longrightarrow {}^3HCCCC^- + {}^1CO$	226
$^1CCCCCHO^- \longrightarrow CCCC^{-\bullet} + {}^\bullet CHO$	497.5
$^3CCCCCHO^- \longrightarrow CCCC^{-\bullet} + {}^\bullet CHO$	178
$^1HCCCCCO^+ \longrightarrow {}^1HCCCC^+ + {}^1CO$	481
$^3HCCCCCO^+ \longrightarrow {}^1HCCCC^+ + {}^3CO$	758.5
$^3HCCCCCO^+ \longrightarrow {}^3HCCCC^+ + {}^1CO$	176.5
$^1CCCCCHO^+ \longrightarrow CCCC^{+\bullet} + {}^\bullet CHO$	410.5
$^3CCCCCHO^+ \longrightarrow CCCC^{+\bullet} + {}^\bullet CHO$	379.5

[a] Energy values were determined from the following theoretically calculated values (Hartrees): $^1HCCCC^-$ = −152.46124, ^1CO = −113.06894, ^3CO = −112.85212, $^3HCCCC^-$ = −152.35966, $CCCC^{-\bullet}$ = −151.76280, $^\bullet CHO$ = −113.58699, $^1HCCCC^+$ = −151.95028, $^3HCCCC^+$ = −151.95520, $CCCC^{+\bullet}$ = −151.27947.

Table 4 Data for singlet and triplet $[HCCCCCO]^+$

	H–C–C–C–C–C–O	H–C–C–C–C–C–O (bent)
State	$^1\Sigma$	$^3A''$
Symmetry	$C_{\infty v}$	C_s
Energy/Hartree[a]	−265.20259	−265.09136
Dipole/debye[b]	3.42	4.81
Bond length/Å[b] or angle/°[b]		
C1C2	1.320	1.308
C2C3	1.237	1.290
C3C4	1.336	1.291
C4C5	1.220	1.276
C1O	1.143	1.161
C5H	1.025	1.079
C1C2C3	180.0	174.2
C2C3C4	180.0	176.9
C3C4C5	180.0	173.8
OC1C2	180.0	177.1
HC5C4	180.0	157.1
C1C2C3C4		180.0
C2C3C4C5		180.0
OC1C2C3		180.0
HC5C4C3		180.0

[a] CCSD(T)/aug-cc-pVDZ level of theory including zero point energy (calculated from vibrational frequencies at the B3LYP/6-31G(d) level of theory and scaled by 0.9804). [b] B3LYP/6-31G(d) level of theory.

The exothermicity of the process involving CO loss suggests that $[HCCCCCO]^-$ is not an appropriate precursor of HCCCCCO.

Since $[HCCCCCO]^-$ cannot be used as a precursor to doublet HCCCCCO, the alternative possibility is to form the neutral by one-electron vertical reduction of the cation $[HCCCCCO]^+$. Cation $[HCCCCCO]^+$ has singlet and triplet forms, with the singlet form being the more stable by 292 kJ mol^{-1} (see Table 4). The data listed in Table 3 indicate that the decompositions of the singlet and doublet cations of $[HCCCCCO]^+$ are unfavourable. Thus we will use $[HCCCCCO]^+$ as the precursor of HCCCCCO and $[CCCCCHO]^-$ as the precursor to CCCCCHO.

$$[\mathrm{H{-}C{\equiv}C{-}C{\equiv}C{-}CO{-}}\textit{iso}\mathrm{{-}Pr}]^{+\bullet} \longrightarrow \mathrm{H{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}O^+} + \textit{iso}\mathrm{{-}Pr^\bullet} \quad (1)$$

$$\mathrm{(CH_3)_3Si{-}C{\equiv}C{-}C{\equiv}C{-}CHO} + \mathrm{F^-} \longrightarrow {}^-\mathrm{CCCCCHO} + \mathrm{(CH_3)_3SiF} \quad (2)$$

