PERKIN 2

The formation of neutral CCC and its radical cation from the CCC radical anion in the gas phase. A joint experimental and theoretical study

Andrew M. McAnoy,[a] Suresh Dua,[a] Detlef Schröder,[b] John H. Bowie *[a] and Helmut Schwarz[b]

[a] *Department of Chemistry, The University of Adelaide, South Australia, 5005.*
E-mail: john.bowie@adelaide.edu.au
[b] *Institut für Chemie, Technische Universität Berlin, D-10623 Berlin, Germany*

Received (in Cambridge, UK) 2nd July 2002, Accepted 30th July 2002
First published as an Advance Article on the web 23rd August 2002

The radical anion $[CC^{13}C]^{-\bullet}$ has been produced by treatment of $[(CH_3)_3SiC{\equiv}C^{13}C(=NNHSO_2C_6H_4\text{-}p\text{-}CH_3)Si(CH_3)_3]$ with HO^-/F^- in the ion source of a mass spectrometer. The stable anion undergoes vertical two-electron oxidation [charge reversal ($^-CR^+$)] in a collision cell to give $[CC^{13}C]^{+\cdot}$ which cyclises to the more stable [*cyclo*-$CC^{13}C]^{+\cdot}$ over a barrier of only 11 kJ mol^{-1} [calculated at the CCSD(T)/aug-cc-pVTZ//B3LYP/6-311G(d) level of theory], effectively scrambling the three carbon atoms of the cation radical. One-electron Franck–Condon oxidation of $[CC^{13}C]^{-\bullet}$ yields neutral $CC^{13}C$. Theoretical calculations suggest that neutral CCC may undergo a degenerate rearrangement through a cyclic C_3 transition state if the excess energy of CCC is ≥104 kJ mol^{-1} (at the CCSD(T)/aug-cc-pVTZ//B3LYP/6-311G(d) level of theory). It is likely that at least a proportion of the $CC^{13}C$ neutrals formed from $[CC^{13}C]^{-\bullet}$ should have sufficient energy to effect this reaction, resulting in the scrambling of the ^{13}C label. The neutralisation/reionisation ($^-NR^+$) spectrum of $[CC^{13}C]^{-\bullet}$ ($[CC^{13}C]^{-\bullet} \longrightarrow CC^{13}C \longrightarrow [CC^{13}C]^{+\cdot}$) shows a pronounced peak corresponding to the parent cation, confirming that neutral $CC^{13}C$ is stable for the time of the NR experiment (10^{-6} s). However due to total scrambling of the label in the cation, possible scrambling in the neutral CCC molecule cannot be probed by this experiment. The corresponding $^-NR^-$ experiment of $[CC^{13}C]^{-\bullet}$ showed a recovery signal but the sensitivity of the instrument was not sufficient to detect the decomposition fragments of the final radical anion.

Introduction

The volume of scientific literature pertaining to carbon clusters is testament to the importance of these unusual species.[1,2] The participation of carbon clusters in circumstellar and interstellar chemistry,[3–5] combustion processes,[6] and material sciences,[7] is well known, but understanding the precise role in each of these systems demands detailed knowledge of the structure and reactivity of such molecules. Small carbon clusters are present in stellar media[3–5] and are considered[8,9] to be the precursors of large carbon molecules[10,11] including aromatic species and fullerenes.[12] To date, C_2, C_3 and C_5 are the only small carbon neutrals definitely identified in the stellar medium: *e.g.* in the circumstellar envelope of the evolved carbon star IRC+10216.[3] A range of linear and cyclic carbon clusters have been made by a number of techniques, and have been characterised,[8,9,13–28] including linear and rhombic C_4[27] and linear C_5.[28]

The smallest polyatomic carbon cluster (cumulene), linear C_3, has been detected in a number of extraterrestrial sources including comets,[29] circumstellar envelopes,[3,30] cold dense molecular clouds,[31] and diffuse molecular clouds.[32] Detection of this molecule in such different environments was effected by using the electronic transition at 4050 Å (comets[29] and diffuse clouds[32]), by the bending mode at 63.42 cm^{-1} (dense clouds[31]), and the anti-symmetrical stretching mode at 2040 cm^{-1} (circumstellar envelopes[3]).

Linear C_3 was first formed in the laboratory from deposited carbon vapour in 1962.[33] It has since been formed in many ways,[34] for example by infrared multiple photon photolysis of allene,[35] and by fast electric discharge in the supersonic expansion of CO.[36] Experimental measurements on linear CCC include the determination of electron affinity of the neutral (1.981 eV) determined by photoelectron spectroscopy,[37] and other spectroscopic measurements[13,34,38] including far infrared measurements[38] which were subsequently used in the successful search for linear C_3 in cold molecular clouds.[31] The stability of C_3 has been demonstrated by it being a dominant photofragment of C_n cations ($4 < n < 20$), while in the particular case of $C_3^{+\cdot}$, no photofragment was observed.[39] Laser ablation TOF mass spectrometry has been used to generate C_3 radical cations,[40] while the linear C_3 radical anion has been formed by laser ablation of graphite deposited in argon matrices and subsequently studied by infrared spectroscopy.[41]

There have been many theoretical studies on isomeric C_3 neutrals,[42–49] the corresponding anions,[23,44,48,50] and cations.[44,51–54] As long ago as 1981, it was realised that the global minimum on the neutral potential surface corresponds to the $^1\Sigma_g{}^+$ ground state of linear C_3, while the C_{2v} cyclic C_3 is a transition state for the degenerate isomerisation of linear C_3.[43]

In previous studies, we have synthesised small carbon clusters by converting negative ions of known connectivity into neutrals in a collision cell of a mass spectrometer and interrogating those neutral species by reionisation using the neutralisation/reionisation process ($^-NR^+$).[55] For example, we have recently made $^{13}CCC^{13}C$[27] and $CC^{13}CCC$[28] from the corresponding anions, and shown that these energised neutrals undergo carbon scrambling within the timeframe of the NR experiment (10^{-6} s). Theoretical studies indicate that the scrambling mechanisms proceed through rhombic C_4 and a carbon substituted rhombic structure respectively.[27,28]

The purpose of the present study is twofold, namely, (i) to make labelled linear neutral $CC^{13}C$ from an anion precursor of known connectivity, and (ii) to determine whether the energised neutral $CC^{13}C$ equilibrates its carbons.

