The syntheses of $C_6CH_2^{\bullet-}$ and the corresponding carbenoid cumulene C_6CH_2 in the gas phase

Suresh Dua, Stephen J. Blanksby and John H. Bowie†

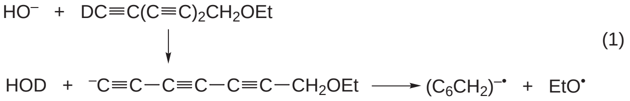
Department of Chemistry, The University of Adelaide, South Australia, 5005, Australia

The ion $(C_6CH_2)^{\bullet-}$ is formed in the gas phase by the process $–C≡C–C≡C–C≡C–CH_2OEt \rightarrow (C_6CH_2)^{\bullet-} + EtO^{\bullet}$, and charge stripping of the product radical anion yields the carbenoid neutral C_6CH_2; this can be either a singlet (the ground state), which is best represented as the carbene :C=C=C=C=C=C=CH$_2$, or a triplet; the adiabatic electron affinity and the dipole moment of the carbenoid neutral are calculated to be 2.82 eV and 7.33 D respectively.

Small cumulenes have been detected in circumstellar gas and dust envelopes which surround red giant stars, in particular, the bright carbon-rich star IRC-10216.[1–3] These include C_n (n = 3 and 5), C_nH (n = 2–8) and C_nH_2 (n = 2–4 and 6), with neutrals where n is even generally being more abundant than those where n is odd.[1–5] The high electron affinities of these neutrals suggests the possibility that the corresponding anions may co-occur with the neutrals in circumstellar envelopes.[6–8] We have reported the syntheses of a number of these anions in the source of a VG ZAB 2HF mass spectrometer [*e.g.* C_5H^{-} [8] and three isomers of $C_5H_2^{\bullet-}$ [9]] and have used collision-induced charge stripping of the anions to effect the syntheses of the appropriate neutrals.[9] Both C_5CH_2 and C_6CH have already been detected in circumstellar envelopes,[3] and it has been suggested that C_6CH_2 should also be present,[10] and that it should be an excellent candidate for detection because of its large dipole moment [calculated to be 7.33 D (Table 1)].[5] The proposed pathways *via* which such hydrocarbons can form in the interstellar environment have been reviewed.[11]

We describe the synthesis and structures of both $(C_6CH_2)^{\bullet-}$ and the corresponding carbenoid cumulene neutral.

The radical anion of C_6CH_2 was synthesised in the source of the ZAB 2HF mass spectrometer as summarised in sequence (1). The reaction between HO^- and DC_6CH_2OEt‡ yields the



$$\begin{array}{l} HO^- + DC{\equiv}C(C{\equiv}C)_2CH_2OEt \\ \quad\downarrow \\ HOD + {}^-C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}CH_2OEt \longrightarrow (C_6CH_2)^{-\bullet} + EtO^{\bullet} \end{array} \qquad (1)$$

anion $^-C_6CH_2OEt$ which undergoes facile loss of EtO· to yield $(C_6CH_2)^{\bullet-}$. Source formed $(C_6CH_2)^{\bullet-}$ ions are then fired through a collision cell containing O_2 (at 2×10^{-7} Torr; 1 Torr = *ca.* 133 Pa) to produce a beam of neutral C_6CH_2 which then proceeds into a second collison containing O_2 (at 2×10^{-7} Torr) which effects ionisation of the neutral to form a decomposing C_6CH_2 radical cation. The resultant neutralisation reionisation spectrum of $(C_6CH_2)^{\bullet-}$ ($^-NR^+$)[16] is shown in Fig. 1. The observation of a pronounced recovery signal (at m/z 86) in the spectrum indicates that the neutral has a lifetime of at least 10^{-6} s, and the similarities between the $^-NR^+$ spectrum and the corresponding charge reversal (CR) spectrum of $C_6CH_2^{\bullet-}$ (listed in the caption to Fig. 1) suggests that the neutral formed has the same connectivity as the radical anion.[17]

