

Fullerenes



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Since they were first isolated in 1985,^[1] fullerenes have been the focus of a great deal of research, and speculation about their properties. For years it had been thought that carbon had only two allotropes in its pure form: graphite and diamond. However, Nobel laureate Harry Kroto and his team managed to isolate this compound after vaporizing graphite in a helium atmosphere. They found that the carbon^[2] nucleates in the gas phase to form these closed spheres.

This picture shows the C₆₀ identified originally. It consists of 12 pentagons, alongside a series of regular hexagons. All spherical fullerenes are characterized by these 12 pentagons which are required for the shell to close, a property discovered by Euler. C₆₀ is the smallest fullerene which is particularly stable, because it is the smallest fullerene in which each pentagon is isolated from each other.

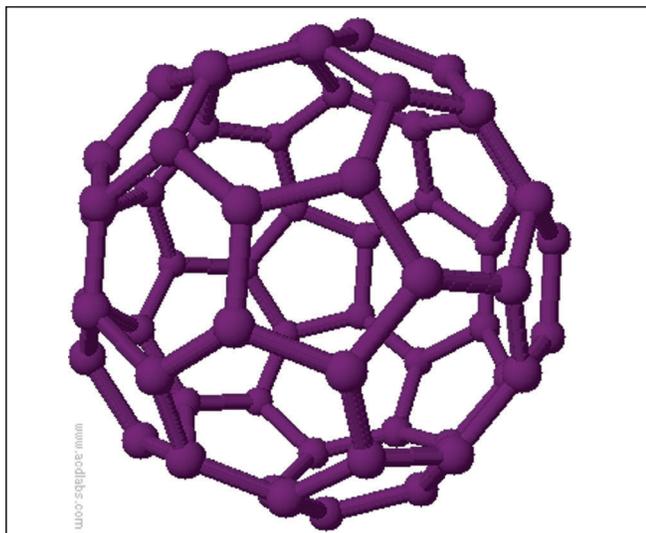


Figure 1: Representation of a C₆₀ “buckyball” fullerene

This is important, as adjacent pentagons experience increased reactivity. As such, C₅₆ and C₅₈ have been found to form derivatives much more easily.^[3] They cannot easily be produced in bulk as a consequence. However, some derivatives have recently been found with a distinct ‘egg-shaped’ distortion^[4].

C₆₀ was determined to be the most stable compound formed by the process by mass spectroscopy. C₆₀ leads to the single large peak corresponding to 60 carbons. There is also a smaller one corresponding to 70 carbons - another quite stable allotrope.

C₆₀ is also unusual in that its ¹³C nuclear magnetic resonance (NMR) spectrum contains only one peak, because every carbon atom is equivalent.^[6]

The C₆₀ was originally thought to be superaromatic:

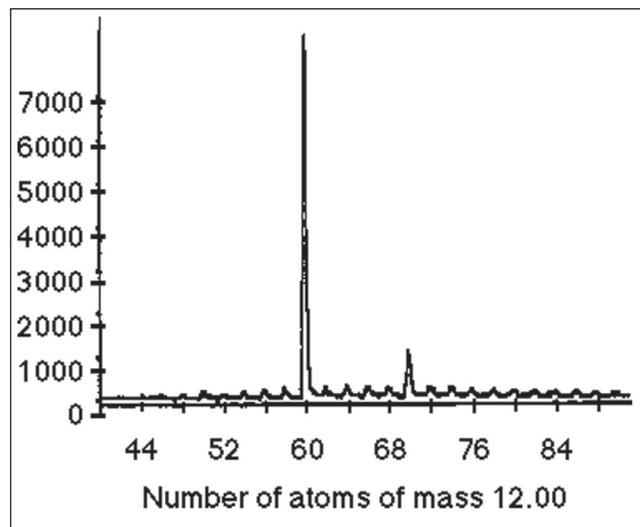


Figure 2: Mass spectrum of carbon atoms in bucky balls. Formation occurs under low energy laser power.⁵