DOI: 10.1039/b206400f

Table 1 Anion geometries and energies[a,b]

	Linear	Cyclic	TS
State	$^2\Pi_g$	$^2A_1$	$^2A'$
Energy/Hartrees	−113.9016615	−113.8851092	−113.842067
Relative energy/kJ mol^{-1}	0	43 (41[c], 60[d])	156 (166[c])
Bond lengths/Å			
C_1C_2	1.306 (1.311[d], 1.307[e], 1.328[c], 1.310[f], 1.322[g])	1.363 (1.385[c], 1.369[d])	1.287 (1.311[c])
C_2C_3	1.306	1.363	1.434 (1.462[c])
C_1C_3	2.612	1.545	2.179
Angles/°			
$C_1C_2C_3$	180.0	69.0 (69.3[c], 68.9[d])	106.3 (104.6[c])

[a] Geometries are optimised at the B3LYP/6-311G(d) level of theory. [b] Energies are calculated at the CCSD(T)/aug-cc-pVTZ//B3LYP/6-311G(d) level of theory and include zero point energy correction [B3LYP/6-311G(d)]. [c] MRD-CI/6-311+G(d)//CASSCF/6-31G(d).[48] [d] B3LYP/6-31G(d).[47] [e] CCSD(T) method (with 255 cGTOs and all electrons correlated).[23] [f] MRCI/(modified)aug-cc-pVQZ.[50] [g] QCISD(T)/6-31G(d).[44]

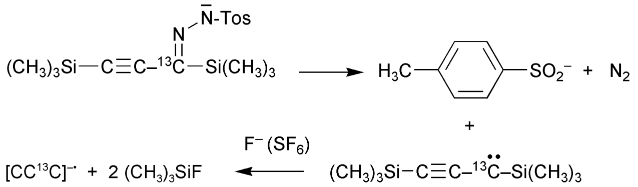
Results and discussion

The formation of linear $[CC^{13}C]^{-\bullet}$ radical anion

It has been shown previously that singlet CCC is the ground state on the C_3 potential surface and that the corresponding singlet cyclic C_3 is not a local minimum on that surface.[43] Triplet CCC is also a stable species, with a singlet–triplet splitting of 201 kJ mol^{-1}.[34] The doublet $[CCC]^{-\bullet}$ radical anion should be a suitable precursor to effect a one-electron oxidation *via* a Franck–Condon vertical process to yield the required linear species CCC. However, there is a complication, because two stable C_3 radical anions exist. One is the required linear species $[CCC]^{-\bullet}$, the other the cyclic C_3 radical anion. The B3LYP/6-311G(d) optimised geometries of these species are given in Table 1, together with their relative energies calculated at the CCSD(T)/aug-cc-pVTZ//B3LYP/6-311G(d) level of theory. Results from previous studies are also listed in Table 1. The highest level theoretical approach to date predicts a CC bond length of 1.307 Å for $[CCC]^{-\bullet}$;[21] this is in excellent agreement with our value of 1.306 Å (Table 1). While the linear C_3 anion radical is the lower in energy of the two anions, the cyclic anion radical is only higher in energy by 42 kJ mol^{-1} at our chosen level of theory (Table 1). Based on this small difference in energy, the possibility must be considered that both anion radicals might be formed in the ion source of the mass spectrometer from a neutral precursor with linear CCC connectivity.

The rearrangement of linear $[CCC]^{-\bullet}$ to $[cyclo\text{-}C_3]^{-\bullet}$ has been computed at the CCSD(T)/aug-cc-pVTZ//B3LYP/6-311G(d) level of theory; geometry and energy data for the two minima and the transition states are recorded in Table 1, together with comparison data from other studies, as appropriate. There is a barrier of 156 kJ mol^{-1} for the conversion of the linear to the cyclic anion: a barrier high enough to suggest that it is unlikely for such a rearrangement to occur in the ion source of the mass spectrometer, following the formation of $[CCC]^{-\bullet}$. In an earlier study,[27] the barrier for rearrangement of $[CCCC]^{-\bullet}$ to rhombic $[C_4]^{-\bullet}$ was calculated to be 132 kJ mol^{-1} at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31(d) level of theory; in fact, this rearrangement does not occur experimentally. Similarly, no rearrangement was noted for the $[CCCCC]^{-\bullet}$ radical anion.[28]

The synthesis of $[CC^{13}C]^{-\bullet}$ was effected by deprotonation of the ^{13}C labelled tosylhydrazone $[(CH_3)_3SiC{\equiv}C^{13}C(NNHTos)(Si(CH_3)_3)]$ to yield the precursor anion shown in Scheme 1. This procedure is analogous to that used previously for the synthesis of $[CC^{13}CCC]^{-\bullet}$;[28] using our SF_6 modification[28] of the Squires double desilylation procedure[56] (which uses F^-/NF_3), together with deprotonation of the tosylhydrazone to effect formation of the carbene intermediate.[57] We do not know the precise sequence for this procedure (just as the intimate mechanism of the Squires bis-desilylation is not known[56]). Scheme 1 shows one possible rationale of the overall reaction. $[M - H]^-$, $p\text{-}CH_3C_6H_4SO_2^-$ and $[CC^{13}C]^{-\bullet}$ species are formed in the ion source of the mass spectrometer, consistent with the process shown in Scheme 1.