The syntheses of the ionic precursors and the formation of HCCCCCO and CCCCCHO

The precursor ions $[HCCCCCO]^+$ and $[CCCCCHO]^-$ were formed in the chemical ionisation source of the VG ZAB 2HF mass spectrometer using standard procedures, namely, (i) the simple α cleavage process of the ketone radical cation shown in eqn. (1), and (ii) the $S_N2(Si)$ reaction using F^- (from SF_6) shown in eqn. (2); a process first reported by DePuy.[37]

The collision induced (CID) mass spectrum (MS/MS) and the $^+NR^+$ spectrum of $[HCCCCCO]^+$ are shown in Figs. 3A and 3B respectively. The MS/MS spectrum (Fig. 3A) of $[HCCCCCO]^+$ shows peaks formed by the losses of $CH^\bullet$, O, CO and CCO from the parent cation. These fragmentations are in accord with a bond connectivity HCCCCCO for the decomposing cations. The $^+NR^+$ spectrum indicates that the process $[HCCCCCO]^+ \longrightarrow HCCCCCO \longrightarrow [HCCCCCO]^+$ occurs without any rearrangement of the cumulene skeleton at either stage of the sequential process. The spectrum is shown in Fig. 3B, and shows similar features to the MS/MS spectrum (Fig. 3A). The presence of a signal at *m*/*z* 77 in the $^+NR^+$ spectrum indicates that some of the doublet HCCCCCO neutrals are stable for the microsecond duration of the NR experiment.

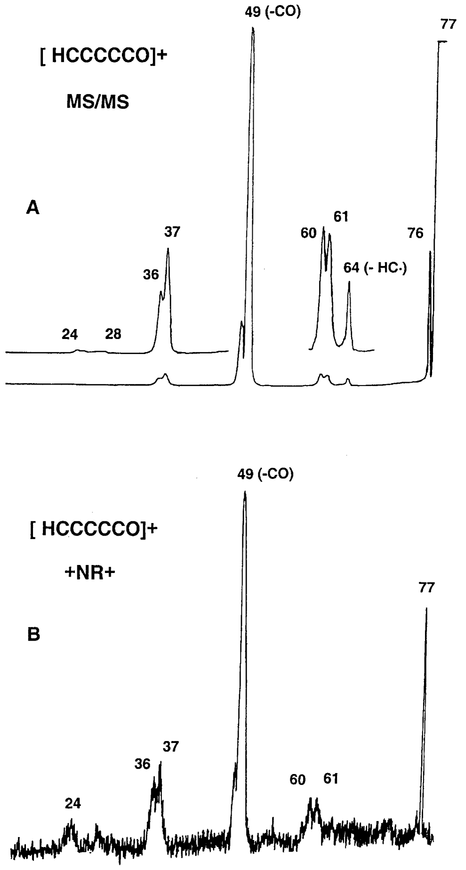


Fig. 3 (A) CID MS/MS of $[HCCCCCO]^+$, (B) $^+NR^+$ spectrum of $[HCCCCCO]^+$. VG ZAB 2HF mass spectrometer. For experimental conditions see Experimental section.

In contrast, the $^-CR^+$ and $^-NR^+$ spectra of $[CCCCCHO]^-$ (Figs. 4A and 4B) show that there are rearrangements occurring at the neutral and cationic stages of the sequential one-electron vertical oxidation processes $[CCCCCHO]^- \longrightarrow CCCCCHO \longrightarrow [CCCCCHO]^+$. The $^-CR^+$ spectrum is that of the (stable and decomposing) cations produced by synchronous two-electron oxidation of the anion $[CCCCCHO]^-$. The peaks formed by losses of O, $[HO^\bullet$ (probably − O − H)], $CHO^\bullet$ and CCHO in Fig. 4A are characteristic of a cation of connectivity CCCCCHO. However, those peaks formed by losses of $HC^\bullet$, $HCC^\bullet$, CO and CCO are formed from rearranged cations in which the H has moved away from the terminal CHO position. In particular, the losses of $HC^\bullet$ and $HCC^\bullet$ suggest the structure of the decomposing cation is $[HCCCCCO]^+$.