Ab initio calculations for both the neutral and radical anion were carried out at the RCCSD(T)/aug-cc-VDZ//B3LYP/6-31G* level of theory using GAUSSIAN94[19] and MOLPRO 96.4.[20] Details are summarised in Table 1. The radical anion and both the singlet and triplet neutrals are best represented as

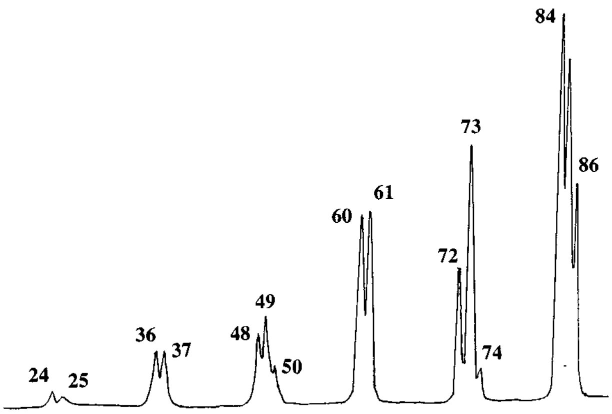
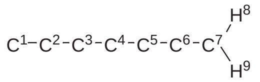


Fig. 1 Neutralisation reionisation ($^-NR^+$) mass spectrum of $C_6CH_2^{\bullet-}$. VG ZAB 2HF mass spectrometer. O_2 in both collision cells (measured pressure outside cells = 2×10^{-7} Torr). CR spectrum of $C_6CH_2^{\bullet-}$ (O_2 in the first collision cell, measured pressure outside cell -2×10^{-7} Torr) as follows [m/z (relative abundance)]: 86(49%), 85(88), 84(100), 74(4), 73(57), 72(13), 62(3), 61(43), 60(29), 50(3), 49(19), 48(9), 37(15), 36(9), 25(1), 24(0.5).

Table 1 *Ab initio* calculations for anions and neutrals



	Anion	Neutral (singlet)	Neutral (triplet)
State	($^2B_1$)	($^1A_1$)	($^3A_2$)
Symmetry	C_{2v}	C_{2v}	C_{2v}
Energy (hartrees)[a]	−266.969928	−266.866186	−266.833462
Rel. energy (kJ mol^{-1})	0	272	358
Adiabatic electron affinity (eV)		2.82	
Dipole moment (Debye)	8.10	7.33	6.40
Bond length (Å)[b]			
C^1C^2	1.272	1.289	1.301
C^2C^3	1.334	1.301	1.301
C^3C^4	1.256	1.270	1.274
C^4C^5	1.323	1.293	1.297
C^5C^6	1.261	1.271	1.272
C^6C^7	1.345	1.320	1.329
C^7H^8	1.090	1.090	1.089
C^7H^9	1.090	1.090	1.089
Bond angles (°)[b]			
$C^1C^2C^3$[c]	180.0	180.0	180.0
$C^6C^7H^8$	121.98	121.61	121.16
$C^6H^7H^9$	121.98	121.61	121.16
$H^8C^7H^9$	116.04	116.78	117.67
$C^6C^7H^8H^9$	180.0	180.0	180.0

[a] RCCSD(T)/aug-cc-p VDZ level of theory including zero point vibrational energy [calculated from vibrational frequencies at the B3LYP/6-31G* level of theory, and scaled by 0.9804 (ref. 18)]. [b] B3LYP/6-31G* level of theory. [c] All other angles along the carbon skeleton are also 180.0°.

simple linear cumulenes. The ground state of neutral C_6CH_2 corresponds to the singlet carbenoid cumulene :C=C=C=C=C=C=CH_2 (*cf.* ref. 21) which has a calculated dipole moment of 7.33 D. The adiabatic electron affinity of this neutral is estimated to be 2.82 eV; thus we propose that $C_6CH_2^{\bullet-}$ as well as the corresponding neutral may be present in the circumstellar environment.