Scheme 1

The collision induced (CID) mass spectrum (MS/MS) of $[CC^{13}C]^{-\bullet}$ shows a pronounced peak due to the parent radical anion together with two weak peaks corresponding to losses of ^{12}C and ^{13}C. The spectrum was scanned at maximum sensitivity over the region containing *m*/*z* 24 and 25 ($CC^{-\bullet}$ and $C^{13}C^{-\bullet}$) giving a peak area ratio (*m*/*z* 24 to *m*/*z* 25) of 1 : 1. This result demonstrates that the carbons of $[CC^{13}C]^{-\bullet}$ are not scrambling prior to or during the losses of ^{12}C and ^{13}C. This is interesting, since the dissociation process $C_3^{-\bullet} \longrightarrow C_2^{-\bullet} + C$, has $\Delta H = +603$ kJ mol^{-1};[58] similar results were obtained for linear C_4 and C_5.[27,28]

In view of the experimental observation that $[CC^{13}C]^{-\bullet}$ may decompose (by loss of ^{12}C and ^{13}C) without prior or accompanying rearrangement of the carbon skeleton, is it possible that the transition state for this process is inaccessible? Renner–Teller splitting of the $^2\Pi_g$ ground state occurs upon symmetrical bending of $[CCC]^{-\bullet}$. This effect has been studied using a number of high level procedures.[19,48] The two Renner–Teller bending potentials ($^2B_2$ and $^2A_2$) increase dramatically in energy upon symmetrical bending of the anion radical. In contrast, the cyclic anion is a local minimum on the $^2A_1$ surface, and this increases in energy with increasing CCC bond angle. The $^2\Pi_g$ excited state is attained some 343 kJ mol^{-1} higher in energy than the $^2\Pi_u$ ground state (calculated at the MRD-CI/6-311+G(d)//CASSCF/6-31G(D) level of theory).[46] Thus, if only symmetrical bending is considered, theory suggests that neither ring-opening nor ring-closing is viable energetically. At first sight this appears to be at variance with the transition state detailed in Table 1. However the transition state is not symmetrical and lies on the $^2A'$ surface near the crossing point of the $^2A_1$ and $^2B_2$ surfaces. Therefore the anion rearrangement not only has a barrier, but it is also dependent on accessing the transition state on the $^2A'$ potential energy surface. In addition, rearrangement of energised $[CCC]^{-\bullet}$ has to compete with collision-induced electron detachment.

The $^-$CR$^+$ and $^-$NR$^+$ mass spectra of $[CC^{13}C]^{-\bullet}$

The $^-$CR$^+$ and $^-$NR$^+$ mass spectra of $[CC^{13}C]^{-\bullet}$ are shown in Figs. 1 and 2 respectively. The spectra are simple, showing recovery signals and fragment peaks corresponding to losses of ^{12}C and ^{13}C together with $^{12}C_2$ and $^{12}C^{13}C$. The spectra are very similar to each other except for the peak at *m/z* 18.5 in the $^-$CR$^+$ spectrum which is due to doubly-charged $CC^{13}C$ [this is our first observation of a peak produced by a doubly-charged cation in a $^-$CR$^+$ spectrum of a cumulene anion: this peak is present in the $^-$CR$^+$ spectra obtained from the ZAB/AMD 604 mass spectrometer (Berlin) and the VG ZAB 2HF instrument (Adelaide)]. The peaks due to losses of ^{12}C and ^{13}C (*m/z* 25 and 24) have an area ratio of 2 : 1, while those corresponding to losses of $^{12}C_2$ and $^{12}C^{13}C$ (*m/z* 13 and 12) have an area ratio of 1 : 2. These ratios indicate that the carbon chain scrambles statistically either during the formation of $[^{12}C_2{}^{13}C]^{+\bullet}$, or accompanying decomposition of the parent radical cation.

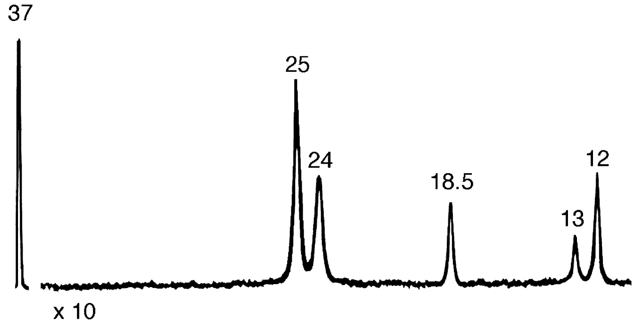


Fig. 1 $^-$CR$^+$ spectrum of $[CC^{13}C]^{-\bullet}$. HF-ZAB/AMD 604 mass spectrometer. Full experimental conditions see Experimental section.

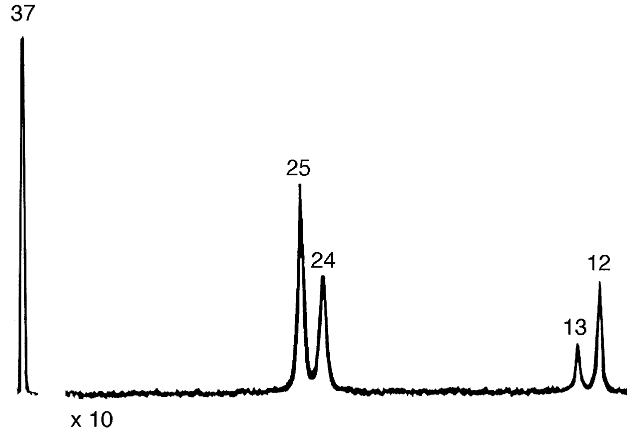


Fig. 2 $^-$NR$^+$ spectrum of $[CC^{13}C]^{-\bullet}$. HF-ZAB/AMD 604 mass spectrometer. Full experimental conditions see Experimental section.