Comparison of the $^-CR^+$ and $^-NR^+$ spectra of $[CCCCCHO]^-$ (Figs. 4A and 4B) provides clear evidence that

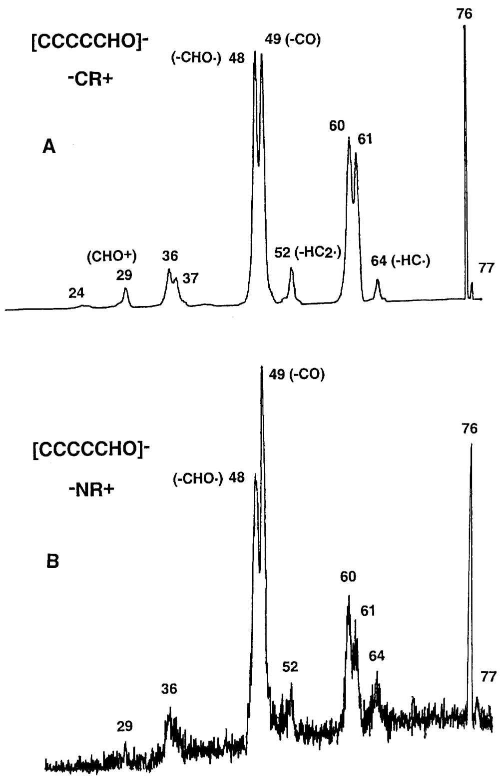


Fig. 4 (A) $^-$CR$^+$ mass spectrum of [CCCCCHO]$^-$. (B) $^-$NR$^+$ spectrum of [CCCCCHO]$^-$. VG ZAB 2HF mass spectrometer. For experimental conditions see Experimental section.

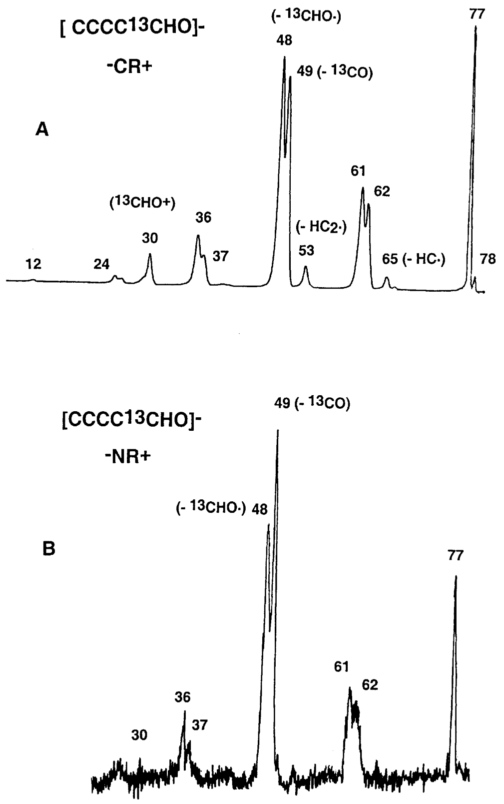


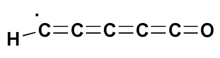
Fig. 5 (A) $^-$CR$^+$ mass spectrum of [CCCC^{13}CHO]$^-$. (B) $^-$NR$^+$ spectrum of [CCCC^{13}CHO]$^-$. VG ZAB 2HF mass spectrometer. For experimental conditions see Experimental section.

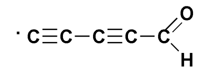
the first-formed neutral CCCCCHO undergoes more rearrangement than the cationic product of the $^-$CR$^+$ process.† The $^-$CR$^+$ and $^-$NR$^+$ spectra are similar except that the $^-$NR$^+$ spectrum shows the larger peak formed by loss of carbon monoxide. This means that either (i) the rearranged neutrals are decomposing by loss of CO, and/or (ii) there are more rearranged cations formed by $^-$NR$^+$ than $^-$CR$^+$ processes. Irrespective of which of these two possibilities is correct, neutral CCCCCHO is rearranging more under NR conditions than [CCCCCHO]$^+$ is under $^-$CR$^+$ conditions.