Notes and References

† E-mail: jbowie@chemistry.adelaide.edu.au

‡ 1-Ethoxy-7-deuteriohepta-2,4,6-triyne was formed by desilyation of the corresponding trimethylsilyl triyne with MeOD/DO^- (*cf.* ref. 12). The trimethylsilyl triyne was prepared by coupling between TMS–C≡C–C≡C–Li (ref. 13) and Br–C≡C–CH_2OEt (ref. 14) using CuBr as catalyst (ref. 15).

1 H. Olofsson, in *Molecules in the Stellar Environment, Lecture Notes in Physics*, ed. O. G. Jorgenson, Springer, Heidelberg, 1994, pp. 114–133, and refs. cited therein.

2 P. F. Bernath, K. H. Hinkle and J. J. Keady, *Science*, 1989, **244**, 562; K. H. Hinkle, in *Molecules in the Stellar Environment, Lecture Notes in Physics*, ed. O. G. Jorgensen, Springer, Heidelberg, 1994, pp. 99–114, and refs. cited therein.

3 A. Omont, in *Molecules in the Stellar Environment, Lecture Notes in Physics*, ed. O. G. Jorgenson, Springer, Heidelberg, 1994, pp. 135–138, and refs. cited therein.

4 M. J. Travers, M. C. McCarthy, C. A. Gottlieb and P. Thaddeus, *Astrophys. J.*, 1996, **465**, L77.

5 Cited as unpublished work in, M. C. McCarthy, M. J. Travers, A. Korvacs, W. Chen, S. E. Novick, C. A. Gottlieb and P. Thaddeus, *Science*, 1997, **275**, 518.

6 J. Natterer, W. Koch, D. Schröder, N. Goldberg and H. Schwarz, *Chem. Phys. Lett.*, 1994, **229**, 429.

7 S. Petrie, *Mon. Not. R. Astron. Soc.*, 1996, **281**, 137.

8 S. J. Blanksby, S. Dua, J. H. Bowie and J. C. Sheldon, *Chem. Commun.*, 1997, 1833.

9 S. J. Blanksby, S. Dua, J. H. Bowie, D. Schröder and H. Schwarz, submitted for publication in *J. Phys. Chem.*

10 M. C. McCarthy, M. J. Travers, C. A. Gottlieb and P. Thaddeus, *Astrophys. J.*, 1997, **483**, L139.

11 D. Smith and P. Spanel, *Mass Spectrom. Rev.*, 1995, **14**, 255.

12 B. N. Ghose, *Synth. React. Inorg. Metal-Org. Chem.*, 1994, **24**, 29.

13 A. B. Holmes, C. L. D. Jennings-White, A. H. Shulthess, B. Akinde and D. R. M. Walton, *J. Chem. Soc., Chem. Commun.*, 1979, 840.

14 C. Cai and A. Vasella, *Helv. Chim. Acta*, 1995, **78**, 2053.

15 J. Miller and G. Zweifel, *Synthesis*, 1983, 128.

16 For an account of neutralisation/reionisation of negative ions, and definitions of nomenclature, see N. Goldberg and H. Schwarz, *Acc. Chem. Res.*, 1994, **27**, 347.

17 For an account of the application of the comparison of $^-NR^+$ and CR spectra of an anion, see C. A. Schalley, G. Hornung, D. Schröder and H. Schwarz, *Chem. Soc. Rev.*, 1998, **27**, 91.

18 M. W. Wong, *Chem. Phys. Lett.*, 1996, **256**, 391.

19 GAUSSIAN94, Revision C3, M. J. Frish, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavavhari, M. A. Al-Latham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. V. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez and J. A. Pople, Gaussian Inc., Pittsburgh, PA, 1995.

20 H.-J. Werner, P. J. Knowles, J. Almlf, R. D. Amos, M. J. O. Deegan, S. T. Elbert, C. Hampel, C. Meyer, K. Peterson, R. Pitzer, A. J. Stone and R. Lindh, MOLPRO 96.4.

21 K. Aoki and S. Ikuta, *J. Mol. Struc.*, 1994, **310**, 229.

Received in Cambridge, UK, 1st June 1998; 8/04070B