The rearrangement of linear $[CC^{13}C]^{+\bullet}$ to the cyclic isomer

The cation potential energy surface has been investigated at the CCSD(T)/aug-cc-pVTZ//B3LYP/6-311(d) level of theory, and the results are listed in Table 2. There has been debate as to whether the linear $^2\Sigma_u$ or the cyclic $^2B_2$ structure is the ground state.[44,45,51,53,54] Our calculations predict that the cyclic $^2B_2$ cation corresponds to the global minimum on the cation potential energy surface, with the linear $^2\Sigma_u$ state lying 24 kJ mol^{-1} above the ground state. The barrier to convert the linear to the cyclic cation is only 11 kJ mol^{-1}. When $[CCC]^{-\bullet}$ undergoes vertical two-electron oxidation to the linear cation, the excess Franck–Condon energy (the difference in energy between the ground-state cation radical $[CCC]^{+\bullet}$ and the radical cation with the anion geometry on the cation potential energy surface) is only 2 kJ mol^{-1} at the B3LYP/6-311(d) level of theory. This small energy difference can be attributed to the similar geometries of the anion and cation (*cf.* data in Tables 1 and 2). This Franck–Condon excess energy of 2 kJ mol^{-1} is not sufficient to surmount the 11 kJ mol^{-1} barrier between the linear and cyclic C_3 cation radicals. However, the actual excess energy of the cation formed will be more than the excess Franck–Condon energy, either as a consequence of some formation energy of the anion radical being carried through to the cation, or by some subsequent collision process of the cation. Thus $[CC^{13}C]^{+\bullet}$ formed initially in the $^-$CR$^+$ process will rearrange over the 11 kJ mol^{-1} barrier to yield the cyclic cation radical in which the ^{13}C label is essentially scrambled.

The conversion of $[CC^{13}C]^{-\bullet}$ to neutral $CC^{13}C$

The $^-$CR$^+$ and $^-$NR$^+$ spectra of $[CC^{13}C]^{-\bullet}$ show the same fragment peaks in the same ratio. The $^-$NR$^+$ spectrum shows the presence of a pronounced recovery signal confirming that a neutral C_3 is stable for the duration of the NR experiment (10^{-6} s). The similarity of the $^-$NR$^+$ and $^-$CR$^+$ spectra of $[CC^{13}C]^{-\bullet}$ suggests that no major decomposition of the neutral occurs on the microsecond timescale [for CCC $\longrightarrow$ CC + C, ΔH = 734 kJ mol^{-1} [58]]. Since complete ^{13}C scrambling is noted for both $^-$CR$^+$ and $^-$NR$^+$ spectra, this means that the $^-$NR$^+$ spectrum (Fig. 2) provides no information concerning the question of carbon scrambling of the neutral. In this context, it has been recently reported that carbon scrambling within the ^{13}C labelled $[C_3]^{+\bullet}$ species produced by dissociative ionisation of $[CH_3{}^{13}C{=}CH_2]^{+\bullet}$ precedes formation of a labelled neutral C_3 by one-electron vertical reduction in an $^+$NR$^+$ experiment.[59]

Since the $^-$NR$^+$ spectrum of $[CC^{13}C]^{-\bullet}$ gives no data concerning the possibility of carbon scrambling occurring during or subsequent to the vertical one-electron oxidation of the anion to the neutral, the next obvious experiment is to measure the $^-$NR$^-$ spectrum. Since the CID mass spectrum of $[CC^{13}C]^{-\bullet}$ shows no carbon scrambling in the anion, rearrangement of the carbon skeleton of the neutral $CC^{13}C$ should be readily identifiable in the $^-$NR$^-$ spectrum of $[CC^{13}C]^{-\bullet}$. Unfortunately, the fragment ions in the CID spectrum of $[CC^{13}C]^{-\bullet}$ are very weak (see earlier), and although a peak corresponding to the parent anion radical is observed in the $^-$NR$^-$ spectrum, no fragment anions were detected using the maximum sensitivity of the instrument.

The geometry of the neutral $^1\Sigma_g$ ground state of CCC has been calculated at the B3LYP/6-311G(d) level of theory. Results are recorded in Table 3, together with data obtained from previous studies. We obtain a value of 1.291 Å for the CC bond length; this should be compared with the experimental value of 1.297 Å,[30] and a 'best' theoretical value of 1.295 Å obtained previously.[45]

A theoretical study of the triplet C_3 neutral potential energy surface predicts the linear $^3\Pi_u$ state to be 226 kJ mol^{-1} higher in energy than the $^1\Sigma_g$ ground state,[48] which should be compared with an experimental value of 201 kJ mol^{-1}.[34] There is also a cyclic neutral of D_{3h} symmetry on the triplet potential energy surface.[41,46] At the CCSD(T)/aug-cc-pVTZ//B3LYP/6-311(d) level of theory, the energies of linear $^3\Pi_u$ and cyclic $^3A_1$ neutrals relative to the ground state singlet are 204 and 85 kJ mol^{-1} respectively (Table 3).