The carbon atoms of energised cumulenes like CCCC[27] and CCCCC[26] are scrambled during NR processes. This is not a feature of cumulene oxides like CCCO[25] and CCC(=O)CC.[10] Does reorganisation of the backbone of CCCCCHO occur during or following rearrangement? The $^-$CR$^+$ and $^-$NR$^+$ spectra of the ^{13}C labelled anion [CCCC^{13}CHO]$^-$ are shown in Fig. 5. These spectra should be compared with the corresponding spectra of the unlabelled anion (Fig. 4). No C scrambling is noted for data provided by either the $^-$CR$^+$ or $^-$NR$^+$ spectra. Both spectra show losses of HC$^•$, HCC$^•$ and ^{13}CO, indicating that the oxygen atom remains attached to the ^{13}C atom during cationic and neutral rearrangements.

Rearrangements of neutral CCCCCHO

The structures of the doublet neutrals HCCCCCO and CCCCCHO are best represented by the valence bond structures shown below (for full details see Table 5). The dipole moments are 2.67 and 2.61 D and the adiabatic electron affinities 1.69 and 4.47 eV respectively at the level of theory used in this study.





Consideration of the $^-$CR$^+$ and $^-$NR$^+$ spectra shown in Figs. 4 and 5 indicates that the initially formed CCCCCHO undergoes rearrangement to an isomer or isomers, which either decompose by loss of CO, or are reionised to a cation which may fragment by loss of CO. In addition, whatever the nature of the rearrangement, it does not involve cleavage of the CO bond.

Possible rearrangement processes of doublet CCCCCHO have been investigated by probing the doublet neutral potential surface at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory. Results are summarised in Fig. 6, with full details of species shown in Fig. 6 given in Table 5. There are three possible mechanisms to consider: that involving successive H rearrangements (Fig. 6A), and those involving six-centre states (Fig. 6B). The reaction sequence shown in Fig. 6A shows that only 75.5 kJ mol^{-1} is needed to convert CCCCCHO to CCCCHCO, with an additional 20 kJ mol^{-1} required to convert CCCHCCO to HCCCCCO. In principle, there are three species formed in this sequence which could lose CO, namely CCCCHCO, CCCHCCO and HCCCCCO. Of these, CCCCHCO and HCCCCCO are formed with sufficient excess energy (182 and 308 kJ mol^{-1} respectively) to effect loss of CO (see Fig. 6A and *cf.* Table 6). However, only one of these, HCCCCCO, can lose HC$^•$, HCC$^•$ and CO as observed in the $^-$NR$^+$ spectra (Figs. 4B and 5B).

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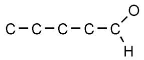
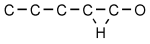
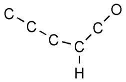
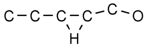
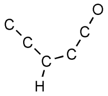
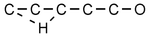
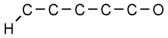
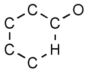
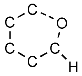
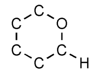
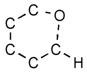
† A reviewer has requested that the CID mass spectrum (MS/MS) of [CCCCHO]$^-$ be included in order that possible rearrangement of [CCCCCHO]$^-$ may be probed experimentally. The CID spectra of [CCCCCHO]$^-$ and [CCCC^{13}CHO]$^-$ follow. [CCCCCHO]$^-$, *m/z* (loss) abundance: 76 (H$^•$) 100, 49 (CO) 22, 48 (HCO$^•$) 20%. [CCCC^{13}CHO]$^-$, 77 (H$^•$) 100, 49 (^{13}CO) 20 and 48 (H^{13}CO$^•$) 17. The reason these data were not included originally is that they provide no data concerning possible rearrangement of [CCCCCHO]$^-$. This is because (i), we do not have the corresponding spectrum of [HCCCCCO]$^-$ for comparison, and (ii) the loss of CO does not necessarily imply rearrangement of the skeleton, because this loss may well occur by the stepwise process [CCCCCHO]$^-$ ⟶ [(CCCC) HCO$^-$] ⟶ HC$_4^-$ + CO. Here, the HCO$^-$ ion in the anion neutral complex acts as a hydride donor. The theoretical data summarised in Fig. 1 show the barrier for rearrangement to be ≥ 250 kJ mol^{-1}. It is most unlikely that [CCCCCHO]$^-$, on formation, will have sufficient excess energy to surmount such a barrier.

