

A POST-BUCKMINSTERFULLERENE VIEW OF CARBON CHEMISTRY

Harold Kroto
School of Chemistry and Molecular Sciences,
University of Sussex, Brighton, BN1 9QJ UK

Keywords: C₆₀. Fullerenes, carbon particles

INTRODUCTION

The discovery of C₆₀ Buckminsterfullerene, Fig 1, has its origins in a research programme involving synthetic chemistry, microwave spectroscopy and radioastronomy¹. In 1975, at Sussex (with David Walton), the long chain polyynes H-C≡C-C≡C-C≡N was synthesised and studied by microwave spectroscopy. Subsequently, with Takeshi Oka and NRC(Ottawa) astronomers, the molecule was discovered in space, Fig 2, by radioastronomy using the laboratory microwave frequencies.

This discovery led on to the detection of the even longer carbon chain molecules HC₇N, HC₉N and HC₁₁N in the space between the stars². Further work aimed at understanding the formation of the chains in space focussed attention on the possibility that they are produced at the same time as carbon dust in red giant stars^{1,2}. During experiments at Rice University in 1985 (with James Heath, Sean O'Brien, Robert Curl and Richard Smalley), designed to simulate the conditions in these stars and explore their capacity for carbon chain formation, the exciting discovery that C₆₀ was remarkably stable was made³. It was found that under conditions where almost all the atoms in a carbon plasma had nucleated to form microparticles the molecule C₆₀ remained behind - together with some C₇₀. This result was, as is now well known, rationalised on the basis of the closed cage structure shown in Fig 1. It was proposed that the geodesic and aromatic factors inherent in such a structure could account for the stability of the molecule.

THE CIRCUMSTANTIAL EVIDENCE FOR THE EXISTENCE OF FULLERENES

Many subsequent experiments, carried out during the period 1985-90 provided compelling evidence for the exceptional stability of C₆₀ whatever its structure might have been^{2,4}. For instance support for the structure had been obtained by showing that the mass spectrometric magic numbers observed in cluster experiments were consistent with the formation of a whole family of closed cages, the fullerenes Fig 3^{5,2}. Particularly convincing was the fact that the smallest cages, in which all the 12 pentagons needed for closure are isolated, are C₆₀ and C₇₀⁵.

To explain the spontaneous creation of such an unexpected species in a chaotic carbon plasma a simple refined nucleation mechanism^{6,7} was developed. It was also recognised that the mechanism could not only account for C₆₀ but it also⁷ explained the detailed structure of carbon microparticles such as those that Iijima⁸ had observed (Fig 4a). In this scheme it is proposed that when carbon nucleates, curved and closing graphitic shells form⁶ (rather than flat sheets as has

traditionally been assumed) and these wrap up under epitaxial control⁷. It predicts that the embryos involved in carbon particle growth are partially closed cages which grow into quasi-icosahedral graphite particles⁷. This mechanism explains the formation of the fullerene cages, C₆₀ in particular, as resulting from closure during the general carbon microparticle formation process. It is proposed that embryos that do not close grow directly into graphite microcrystals essentially consisting of imperfect, concentric quasi-icosahedral spirally interconnected shells. The mechanism is supported by simulated TEM images (Fig. 4b) derived for the structures predicted by the new scheme⁹ which show excellent agreement with the elegant electron microscope images of carbon microparticles obtained by Iijima⁸ in 1980, Fig 4a.

It was also recognised that there were significant similarities between the structures of the pure carbon particles and soot particles and that both could be explained by essentially the same scheme (albeit in perturbed form for soot). This proposal has been criticised on various grounds¹⁰, however detailed analysis of soot¹¹ reveals that there are numerous serious gaps in our understanding of the formation process, indeed sufficient to show that the new scheme cannot be discounted readily¹². Harris and Weiner¹¹ said, in 1985, that "...knowledge of the chemistry (of soot formation) has been totally absent." so there would appear to be some room for some fresh ideas on the chemistry involved. The new mechanism does appear able to explain many observations more simply than some previous models such as those involving liquid droplet formation in which it appears the substructure is thought to be held in place van der Waals forces. The mechanism predicts that C₆₀ should be a by-product of the soot formation process⁶. Interestingly Gerhardt, Löffler and Homann¹³ subsequently showed that C₆₀⁺ is the major ion in a sooting flame. Homann has however pointed out that this observation is not necessarily to be taken as support for the new scheme.