The degenerate rearrangement of neutral $^1\Sigma_g$ CCC *via* the $^1A_1$ cyclic transition state is calculated to require 104 kcal mol^{-1} (Table 3). This should be compared with the barrier of 157 kJ mol^{-1} on the triplet neutral surface for the conversion of the $^3\Pi_u$ state to the more stable $^3A_1$ (Table 3). Since we cannot control the energy of the $^-$NR$^+$ procedure, both the $^1\Sigma_g$ and $^3\Pi_u$ CCC neutrals could be accessible in the one-electron vertical oxidation from $[CCC]^{-\bullet}$.[60] In our previous studies of the carbon scrambling observed for singlet forms of neutral CCCC[27] and CCCCC,[28] the respective barriers for the scrambling processes were calculated to be 120 and 224 kJ mol^{-1} at the CCSD-(T)/aug-cc-pVDZ//B3LYP/6-31(d) level of theory, energies significantly higher than the Franck–Condon excess energies

Table 2 Cation geometries and energies[a,b]

	Linear	Cyclic	TS
State	$^2\Sigma_u$	$^2B_2$	$^2B_2$
Energy/Hartrees	−113.389070	−113.398386	−113.384757
Relative energy/kJ mol^{-1}	24 (12.5[c], 28[d], 17[e], 22[f])	0	36
Bond lengths/Å			
C_1C_2, C_2C_3	1.290 (1.318[c], 1.307[d], 1.283[e], 1.314[f])	1.316 (1.333[c], 1.324[d], 1.296[e], 1.331[f])	1.293
C_1C_3	2.580	1.446	2.333
Angles/°			
$C_1C_2C_3$	180.0	66.6 (67.2[c], 67.8[d], 71.0[e], 66.6[f])	128.9

[a] Geometries are optimised at the B3LYP/6-311G(d) level of theory. [b] Energies are calculated at the CCSD(T)/aug-cc-pVTZ//B3LYP/6-311G(d) level of theory. [c] QCISD(T)/6-311+G(2df)//QCISD(T)/6-31G(d).[44] [d] CCSD(T)/[5s4p3d2f1g]//CCSD(T)/[4s3p2d1f].[53] [e] CISD/TZ2P.[51] [f] CASSCF[5s3p2d1f].[54]

Table 3 Neutral geometries and energies[a,b]

	Singlet linear	Singlet TS	Triplet linear	Triplet cyclic	Triplet TS
State	$^1\Sigma_g$	$^1A_1$	$^3\Pi_u$	$^3A_1'$	$^3A'$
Energy/Hartrees	−113.830199	−113.797685	−113.752653	−113.797674	−113.692625
Relative energy/kJ mol^{-1}	0	104 (125[c])	204 ([204][d], 226[e], 197[f])	85 (102[c], 97[e])	361 (367[e])
Bond lengths/Å					
C_1C_2	1.291 ([1.297][g], 1.278[c], 1.311[e], 1.295[h], 1.310[i], 1.308[f])	1.260 (1.250[c])	1.294 ([1.298][d], 1.317[e], 1.311[f])	1.370 (1.346[c], 1.393[e])	1.376 (1.387[e])
C_2C_3	1.291	1.471 (1.461[c])	1.294	1.370	1.301 (1.335[e])
C_1C_3	2.582	1.471 (1.461[c])	2.588	1.370	2.146
Angles/°					
$C_1C_2C_3$	180.0	64.7 (64.7[c])	180.0	60.0 (60.0[c,e])	106.5 (103.2[e])

[a] Geometries are optimised at the B3LYP/6-311G(d) level of theory. [b] Energies are calculated at the CCSD(T)/aug-cc-pVTZ//B3LYP/6-311G(d) level of theory and include zero point energy correction [B3LYP/6-311G(d)]. [c] MP4SDTQ/6-31G(d)//HF/6-31G(d).[43] [d] Experimental value.[34] [e] MRD-CI/6-311+G(d)//CASSCF/6-31G(d).[48] [f] MRD-CI.[42] [g] Experimental value.[30] [h] CCSD(T) method (with 255 cGTOs and all electrons correlated).[45] [i] QCISD(T)/6-31G(d).[44]

imparted to those neutrals during the one-electron oxidation processes. Both of these barriers are greater than that required for the degenerate rearrangement of singlet CCC. It therefore seems likely that at least a proportion of the $CC^{13}C$ neutrals formed from $[CC^{13}C]^{-\bullet}$ will undergo the degenerate rearrangement (Table 3), with consequent randomisation of the carbons. Unfortunately we have no experimental probe to substantiate this proposal.

Conclusions

(i) The radical anion $[CC^{13}C]^{-\bullet}$ has been prepared by an unequivocal gas-phase synthesis, and this anion retains its skeletal integrity under the collision conditions necessary to effect one-electron vertical oxidation to the corresponding CCC neutral molecule.

(ii) The radical anion $[CC^{13}C]^{-\bullet}$ is converted by two-electron vertical oxidation to $[CC^{13}C]^{+\bullet}$ which requires an excess energy of only 11 kJ mol^{-1} to interconvert to the more stable [*cyclo*-$C_2{}^{13}C]^{+\bullet}$.

(iii) The radical anion $[CC^{13}C]^{-\bullet}$ is converted to neutral $CC^{13}C$ by Franck–Condon one-electron vertical oxidation. Theoretical calculations indicate that the neutral singlet requires an excess energy of 104 kJ mol^{-1} to effect a degenerate rearrangement through a cyclic $C_2{}^{13}C$ transition state; a process which essentially randomises the three carbon atoms. It is likely that some neutrals will equilibrate the carbons by this process, but no experimental probe was available to substantiate this proposal.

