

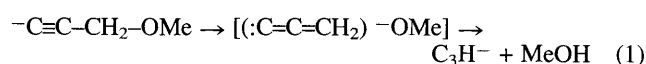
The Synthesis and Structures of C_5H^- and C_5^{--}

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The ion C_5H^- is formed in the gas phase by the process $-(C\equiv C)_2CH_2OMe \rightarrow C_5H^- + MeOH$; *ab initio* calculations indicate a ground state triplet structure with a near linear carbon skeleton, but with the terminal H at a marked angle to the carbon backbone.

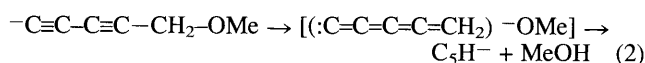
Unusual organic molecules have been detected in circumstellar gas and dust envelopes which surround red giant stars.¹ These include C_3 , C_5 and the hydrocarbons C_nH ($n = 2-6$), which have been identified around the bright carbon-rich star IRC + 10216.¹⁻³ It is proposed that such neutrals are formed following photoionisation of acetylene, but the reaction sequences are not known.³ We are interested in synthesising anions corresponding to these neutrals and in investigating their structures and reactivities. We have already prepared C_3H^- in the gas phase by the collision induced process shown in eqn. (1). *Ab initio*



calculations indicate that C_3H^- has a ground state triplet diradical structure with allenic type geometry: the two unpaired electrons occupy the two lowest antibonding and orthogonal π -orbitals which extend along the carbon chain, with most of the electron density being concentrated on the carbon which bears hydrogen.⁴

The linear C_5H^- ion has been synthesised by a similar and unambiguous route. Reaction of $DC\equiv C-C\equiv CCH_2OMe$ with NH_2^- in the chemical ionization source of a VG ZAB 2HF reverse-sector mass spectrometer yields an (M - D)⁻ anion exclusively. A proportion of these parent anions have sufficient energy to undergo loss of MeOH to form an abundant C_5H^-

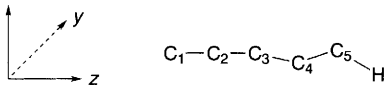
species as the major decomposition product. The reaction is summarised in eqn. (2).



When source-formed C_5H^- ions are fired through a collision cell (situated between the magnetic and electric sectors) containing He [at a pressure of 2×10^{-7} Torr (1 Torr is ca. 133 Pa)], the resultant negative-ion tandem mass spectrum (CID MS/MS) exhibits only loss of H⁺, *i.e.* $C_5H^- \rightarrow C_5^{--} + H^+$. Under precisely the same experimental conditions, collisional activation of C_5H^- also effects charge stripping to form C_5H^+ . Some of the resulting parent C_5H^+ ions have excess energy and undergo decomposition: the resultant spectrum is called a charge reversal mass spectrum [CR MS/MS (for descriptions of the technique, see refs. 5, 6)]. The CR MS/MS data for C_5H^- are [m/z (composition) relative abundance]: $61(C_5H^+)100$, $60(C_5^{++})76$, $49(C_4H^+)27$, $48(C_4^{++})28$, $37(C_3H^+)27$, $36(C_3^{++})33$, $25(C_2H^+)1$, $24(C_2^{++})3$, $13(CH^+)0.5$, $12(C^+)1$. This spectrum is quite characteristic, with C_5H^+ forming the major peak, together with less abundant peaks corresponding to the fragment cations C_n^{++} ($n = 1-5$) and C_nH^+ ($n = 1-4$).

We have carried out *ab initio* calculations using GAUSSIAN 92⁷ on C_5H^- and its decomposition product C_5^{--} : these data are

Table 1 *Ab initio* calculations for C_5H^- and C_5^{--a}

					
C_5H^-					
Bond/Å	triplet	singlet	Angle/°	triplet	singlet
C ₁ -C ₂	1.2854	1.2461	C ₁ -C ₂ -C ₃ (yz) ^b	180.0	180.0
C ₂ -C ₃	1.3095	1.3308	C ₁ -C ₂ -C ₃ (xz) ^c	180.0	180.0
C ₃ -C ₄	1.3003	1.2492	C ₂ -C ₃ -C ₄ (yz)	177.4	178.5
C ₄ -C ₅	1.2912	1.3236	C ₂ -C ₃ -C ₄ (xz)	180.0	180.0
C ₅ -H	1.0615	1.0945	C ₃ -C ₄ -C ₅ (yz)	173.2	175.7
			C ₃ -C ₄ -C ₅ (xz)	178.7	179.5
			C ₄ -C ₅ -H(yz)	150.2	110.6
			C ₄ -C ₅ -H(xz)	185.7	190.7
			triplet	singlet	
			C ₁ symmetry	C ₁ symmetry	
	HF/6-311G**		-189.77870 ^d	-189.72855	
	Zero-point vibrational energy		0.02633	0.02853	
	Total thermal energy (298.15 K)		0.032080	0.033860	
	CISD/6-311G**		-190.28989	-190.273615	
C_5^{--}					
C ₁ -C ₂ -C ₃ -C ₄ -C ₅					
Bond/Å					
C ₁ -C ₂	1.2765	$D_{\infty h}$ symmetry			
C ₂ -C ₃	1.2950	HF/6-311G**		-189.15323	
C ₃ -C ₄	1.2765	Zero-point vibrational energy		0.01901	
C ₄ -C ₅	1.2950	Total thermal energy (298.15 K)		0.02306	
		CISD/6-311G**		-189.66782	

^a *Ab initio* optimization used the Berny procedure at HF6-311G**, GAUSSIAN 92.⁷ 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. ^b This is the angle in the plane of the page. ^c This is the angle in the plane perpendicular to the page. ^d All energies in hartrees.

collected in Table 1. There are triplet and singlet forms of C_5H^- with the ground state corresponding to the triplet state [53 kJ mol^{-1} lower in energy than the singlet (CISD level, zero-point energy corrected and at 298.15 K)]. The energy necessary to remove an electron from triplet C_5H^- (*i.e.* the electron affinity of C_5H) is calculated as 229 kJ mol^{-1} . The atomic linkages are similar in both triplet and singlet states with the carbon atoms forming a near to linear chain, but with the hydrogen being at a marked angle to the carbon skeleton. The triplet state is characterised by small differences in carbon-carbon distances along the chain [1.27–1.30 Å (these distances are similar to those reported⁸ for CH_2CCH_2 and $OCCCCO$)]. In valence bond terms the geometry approximates to $[C=C=C=C=CH]^-$: in MO terms, there are two unpaired electrons occupying the two lowest and mutually orthogonal antibonding π orbitals along the length of the carbon chain. Thus, the ground state structures of C_3H^- and C_5H^- are comparable. In contrast, the singlet state of C_5H^- is marked by alternation of carbon-carbon distances [1.25 and 1.33 Å ($C\equiv C$ distance in $Me(C\equiv C)_2H$ is 1.212 Å⁸)], suggesting that there is partial di-yne character, *i.e.* $(C\equiv C-C\equiv C-CH)^-$. Finally, *ab initio* calculations indicate that the ground doublet state of the odd-electron species C_5^- is $:C=C=C=C=C\dot{C}:^-$.

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