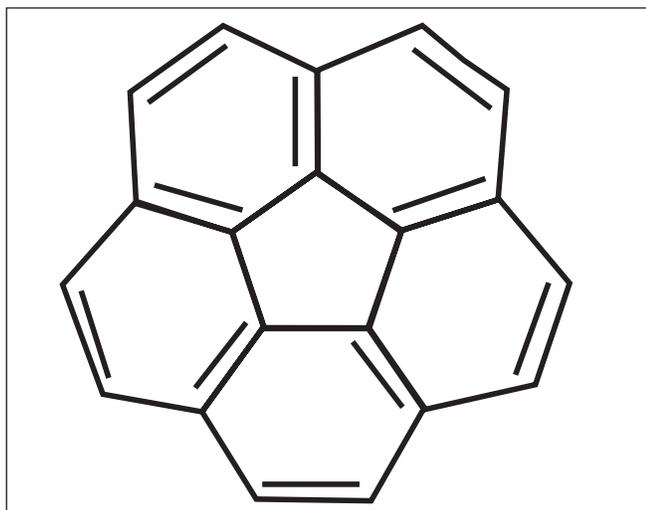


Figure 3: Example of a fullerene spectrum

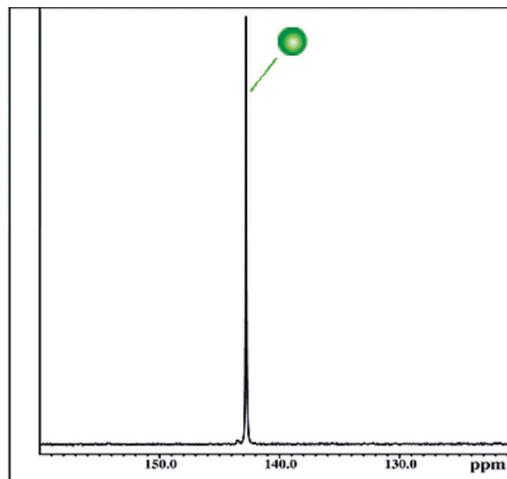
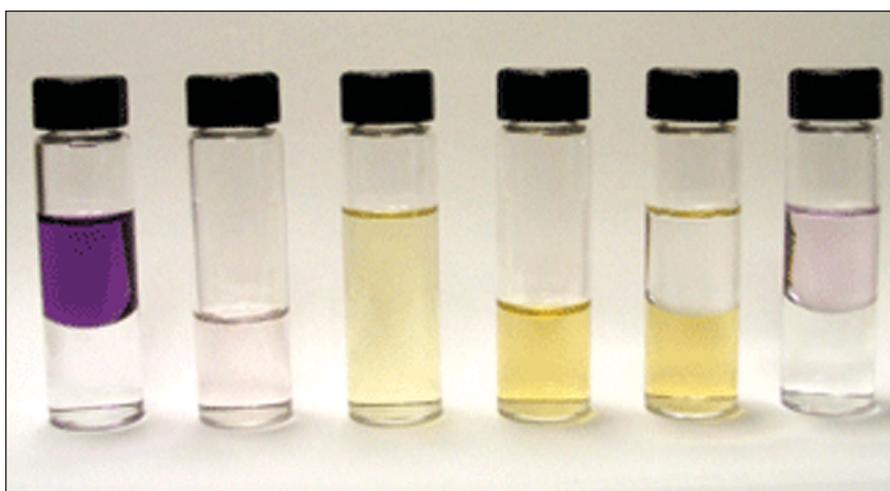


Figure 4: Structure of corannulene ($C_{20}H_{10}$). It is of interest because it can be considered a fragment of a fullerene. This structure is known as a "buckybowl".^[12]



Far left: dissolved in toluene
 2nd: in tetrahydrofuran (THF)
 3rd: in water and THF
 4th: suspension in water
 5th: in water and toluene
 6th: after addition of a mild oxidant, in toluene^[12]

the three dimensional configuration of the molecule allows for greater delocalization of the p-orbitals than even benzene. However, research has suggested that the conjugative effect in C_{60} is less than might be expected, as the pentagons avoid containing double bonds^[7]. The bonding is therefore better described as superalkene. They are therefore able to react with nucleophiles to a greater extent than might be assumed. Therefore the p-orbital delocalization about each hexagon can be approximated as:

One of the principal reasons for interest in the fullerenes, especially in the field of material science, is that one can intuitively see how smaller molecules can be placed inside the shell.^[8] This has been suggested as a possible method of drug insertion, or even as a medical treatment in its own right,^[9] though great care would have to be taken with fragile endohedral

complexes, as the contents are susceptible to influence from the magnetic environment of both the inside and outside (including any added groups) of the fullerene cage.^[10]

Fullerenes have also been put forward as candidates for organic superconductors.^[11] At low temperatures (18K), fullerenes doped with potassium have been shown to experience very little electrical resistance; near 5K, the resistance is negligible.

They are also notable for their wide variety of colors in different solvents:

Fullerenes need not necessarily take the form of spheres either. Nanotubes also exist, in which the sphere is replaced by a long cylinder, with hemispherical ends. Even more elaborate shapes

have been created, such as a 'pillared graphene', with many nanotube pores, designed for hydrogen storage^[13]. This represents the new wave of fullerene research: moving on from the original spheres to increasingly intricate structures, with a more practical bent.

Bibliography

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About the Author

Chris Slaney already has A-level chemistry, biology and maths, and is doing further maths and economics. He has an unconditional place at Oriel, Oxford next year to read chemistry.