Experimental

A. Mass spectrometric methods

For a detailed description of the experiment and the instrument used see.[61] In brief, the experiments were performed using a four-sector modified ZAB/AMD 604 mass spectrometer with BEBE configuration, where B and E represent magnetic and electric sectors respectively. The $[CC^{13}C]^{-\bullet}$ radical anion was generated by chemical ionisation (CI) in the negative ion mode, with typical source conditions as follows: source temperature 200 °C, repeller voltage −0.5 V, ion extraction voltage 8 kV, mass resolution $m/\Delta m \geqslant 1500$. The precursor, 1,3-bis(trimethylsilyl)-1-^{13}C-prop-2-yne-1-*p*-tosylhydrazone, was placed in a small glass capillary tube which was then drawn out in a flame to create a very fine aperture, allowing for a slow steady release of sample vapour upon heating. The capillary was inserted into the CI source *via* the direct probe; the probe tip was heated to 60–80 °C to generate a background pressure of *ca.* 10^{-5} Torr inside the source housing. The $[CC^{13}C]^{-\bullet}$ radical anion was formed as suggested in Scheme 1, utilising a 1 : 1 mixture of H_2O and SF_6 as CI reagent gases [to liberate the reagent ions HO^- and F^- respectively—a modification[28] of the Squires bis $S_N2(Si)$ reaction with F^-/NF_3[56]] at a pressure of *ca.* 10^{-4} Torr inside the source housing.

Collisional induced dissociation (CID) of B(1) mass selected ions was effected in the second of the tandem collision cells positioned between B(1) and E(1). Helium was used as a target gas. The pressure of the collision gas in the 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.[62] Product ions resulting from CID were recorded by scanning E(1).

Neutralisation–reionisation[55] ($^-$NR$^+$ and $^-$NR$^-$) experiments were performed for B(1) mass-selected [CC^{13}C]$^{-\bullet}$ utilising the dual collision cells located between sectors B(1) and E(1). Neutralisation of the anions was achieved by collisional electron detachment using O_2 at 80% transmittance as collision gas, while reionisation to cations was achieved by collision of the neutrals with O_2, again at 80% transmittance.

Reionisation to anions was effected using xenon, at 80% transmittance. Any ions remaining after the first collision event were deflected from the primary neutral beam using an electrode maintained at a high voltage (1.0 kV) positioned before the second collision cell. In order to detect a reionisation signal due to the parent, the neutral species must be stable for approximately one microsecond. Charge reversal ($^-$CR$^+$) spectra[63] were recorded using single collision conditions in collision cell 1 (O_2, 80% transmission of main beam).

1,3-Bis(trimethylsilyl)-1-^{13}C-prop-2-yne-1-*p*-tosylhydrazone was prepared by a known procedure (^{13}C = 99.5%).[64,65]

B. Theoretical methods

Geometry optimisations were carried out with the Becke 3LYP method[66,67] using the 6-311G(d) basis set within the GAUSSIAN 98 suite of programs.[68] 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. Some problems have been highlighted in the literature regarding the use of the B3LYP method for the accurate prediction of molecular energies for carbon clusters,[69] even though the method continues to be used with success.[70,71] † More accurate energies for the B3LYP geometries were determined using the CCSD(T) method[72] together with the Dunning aug-cc-pVTZ basis set.[73] The CCSD(T)/aug-cc-pVTZ//B3LYP/6-311G(d) approach used in this study computes the adiabatic electron affinity of linear C_3 to be 1.945 eV in good agreement with the experimentally measured value of 1.981 eV.[37] All calculations were carried out on the Alpha Server at the Australian Partnership for Advanced Computing (APAC) National Facility (Canberra).

Acknowledgements

This project was supported by an international linkage grant funded jointly by the Australian Research Council, the Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie. A.M.McA. acknowledges the award of an APRA PhD scholarship. We thank the Australian Partnership for Advanced Computing (APAC) National Facility (Canberra) for a generous allowance of super computer time.