THE PRODUCTION AND CHARACTERISATION OF BUCKMINSTERFULLERENE

In August 1990 the scepticism which surrounded the original fullerene-60 proposal was finally laid to rest by the breakthrough made by two groups, Krättschmer, Lamb, Fostiropoulos and Huffman¹⁴ (Heidelberg/ Tucson) and Taylor et al¹⁵ (Sussex). From the carbon deposit produced from arc processed graphite Krättschmer et al¹⁴ obtained a crystalline material. X-ray analysis showed it to consist of arrays of spherical C₆₀ molecules of exactly the expected size. Mass spectrometric and infrared data were further confirmation. From similarly processed graphite Taylor et al¹⁵ also obtained mass spectrometric evidence for fullerene-60 and also extracted a red solution (in benzene) independently. Subsequently they chromatographically separated the material into two components C₆₀ and C₇₀. The ¹³C NMR analysis of the beautiful magenta solution of C₆₀ yielded a single line resonance (Fig 5) indicating that all the C atoms in the molecule are equivalent! A result perfectly commensurate with the proposed fullerene-60 structure. Elegant support came from the spectrum of C₇₀ which showed that it had five lines (Fig 5), again in perfect agreement with expectation. This result was also important as it showed that other members of the fullerene family existed.

POSTBUCKMINSTERFULLERENE CHEMISTRY

Since this breakthrough was made in September 1990 the field has exploded and all aspects of the chemical and physical properties of the fullerenes are now being investigated in minute detail. The fact that this new, third form of carbon exists, is created spontaneously and has been under our noses since time immemorial is somewhat difficult to accept. Indeed fullerenes appear to make up some 10-30% of the material produced by the carbon arc and it has now been shown to reside in soot. Howard and co-workers who have found the fullerene content of soot from a benzene flame can be as high as 7% under certain conditions.

These observations have major implications; in particular for:

- 1) The composition of carbon vapour,
- 2) The mechanism of carbon nucleation,
- 3) The structure of graphitisable carbons,
- 4) Fluid carbon phases,
- 5) Soot formation,
- 6) The structure of interstellar and circumstellar grains,
- 7) Structure and synthesis of new polyaromatic hydrocarbons,
- 8) New metal-carbon complexes and intercalation compounds

New advances are made every day as the material becomes more and more accessible and a complete review of the material published on C₆₀ Buckminsterfullerene by the end of 1990 has been written⁴.

ACKNOWLEDGEMENTS

The success in the most recent work at Sussex was made possible by the expertise, effort and help of: Wahab Allaf, Simon Balm, John Dennis, Laurence Dunne, Richard Hallett, Jonathan Hare, Ken McKay, A Abdul-Sada, Amit Sarkar, Roger Taylor, David Walton and Steve Wood. We also thank the SERC.

LITERATURE CITED

1. H W Kroto, Chem. Soc. Revs., 11, 435-491 (1982).
2. H W Kroto, Science, 242, 1139-1145 (1988)
3. H W Kroto, J R Heath, S C O'Brien, R F Curl and R E Smalley, Nature, 318, 162-163, (1985).
4. H W Kroto, A W Allaf and S P Balm, Chem Revs (in press)
5. H W Kroto, Nature, 329, 529-531 (1987)

6. Q L Zhang, S C O'Brien, J R Heath, Y Liu, R F Curl, H W Kroto and R E Smalley, *J Phys Chem.*, 90, 525-528 (1986)
7. H W Kroto and K McKay, *Nature*, 331, 328-331 (1988)
8. S Iijma, *J Cryst Growth* 50 675-683 (1980)
9. K G McKay, D Wales and H W Kroto, in preparation
10. L B Ebert, R V Kastrup, J C Scanlon and R D Sherwood, 19th Biennial Conf. Carbon (Penn State) 396-397
11. S J Harris and A M Weiner, *Ann. Rev. Phys. Chem.*, 36, 31-52 (1985)
12. H W Kroto (in preparation)
13. P H Gerhardt, S Löffler and K H Homann, *Chem Phys Letts* 137, 306 (1987)
14. W Krätschmer, L D Lamb, K Fostiropoulos and D Huffman, *Nature*, 347, 354-358 (1990)
15. R Taylor, J P Hare, A K Abdul-Sada and H W Kroto, *J. C. S. Chem. Comm.*, 1423-1425 (1990)
16. J B Howard, J T McKinnon, Y Makarovsky, A L Lafleur and M E Johnson, *Nature* (in press)

