

The discovery of buckminsterfullerene

Topics

Allotropy, organic chemistry, chemists

In 1985, virtually all school chemistry textbooks became out of date overnight. Prior to this, textbooks stated that there were two allotropes of carbon – diamond and graphite. Allotropes are forms of the same element which differ in the way their atoms are arranged. Diamond and graphite are classic examples of allotropy. In diamond the carbon atoms are arranged tetrahedrally and in graphite they form two-dimensional layers of interlinked hexagons.

Picture Diamond and graphite structures

In 1985 the discovery was announced of a third allotrope in which the atoms form C_{60} molecules in the shape of a football. This led to the award of the 1996 Nobel Prize to Harry (now Sir Harry) Kroto of Sussex University, Robert Curl and Richard Smalley (both of Rice University in Houston, USA).

Harry Kroto had an interest in molecules found in interstellar space which can be identified from their microwave spectra – by comparing signals obtained from outer space with those measured for known compounds in the laboratory. He was particularly interested in polyynes (molecules with several carbon-carbon triple bonds) but these are difficult to make conventionally. In 1984, Kroto began a collaboration with Smalley and Curl in Houston who had an apparatus called AP2 ('App-two'). This used a laser to blast clusters of atoms off solid targets and then led the clusters into a mass spectrometer where their relative molecular masses could be measured. Kroto hoped that if a graphite target were used, small sections of graphite layers might rearrange themselves into polyynes whose spectra could then be measured.

Clusters of carbon atoms were indeed formed, and unexpectedly large peaks were found in the mass spectra with masses corresponding to C_{60} and (at a lesser intensity) C_{70} . These peaks always appeared together, and Kroto started to refer to them as the Lone Ranger and Tonto.

Why were these molecules so stable? Sheets of graphite in which the carbon atoms are arranged in hexagons would be expected to be very *unstable* because they would have so many 'dangling bonds' with unpaired electron at the edges. Inspired by geodesic dome structures made up of hexagons designed by the architect Richard Buckminster Fuller, the team began to consider the possibility that a sheet of graphite hexagons might curl up into a spherical shape so that all the 'dangling bonds' could link up. However, work with crude paper molecular models showed that this was impossible if all the atoms were linked in hexagons. Kroto recalled a spherical 'stardome' made of cardboard shapes that he had built for his children and believed that it contained pentagons. This was a vital clue. More late night work with the paper models showed that a spherical shape could be made with 20 hexagons and 12 pentagons. A quick counting of bonds showed that this structure was chemically reasonable in that each carbon atom was forming four covalent bonds – one double and two single. Having made the model, the team did not know what the geometrical shape was and the story goes that a phone call to the chairman of the Rice University Mathematics Department for advice elicited the reply 'what you've got there boys is a soccer ball'. However, Kroto remembers a less laconic reply.

'We were sitting in Rick Smalley's office. We were extremely high, on a roll at the time as you might imagine, only just recovering from the realisation

of what the bloody thing might be.

Jim Heath [a student of Smalley's] and I and almost certainly Sean O'Brien [another student of Smalley's] and probably Bob Curl too were there. Rick was definitely not there at the time and that is why Jim was sitting in Rick's chair at Rick's desk when the phone rang. Jim answered it. Then a sort of stunned expression came over his face and Jim said 'It's soccerball', or he may have said 'He says it's soccerball'. I am pretty sure he did not say 'It's a soccerball'.

This appeared to be a return call from a mathematician that Rick must have called up earlier in the day to ask what the structure might be.'

Picture The 'soccerball' structure of buckminsterfullerene

At this stage, the soccer ball structure (and a similar 'rugby ball structure for C_{70}) was no more than inspired speculation. Confirmation had to wait until enough C_{60} , now christened buckminsterfullerene (buckminsterfuller after the architect and ene because it had double bonds), could be made to allow, ultraviolet / visible, infrared and ^{13}C NMR spectra to be measured as well as X-ray diffraction studies. App-two produced only minute amounts of molecules at a time. Theorists predicted that a 'soccer ball structure' should have just four lines in its IR spectrum (at specific wavelengths) and that its ^{13}C NMR spectrum should have just one line because all the carbon atoms are in exactly equivalent positions. NMR is one of the most important techniques for organic chemists. The saying goes that 'when the NMR breaks down, the chemists go home.'

To produce enough buckminsterfullerene for these tests, a different approach was used. Two graphite rods inside a bell jar containing an inert gas at low pressure were connected to an electrical supply, and an electrical arc formed between the two electrodes (one experimenter described this apparatus as 'a battery and a pencil'). This produced a soot which was found to contain about 1% of a mixture of C_{60} and C_{70} . These could be separated from the soot by sublimation or by extraction into benzene (in which the soot was insoluble) and from each other by chromatography. At Sussex Kroto and his student Jonathan Hare (now the presenter of TV programmes, *Rough Science* and *Hollywood Science*) together with Roger Taylor and Abdul Sada were the first to measure the single line ^{13}C NMR spectrum (Kroto called it 'the one line proof'). Wolfgang Krätschmer and Donald Huffman, working at the Max Planck Institute for Nuclear Physics in Germany and in Arizona State University, extracted the molecule and measured its X-ray pattern just ahead of the Sussex team and measured the IR and UV / visible spectra. Both events occurred in 1990. Krätschmer and Huffman had in fact observed the UV / visible spectrum some years earlier but without realising its significance.

Further information

This is a much simplified account both in detail of the actual experiments and the number of people, and indeed research teams, working on buckminsterfullerene. There is a much more detailed but highly readable account in J Baggott, *Perfect Symmetry*, Oxford: Oxford University Press, 1994. This was written before the award of the Nobel Prize, of course. As well as the story of the discovery, it deals with some of the chemistry and properties of the family of fullerenes and their derivatives. The Nobel lectures of the three laureates are available at www.nobel.se.

Postscript

Rick Smalley died in November 2005 after a long fight against leukaemia.