The synthesis and structure of the symmetrical isomer of C_5H^-

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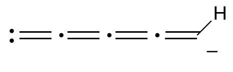
The ion $(C_2CHC_2)^-$ is formed in the gas phase by the process $^{-}C{\equiv}C{-}CH(OCOR){-}C{\equiv}CD \rightarrow (C_2CHC_2)^- + (\text{'}RDCO_2\text{'})$ [R = H, Me or Et]; the ground state structure is a singlet, with C_{2v} symmetry.

Unusual organic molecules have been detected in circumstellar gas and dust envelopes which surround red giant stars.[1] These include C_3, C_5 and the hydrocarbons C_nH (n = 2–6), which have been identified around the bright carbon-rich star IRC + 10216.[1–3] The high electron affinities of these neutrals suggest the possibility that the corresponding anions may co-occur with the neutrals in circumstellar envelopes,[4,5] and it is of interest in this context that negative ions are present in the coma of comet Halley.[6] We have reported the syntheses of C_3H^-,[7] $C_5^{-\cdot}$,[8] and linear $C_5H^{-\cdot}$[8] (and their conversion through the appropriate neutral to decomposing positive ions) in the ion source of a VG ZAB 2HF mass spectrometer. *Ab initio* calculations [at CISD/6-311G (d,p) level] indicate that linear C_5H^- has both singlet and triplet states, with triplet **1** being the ground state, and that the corresponding neutral has an electron affinity of 2.4 eV.[8]



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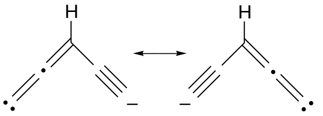

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Ab initio calculations [GAUSSIAN 94[9] at CISD/6-311G (d,p) level] indicate further that (i) there is a stable symmetrical isomer $C_2CHC_2^-$, and that this isomer (like linear C_5H^-) also has stable singlet and triplet forms, and (ii) there is no energy and stable species C_3CHC^-. *Ab initio* data for $C_2CHC_2^-$ are summarised in Tables 1 and 2. In this case the singlet is significantly more stable than the triplet. The geometry of the central carbon of the ground-state singlet approximates to trigonal planar (the C_2–C_3–C_4 angle is close to 130°), and the C_1–C_2 and C_2–C_3 bonds have significant triple and double bond character respectively (see Table 2). The structure is depicted (in valence bond form) as **2**. Isomer **2** is less stable than isomer **1** by 170 kJ mol^{-1} at the level of theory indicated. The electron affinity of the neutral corresponding to **2** is calculated to be 4.2 eV.

Table 1 *Ab initio* calculations for $C_2CHC_2^{-\,a}$

State	Singlet	Triplet
Symmetry	C_{2v}	C_{2v}
HF/6-311G (d,p)	−189.74150	−189.67132
Zero point vibrational energy	0.03188	0.02767
Total thermal energy	0.03685	0.03282
CISD/6-311G (d,p)	−190.286804	−190.20186

[a] *Ab initio* optimization used the Berny procedure (ref. 12) at HF/6-311G (d,p), GAUSSIAN 94 (ref. 9). The correctness of the geometries was confirmed by the lack of negative analytical computed harmonic vibration frequencies. The post Hartree–Fock energies (CISD) were calculated at the Hartree–Fock geometries. All energies are recorded in hartrees.

We initially attempted to form the elusive **2** in the ion source of the VG 2HF mass spectrometer by a number of methods related to that shown in eqn. (1):

$$^{-}(C{\equiv}C){-}CH(OMe){-}C{\equiv}CD \rightarrow [(:C{=}C{=}CH{-}C{\equiv}CD)\ ^{-}OMe] \rightarrow C_5D^- + MeOH \qquad (1)$$

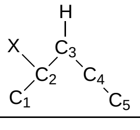
$$^{-}(C{\equiv}C){-}CH(OCOR){-}C{\equiv}CD \rightarrow (C_2CHC_2)^- + [RCDO_2] \qquad (2)$$

$$^{-}(C{\equiv}C){-}CD(OCOR){-}C{\equiv}CH \rightarrow (C_2CDC_2)^- + [RCHO_2] \qquad (3)$$

unfortunately, the base deprotonates exclusively at the central position to yield linear C_5D^- (*cf.* **1**) rather than remove D^+ to form $C_2CHC_2^-$. However the energised precursor anions shown in eqns (2) and (3) (R = H, Me, Et) [formed by the reaction of HO^- with $DC{\equiv}C{-}CH(OCOR){-}C{\equiv}CD$ and $HC{\equiv}C{-}CD(OCOR){-}C{\equiv}CH$] decompose to yield $(C_2CHC_2)^-$ and $(C_2CDC_2)^-$ respectively and exclusively. We are not sure whether this process involves incipient R^- deprotonating at the terminal position (to yield CO_2 and RH as neutral products) or whether the acetylenic H transfers to oxygen to yield RCO_2H as the neutral products.

When source formed $(C_2CHC_2)^-$ ions are fired through a collision cell containing Ar (at 2×10^{-7} Torr; 1 Torr = *ca.* 133 Pa) the resultant tandem negative ion mass spectrum exhibits only loss of $H^\cdot$ to form $C_5^{-\cdot}$ (*cf.* ref. 8). Under the same experimental conditions, charge stripping of $(C_2CHC_2)^-$ ions yields energised parent cations C_5H^+, whose resultant spectrum [the charge reversal spectrum[10,11] of $(C_2CHC_2)^-$] is *m/z* (composition relative abundance) 61 (C_5H^+, 35), 60 ($C_5^{+\cdot}$, 100), 49 (C_4H^+, 77), 48 ($C_4^{+\cdot}$, 62), 37 (C_3H^+, 81), 36 ($C_3^{+\cdot}$, 69), 25 (C_2H^+, 4), 24 ($C_2^{+\cdot}$, 21), 12 ($C^{+\cdot}$, 0.2). Although this spectrum shows the same peaks as those observed in the corresponding spectrum of isomer **1** (*cf.* ref. 8), the peak abundances in the two spectra are significantly and reproducibly different. In particular, the abundances of *m/z* 61 (C_5H^+) and 60 ($C_5^{+\cdot}$) are 35 and 100 for **2**, and 100 and 76 for **1**. Since the two charge reversal spectra are different, we conclude that isomers **1** and **2** are stable. However, the data cannot exclude the possibility of

Table 2 Bond lengths and angles for $C_2CHC_2^-$ taken from *ab initio* calculations



	Singlet	Triplet
Bond length/Å		
C_1–C_2	1.2425	1.2746
C_2–C_3	1.3679	1.3636
C_3–H	1.0843	1.1048
Bond angle (°)		
C_1–C_2–X	85.3	80.0
X–C_2–C_3	90.0	90.0
C_2–C_3–H	115.3	107.2

minor interconversion of **2** to **1** under the experimental conditions.

The neutral analogue of **1** has already been detected in the interstellar environment:[1–3] it would be of interest to search for anions **1**, **2** and the neutral corresponding to **2**.

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Footnote and References

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