Table 5 Doublet neutral potential surface

											
State	$^2A'$	$^2A'$	$^2A'$	$^2A'$	$^2A'$	$^2A'$	$^2A'$	$^2A'$	$^2A'$	$^2A'$	$^2A'$
Symmetry	C_s	C_s	C_s	C_s	C_s	C_s	C_s	C_s	C_s	C_s	C_s
Energy/Hartree[a]	−265.37492	−265.34625	−265.41554	−265.33899	−265.37473	−265.34619	−265.45639	−265.30782	−265.32274	−265.36027	−265.36043
Dipole/debye[b]	2.61		5.49		3.59		2.67			1.65	
Adiabatic electron affinity/eV	4.47		4.33		4.32		1.69			2.34	
Bond length/Å[b] or angle/°[b]											
C1C2	1.437	1.306	1.355	1.312	1.288	1.282	1.292	1.423	1.43	1.356	1.299
C2C3	1.243	1.296	1.379	1.313	1.359	1.283	1.267	1.278	1.296	1.315	1.328
C3C4	1.322	1.286	1.279	1.304	1.375	1.327	1.326	1.329	1.298	1.308	1.299
C4C5	1.296	1.302	1.309	1.288	1.283	1.332	1.233	1.289	1.343	1.377	1.41
C1O	1.218	1.186	1.158	1.180	1.176	1.174	1.181	1.187	1.261	1.435	1.716
C5O									1.994	1.304	1.243
C1H	1.106	1.349						1.388	1.095	1.084	1.078
C2H		1.434	1.088	1.304							
C3H				1.334	1.091	1.350					
C5H						2.289	1.067	1.585			
C1C2C3	178.8	178.7	112.5	166.6	159.9	178.4	178.9	111.6	112.5	105.6	114.7
C2C3C4	179.3	177.4	162.7	176.6	114.1	176.1	179.6	151.2	132.8	149.1	147.3
C3C4C5	179.5	179.7	176.2	178.8	177.3	177.5	178.4	108.6	134.6	98.7	98.1
OC1C2	122.2	169.8	174.6	164.4	174.2	179.6	179.2	142.9	122.7	118.9	110.7
HC1C2	115.0	65.3						101.4	120.6	132.5	114.9
HC2C3			126.3	61.3							
HC3C4					123.3	58.6					
HC5C4							170.5	106.3			
C1C2C3C4	180.0	180.0	0.0	0.0	0.0	180.0	180.0	0.0	0.0	0.0	0.0
C2C3C4C5	0.0	180.0	180.0	180.0	180.0	0.0	180.0	0.0	0.0	0.0	0.0
OC1C2C3	0.0	0.0	0.0	180.0	180.0	180.0	180.0	180.0	0.0	0.0	0.0
HC1C2C3	0.0	180.0						0.0	180.0	180.0	180.0
HC2C3C4			180.0	180.0							
HC5C4C3					0.0	180.0	180.0				

[a] CCSD(T)/aug-cc-pVDZ level of theory including zero point energy (calculated from vibrational frequencies at the B3LYP/6-31G(d) level of theory and scaled by 0.9804). [b] B3LYP/6-31G(d) level of theory.

Table 6 Decomposition pathways of doublet neutral isomers C_5HO [CCSDT/aug-cc-pVDZ//B3LYP-6-31G(d) level of theory][a]

CCCCCHO ⟶ ^{1}CCCC + $^{\bullet}$CHO	339 kJ mol^{-1}
CCCCHCO ⟶ HCCCC$^{\bullet}$ + ^{1}CO	63
CCCHCCO ⟶ CCCHC$^{\bullet}$ + ^{1}CO	130.5
HCCCCCO ⟶ HCCCC$^{\bullet}$ + ^{1}CO	170.5

[a] Energy values were determined from the following theoretically calculated values (Hartrees): ^{1}CCCC = −151.65884, HCCCC$^{\bullet}$ = −152.32257, CCCHC$^{\bullet}$ = −152.25762, HCCCC$^{\bullet}$ = −152.32257.