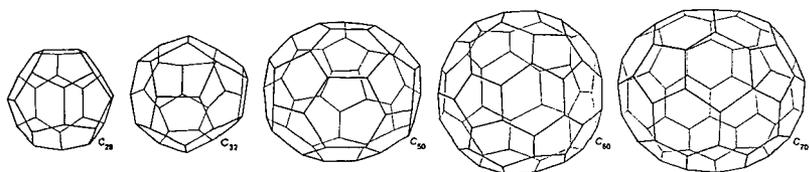


Fig 3 Family of relatively stable Fullerenes⁵

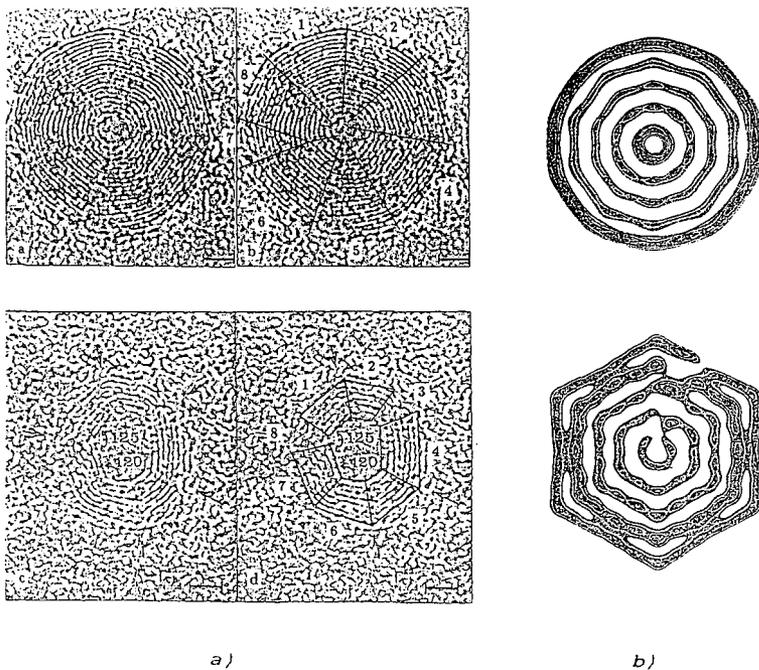


Fig 4 Comparison between TEM images of polyhedral graphite microparticles observed by Iijima⁸ a) and simulated images for a hypothetical icospiral microparticle (two different angles) b)

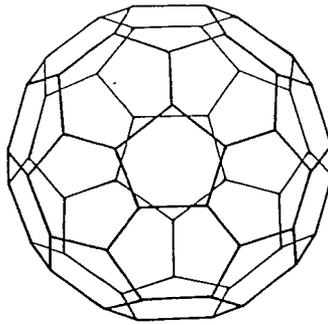


Fig. 1 C_{60} Buckminsterfullerene.

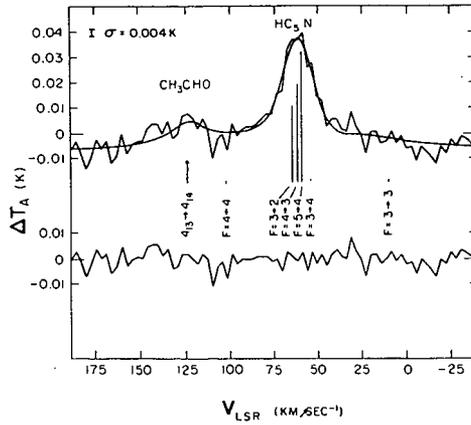


Fig. 2 Radio line of HC_5N observed in a giant molecular cloud SgrB2 near the center of the Galaxy

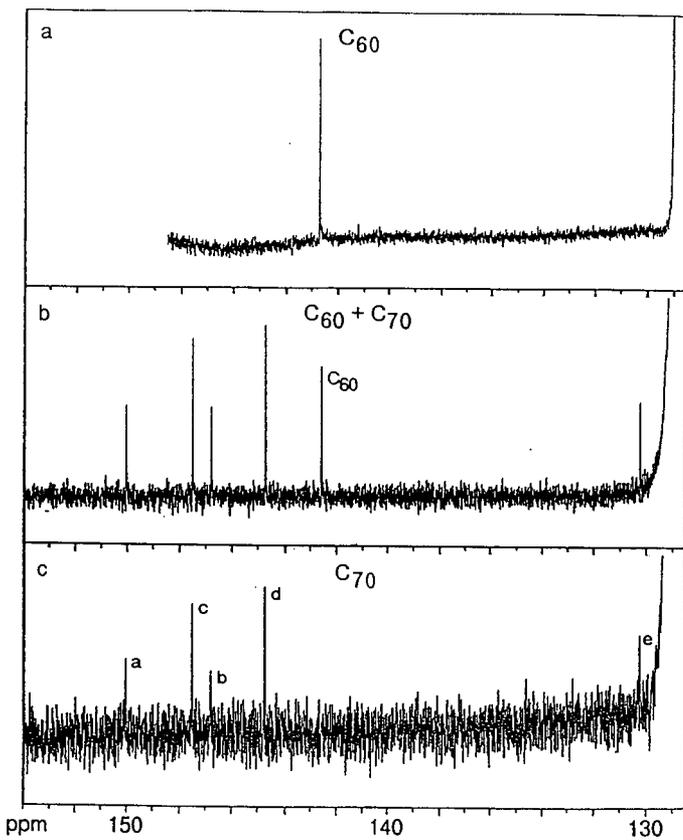


Fig 5 ^{13}C NMR spectrum of Fullerene-60