References

1 W. Weltner and R. J. Van Zee, *Chem. Rev.*, 1989, **89**, 1713 and references cited therein.
2 A. Van Orden and R. J. Saykally, *Chem. Rev.*, 1998, **98**, 2313 and references cited therein.
3 P. F. Bernath, K. H. Hinkle and J. J. Keady, *Science*, 1989, **244**, 562.
4 P. Ehrenfreund and B. H. Foing, *Astron. Astrophys.*, 1996, **307**, L25.
5 B. P. A. Bettens and E. Herbst, *Astrophys. J.*, 1997, **478**, 545.
6 H. W. Kroto and K. McKay, *Nature*, 1988, **332**, 328.
7 R. Levi Guyer and D. E. Koshland, *Science*, 1990, **250**, 1640.
8 G. von Helden, P. R. Kemper, N. G. Gotts and M. T. Bowers, *Science*, 1993, **259**, 1300.
9 G. von Helden, N. G. Gotts and M. T. Bowers, *Nature*, 1993, **363**, 60.
10 R. F. Baddour and R. S. Timmins (Eds.), *The Application of Plasmas to Chemical Processing*, MIT Press, Cambridge, MA, 1967.
11 J. M. Jones, R. P. Malcolm, K. M. Thomas and S. H. Botrell, *Carbon*, 1996, **34**, 231.
12 H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl and R. E. Smalley, *Nature*, 1985, **318**, 162.
13 (*a*) I. Cermac, M. Förderer, I. Cermakova, S. Kalhofer, H. Stopkaebeler, G. Monninger and W. Krätschmer, *J. Chem. Phys.*, 1998, **108**, 10129; (*b*) G. Monninger, M. Förderer, P. Gürtler, S. Kalhofer, S. Petersen, L. Nemes, P. G. Szalay and W. Krätscher, *J. Phys. Chem. A*, 2002, **106**, 5779.
14 W. Weltner and R. J. Van Zee, *Chem. Rev.*, 1989, **89**, 1713.
15 A. N. Raghavachari, *J. Chem. Phys.*, 1990, **93**, 2099.
16 L. Adamowicz, *Chem. Phys. Lett.*, 1991, **182**, 45.
17 J. D. Watts and R. J. Bartlett, *J. Chem. Phys.*, 1992, **97**, 3445.
18 (*a*) R. H. Kranz and W. R. M. Graham, *J. Chem. Phys.*, 1992, **96**, 2517; (*b*) R. H. Kranz and W. R. M. Graham, *J. Chem. Phys.*, 1993, **98**, 71; (*c*) R. H. Kranz, C. M. L. Rittby and W. R. M. Graham, *J. Chem. Phys.*, 1995, **103**, 6841; (*d*) R. H. Kranz, C. M. L. Rittby and W. R. M. Graham, *J. Chem. Phys.*, 1996, **105**, 5313.
19 J. Sun, H.-F. Grutzmacher and C. Lifshitz, *J. Am. Chem. Soc.*, 1993, **115**, 8382 and references cited therein.
20 (*a*) J. R. Heath and R. J. Saykally, *On Clusters and Clustering*; P. J. Reynolds, Ed.; Elsevier, Amsterdam, 1993, p. 7; (*b*) A. V. Orden and R. J. Saykally, *Chem. Rev.*, 1998, **98**, 2313.
21 S. Schmatz and P. Botschwina, *Chem. Phys. Lett.*, 1995, **235**, 8; S. Schmatz and P. Botschwina, *Chem. Phys. Lett.*, 1995, **235**, 136.
22 W. Weltner, R. J. Van Zee and S. Li, *J. Phys. Chem.*, 1995, **99**, 6277.
23 S. Schmatz and P. Botschwina, *Int. J. Mass Spectrom. Ion Processes*, 1995, **149/150**, 621.
24 (*a*) Y. Zhao, E. deBeer, C. Xu, T. Taylor and D. M. Neumark, *J. Chem. Phys.*, 1996, **105**, 4905; (*b*) Y. Zhao, E. deBeer and D. M. Neumark, *J. Chem. Phys.*, 1996, **105**, 2575.
25 J. P. Maier, *Chem. Soc. Rev.*, 1997, **26**, 21.
26 S. J. Blanksby and J. H. Bowie, *Mass Spectrom. Rev.*, 1999, **18**, 131.
27 S. J. Blanksby, D. Schröder, S. Dua, J. H. Bowie and H. Schwarz, *J. Am. Chem. Soc.*, 2000, **122**, 7105.
28 S. Dua and J. H. Bowie, *J. Phys. Chem. A*, 2002, **106**, 1374.
29 P. Swings, *Rev. Mod. Phys.*, 1942, **12**, 190.
30 K. W. Hinkle, J. J. Keady and P. F. Bernath, *Science*, 1988, **241**, 1319.
31 T. F. Giesen, A. O. Van Orden, J. D. Cruzan, R. A. Provencal, R. J. Saykally, R. Gendriesch, F. Lewen and G. Winnewisser, *Astrophys. J.*, 2001, **551**, L181.
32 J. P. Maier, N. M. Lakin, G. A. H. Walker and D. A. Bohlender, *Astrophys. J.*, 2001, **553**, 267.
33 R. H. Barger and H. P. Broida, *J. Chem. Phys.*, 1962, **37**, 1152.
34 H. Sasada, T. Amano, C. Jarman and P. F. Bernath, *J. Chem. Phys.*, 1991, **94**, 2401 and references cited therein.
35 M. L. Lesieki, H. W. Hicks, A. Orenstein and W. A. Guillory, *Chem. Phys. Lett.*, 1980, **71**, 72.
36 J. Szczepanski, C. Wehlburg and M. Vala, *J. Phys. Chem. A*, 1997, **101**, 7039.
37 J. M. Oakes and G. B. Ellison, *Tetrahedron*, 1986, **42**, 6263.
38 C. A. Schumuttermaer, R. C. Cohen, N. Pugliano, J. R. Heath, A. L. Cooksy, K. L. Busarow and R. J. Saykally, *Science*, 1990, **249**, 897.
39 M. E. Geusic, T. J. McIlrath, M. F. Jarrold, L. A. Bloomfield, R. R. Freeman and W. L. Brown, *J. Chem. Phys.*, 1986, **84**, 2421.
40 J. Baker, S. K. Bramble and P. A. Hamilton, *J. Mol. Spectrosc.*, 1997, **101**, 7039.
41 J. J. Gaumet, A. Wakisaka, Y. Shimizu and Y. Tamori, *J. Chem. Soc., Faraday Trans.*, 1993, **89**, 1667.
42 J. Peric-Radic, J. Roemelt, S. D. Peyerimhoff and R. J. Buenker, *Chem. Phys. Lett.*, 1977, **50**, 344.
43 R. A. Whiteside, R. Krishnan, M. J. Frisch, J. A. Pople and P. v. R. Schleyer, *Chem. Phys. Lett.*, 1981, **80**, 547.
44 K. Raghavachari, *Chem. Phys. Lett.*, 1990, **171**, 249.

---

† A reviewer has asked that we make a statement concerning "the bias possibly introduced by the selected type of calculation in the relative energies of linear *versus* cyclic forms." Plattner and Houk[69] have investigated large cyclic carbon systems and found density functional theory to incorrectly favour allenic structures over polyacetylenic structures by about 25 kJ mol^{-1} per C≡C–C to C=C=C transformation. This is also true for smaller systems,[69] for example B3LYP/6-31G(d) favours allene to prop-1-yne, reversing their order of stability by 19 kJ mol^{-1}. We do not know if there is a bias towards linear over cyclic cumulenic systems of the type we are considering, because the experimental data are not available. However, we believe this perceived problem is circumvented using the CCSD(T) method together with the Dunning aug-cc-pVTZ basis set as outlined below.