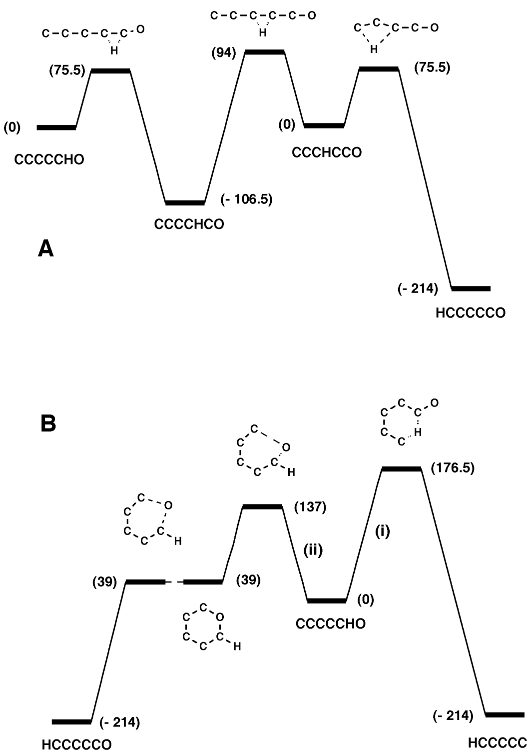


Fig. 6 Rearrangement processes of doublet neutral CCCCCHO. Energies at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory. Structures drawn indicate bond connectivities not bond multiplicity. For full details of structure including geometries and energies see Table 5. Relative energies in kJ mol^{-1}. (A) The sequential H transfer mechanism. (B) Six-centre cyclisation processes, (i) the concerted H transfer mechanism, and (ii) the O transfer process.

Processes **(i)** and **(ii)** (shown in Fig. 6B) both involve six-centre transition states. The concerted process **(i)** has a barrier of 176.5 kJ mol^{-1}, significantly more than the maximum barrier of 94 kJ mol^{-1} required to effect the sequential H transfer process (Fig. 6A). Process **(ii)**, which requires an excess energy of ≥ 137 kJ mol^{-1}, involves O transfer; a process ruled out by the experimental ^{13}C labelling data outlined above.

Finally, the vertical Franck–Condon oxidation of [CCCCCHO]$^-$ to CCCCCHO will initially give a structure on the neutral potential surface with the geometry of the anion precursor. Theoretical calculations indicate that such a structure has 54 kJ mol^{-1} of excess energy at the B3LYP/6-31G(d) level of theory. This is insufficient to cause rearrangement of CCCCCHO. A CCCCCHO neutral must have ≥ 75.5 kJ mol^{-1} to form CCCCHCCO, and ≥ 94.5 kJ mol^{-1} of excess energy to form HCCCCCO. The extra energy is presumably provided by additional collision(s) of CCCCCHO during or following the NR process.[26,27]

Summary and conclusions

1 One-electron vertical reduction of [HCCCCCO]$^+$ gives the doublet radical HCCCCCO. This neutral is stable for the microsecond duration of the NR experiment.

2 One-electron vertical oxidation of [CCCCCHO]$^-$ gives the radical CCCCCHO which is stable for the microsecond duration of the NR experiment provided that CCCCCHO is formed with less than 75.5 kJ mol^{-1} of excess energy.

3 If CCCCCHO has ≥ 75.5 kJ mol^{-1} of excess energy it may rearrange to CCCCHCO which has sufficient excess energy to cause decomposition to HCCCC and CO.

4 If CCCCCHO has ≥ 94 kJ mol^{-1} of excess energy it may rearrange through CCCCHCO to form HCCCCCO in a reaction sequence which is exothermic by 214 kJ mol^{-1}. Experimental and theoretical data show that neutral HCCCCCO is formed from CCCCCHO, and that HCCCCCO is formed with sufficient excess energy to cause decomposition to give HCCCC and CO.