45 M. Mladenovic, S. Schmatz and P. Botschwina, *J. Chem. Phys.*, 1994, **101**, 5891.

46 J. M. L. Martin and P. R. Taylor, *J. Phys. Chem.*, 1996, **100**, 6047.

47 J. Szczepanski, S. Ekern and M. Vala, *J. Phys. Chem. A*, 1997, **101**, 1841.

48 H. Fueno and Y. Taniguchi, *Chem. Phys. Lett.*, 1999, **312**, 65.

49 E. E. Pasqualini and M. Lopez, *Chem. Phys. Lett.*, 2000, **320**, 415.

50 C. Leonard, D. Panten, N. M. Lakin, G. Chambaud and P. Rosmus, *Chem. Phys. Lett.*, 2001, **335**, 97.

51 R. S. Grev, I. L. Alberts and H. F. Schaefer, *J. Phys. Chem.*, 1990, **94**, 3379, 8744.

52 J. D. Watts, J. F. Stanton, J. Gauss and R. L. Bartlett, *J. Chem. Phys.*, 1991, **94**, 4320.

53 G. E. Scuseria, *Chem. Phys. Lett.*, 1991, **176**, 27.

54 (*a*) P. R. Taylor, J. M. L. Martin, J. P. Francois and B. Gijbels, *J. Phys. Chem.*, 1991, **95**, 6530; (*b*) P. R. Taylor, *J. Phys. Chem.*, 1991, **95**, 6534.

55 (*a*) C. Wesdemiotis and F. W. McLafferty, *Chem. Rev.*, 1987, **87**, 485; (*b*) D. V. Zagorevskii and J. L. Holmes, *Mass Spectrom. Rev.*, 1994, **13**, 133; (*c*) N. Goldberg and H. Schwarz, *Acc. Chem. Res.*, 1994, **27**, 347; (*d*) For more recent reviews, including NR nomenclature, see C. A. Schalley, G. Hornung, D. Schröder and H. Schwarz, *Chem. Soc. Rev.*, 1998, **27**, 91; (*e*) D. V. Zagorevskii and J. L. Holmes, *Mass Spectrom. Rev.*, 1999, **18**, 87.

56 P. G. Wenthold, J. Hu and R. R. Squires, *J. Am. Chem. Soc.*, 1994, **116**, 6961.

57 Y. Z. An, Y. Rubin, C. Schaller and S. W. McElvany, *J. Org. Chem.*, 1994, **59**, 2927.

58 http://webbook.nist.gov/ – $C_3^{-\bullet}$, 638; C_3, 820; $C_2^{-\bullet}$, 525; C_2, 838; C, 717 kJ mol^{-1}. In addition, EA C_2, 3.273 ± 0.008 eV[46] and C, 1.262 eV[57].

59 A. Fura, F. Turecek and F. W. McLafferty, *Int. J. Mass Spectrom.*, 2002, **217**, 81.

60 D. W. Arnold, S. E. Bradforth, T. N. Kitsopoulos and D. M. Neumark, *J. Chem. Phys.*, 1991, **95**, 8753.

61 C. A. Schalley, G. Hornung, D. Schröder and H. Schwarz, *Chem. Soc. Rev.*, 1998, **27**, 91.

62 J. L. Holmes, *Org. Mass Spectrom.*, 1985, **20**, 169.

63 (*a*) J. H. Bowie and T. Blumenthal, *J. Am. Chem. Soc.*, 1975, **97**, 2959; (*b*) J. E. Szulejko, J. H. Bowie, I. Howe and J. H. Beynon, *Int. J. Mass Spectrom. Ion Phys.*, 1980, **13**, 76; (*c*) M. M. Bursey, *Mass Spectrom. Rev.*, 1990, **9**, 555.

64 W. E. Billups and M. M. Haley, *J. Am. Chem. Soc.*, 1991, **113**, 5084.

65 K. J. H. Kruithof, R. F. Schmitz and G. W. Klumpp, *Tetrahedron*, 1983, **39**, 3073.

66 A. D. Becke, *J. Phys. Chem.*, 1993, **98**, 5648.

67 P. J. Stevens, F. J. Devlin, C. F. Chablowski and M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623.

68 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tamasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adama, S. Clifford, J. Ochterski, B. Morokuma, D. K. Malich, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Latham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle and J. A. Pople, GAUSSIAN 98, Gaussian, Inc.; Pittsburgh, PA, 1998.

69 D. A. Plattner and K. N. Houk, *J. Am. Chem. Soc.*, 1995, **117**, 4405 and references cited therein.

70 (*a*) J. M. L. Martin, J. El-Yazal and J.-P. François, *Chem. Phys. Lett.*, 1995, **242**, 570; (*b*) J. M. L. Martin, J. El-Yazal and J.-P. François, *Chem. Phys. Lett.*, 1996, **252**, 9; (*c*) J. M. L. Martin and P. R. Taylor, *J. Phys. Chem.*, 1996, **100**, 6047.

71 E. E. Pasqualini and M. López, *Chem. Phys. Lett.*, 2000, **320**, 415.

72 (*a*) J. Cizek, *Adv. Chem. Phys.*, 1969, **14**, 35; (*b*) K. Raghavachari, G. W. Trucks, J. A. Pople and M. Head-Gordon, *Chem. Phys. Lett.*, 1989, **157**, 479; (*c*) M. J. O. Deegan and P. J. Knowles, *Chem. Phys. Lett.*, 1994, **227**, 321 and references cited therein.

73 (*a*) T. H. Dunning, *J. Chem. Phys.*, 1989, **90**, 1007; (*b*) D. E. Woon and T. H. Dunning, *J. Chem. Phys.*, 1993, **98**, 1358.