Experimental section

A Mass spectrometric methods

For a detailed description of the instrument used, see reference 26. In brief, the experiments were performed using a two-sector modified VG ZAB 2HF mass spectrometer with BE configuration, where B and E represent magnetic and electric sectors, respectively. Typical source conditions were as follows: source temperature 200 °C, repeller voltage −0.5 V, ion extraction voltage 7 kV, mass resolution $m/\Delta m \geq 1500$. Each neutral precursor was inserted into the ion source through the septum inlet, which was heated to 120 °C to give a measured pressure of *ca.* 10^{-6} Torr inside the source housing. For the anion, reagent gas [SF_6 (for F^-)] was introduced through a gas inlet into the ion source, to give a measured total pressure of *ca.* 10^{-5} Torr in the source housing. The estimated total pressure in the ion source is 10^{-1} Torr for the system shown in eqn. (2). Collisional induced (CID) spectra (MS/MS) were determined using B to select the parent ion in each case, and utilising argon as the target gas in the first collision cell following B. The pressure of argon in the first cell was maintained such that 80% of the parent ion beam was transmitted through the cell. This corresponds to an average of 1.1–1.2 collisions per ion.[38] Product ion peaks resulting from CID processes were recorded by scanning E.

Neutralisation–reionisation ($^+$NR$^+$ or $^-$NR$^+$)[39–41] experiments were performed for mass-selected ions utilising the dual collision cells located between the magnetic and electric sectors. Neutralisation was effected using O_2 at 80% transmittance (of the main beam) as the collision gas in the first collision cell, while reionisation to cations was achieved by collision of the neutrals with O_2 (80% transmittance) in the second collision cell. In order to detect a reionisation signal due to the parent neutral, the neutral species must be stable for the one microsecond timeframe of this experiment. Charge reversal ($^-$CR$^+$) spectra[42,43] were recorded using single collision conditions in collision cell 1 (O_2, 80% transmission of main beam).

B Synthetic procedures

2-Methylhepta-4,6-diyn-3-one (HC≡C–C≡C–CO–*iso*C_3H_7) was prepared by a reported procedure.[44,45]

$(CH_3)_3$Si–C≡C–C≡C–CHO. Methyllithium complexed with lithium bromide (1.5 M in diethyl ether, 3.46 cm^3) was added to bis(trimethylsilyl)butadiyne (1.01 g) at −10 °C in dry tetrahydrofuran (25 cm^3) and under nitrogen. The reaction mixture was allowed to warm to 20 °C and stirred at that temperature for 15 h under nitrogen. Anhydrous dimethylformamide (0.53 cm^3) was added at 0 °C, the solution warmed to 20 °C and stirred at that temperature for a further 3 h under nitrogen. The reaction mixture was poured into a vigorously stirring biphasic solution of aqueous potassium dihydrogen phosphate (10%, 50 cm^3) and diethyl ether (25 cm^3), the organic layer was separated, dried ($MgSO_4$), and the solvent removed *in vacuo* to give 5-(trimethylsilyl)penta-2,4-diyn-1-al as a colourless oil. Yield 0.48 g, 62%. $(M^{+\bullet} - H)^+$ ion, found 149.0428; C_8H_9SiO requires 149.0422. ^{1}H NMR [200 MHz, δ($CDCl_3$)]: 0.18 [9H, s, $Si(CH_3)_3$], 9.19 (1H, s, CHO).

$(CH_3)_3Si–C{\equiv}C–C{\equiv}C–^{13}CHO$. Prepared as for the unlabelled compound (above) except that $H^{13}CONMe_2$ (^{13}C = 99%) was used in place of unlabelled dimethylformamide. Yield 75%, ^{13}C = 99% by positive ion mass spectroscopy.

C Theoretical methods

Geometry optimisations were carried out with the Becke 3LYP method[46,47] using the 6-31G(d) basis set within the GAUSSIAN 98 suite of programs.[48] Stationary points were characterised as either minima (no imaginary frequencies) or transition structures (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 zero-point vibrational energies which were used as a zero-point correction for the electronic energies. We have previously reported the success of the B3LYP method in predicting geometries of unsaturated chain structures, and that this method produces optimised structures, at low computational cost, that compare favourably with higher level calculations.[49] More accurate energies for the B3LYP geometries were determined using the couple cluster method, CCSD(T) method[50] using the Dunning aug-cc-pVDZ basis set.[51] All calculations were carried out on the Alpha Server at the Australian Partnership for Advanced Computing (APAC) National Facility (Canberra).

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