Dalton Perspectives

The Post-Buckminsterfullerene Graphite Horizon

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The discovery that closed carbon cages form spontaneously suggests that our ideas about the stability of extended carbons such as graphite are not perfect and may need revision. Addressed here are the pre-buckminsterfullerene assumptions about structure-determining factors such as out-of-plane strain which may have been primarily responsible for it being overlooked that non-planar organic chemistry has been under our noses all the time.

The discovery, in 1985, that C_{60} Buckminsterfullerene (Fig. 1) forms spontaneously[1] was a surprise to most chemists and for a few a somewhat difficult proposal to accept, only partly because it appeared to have been based on insufficient evidence. The observation of but a single strong mass spectrometric line, Fig. 2, and an intuitive belief that the truncated-icosahedral cage solution was too elegant to be wrong was not enough for some. During the period 1985–1990 the original mass spectrometric evidence (Fig. 2) was however complemented by a range of ultimately convincing experimental and theoretical evidence[3–5] the strength of which was perhaps not fully recognised outside the Chemical Physics community. Indeed it is interesting to identify some of the reasons for misgivings about the structure proposal. Of course ultimately the convincing proof has been the production, in 1990, of macroscopic amounts of fullerenes and the unequivocal characterisation of their structures by Krätschmer *et al.*[6] and Taylor *et al.*[7]

As long ago as 1970 Osawa and Yoshida[8,9] had considered that, if it could be made, the C_{60} molecule might be stable and possibly 'superaromatic'. Indeed Jones[10,11] had considered graphite balloons even earlier and Bochvar and Gal'pern[12] had done Hückel calculations a little later. It might have been thought that entropy factors should preclude the spontaneous formation of so symmetric a species, after all the creation of $C_{20}H_{20}$ (20-hydrofullerene-20) by Paquette's group[13] had been a synthetic tour de force. This molecule is the perhydro derivative of C_{20} (dodecahedrene or fullerene-20) which can be considered to be the first fullerene, though not the archetypal species as it has no hexagons at all. The fullerenes conform to the rule (based on Euler's law) that a closed cage can form as long as it has 12 pentagons and an unlimited number of hexagons (other than one). With a little thought one also realises that a *flat* sheet of 60 hexagonally bonded carbon atoms must have 20 or more dangling bonds and closure would release a considerable amount of associated binding energy. As a consequence one concludes that the most stable form of an aggregate of 60 carbon atoms is most probably the fullerene cage. Numerous theoretical studies during 1985–1990 confirmed this supposition.[5,14] Apart from excellent evidence that endohedrally encapsulated metal complexes, such as $C_{60}La$, had been produced in a cluster beam,[15] neat and convincing support was also provided when the *Pentagon Isolation Rule* was discovered.[16,17] This rule indicated that the primary gauge of fullerene stability was the absence of abutting pentagons. As fullerene-60 was the first (smallest) cage able to have isolated pentagons ($5 \times 12 = 60$) and fullerene-70 discovered to be the second, the rule correctly explained the two magic numbers originally observed,[1] Fig. 2. The fact that 70 was in fact the second most important magic number allayed, at a stroke, each and every suspicion that might have lingered in the mind of the present author over the correctness of the cage structure proposal.[2]

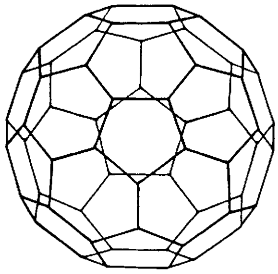
Fig. 1 C_{60}, Buckminsterfullerene

After it seemed clear that the entropy factor must have been overcome by energetics (as usual?) the main stumbling block, in the minds of many, was the part played by out-of-plane strain. This concept is worthy of more detailed consideration. Why had not this factor precluded the formation of this most perfectly non-flat of molecules? Some idea of how our ideas on out-of-plane strain are moulded can be obtained from consideration of the relevant familiar molecules which appear to have structures governed by this factor; the polycyclic aromatic hydrocarbons which are almost invariably flat. For instance naphthalene and coronene are archetypal polycyclic aromatic hydrocarbons and they are flat. If C_{60} is a ball which forms spontaneously it urges us to reconsider our ideas as perhaps there is some flaw in our assumptions about how the out-of-plane strain factor applies to *pure* carbon networks. In fact as soon as one recognises the fact that a flat pure carbon network has dangling bonds on the edge and considers the implications one suddenly realises that out-of-plane strain is not so well defined for such systems. For instance if benzyne-like peripheral bonds are used to represent the edge electrons the puzzle becomes rather interesting and perhaps more understandable. Such triple bonds would of course be shorter than double bonds and probably cause 'crinkling' at the edge causing a 'flat' sheet to pucker.[18] A C_{24} coronene sheet might actually be saucer shaped; indeed one begins to wonder whether there is such a thing as a 'flat' sheet of pure graphite at all. Attention has already been drawn[3] to the implication in Barth and Lawton's

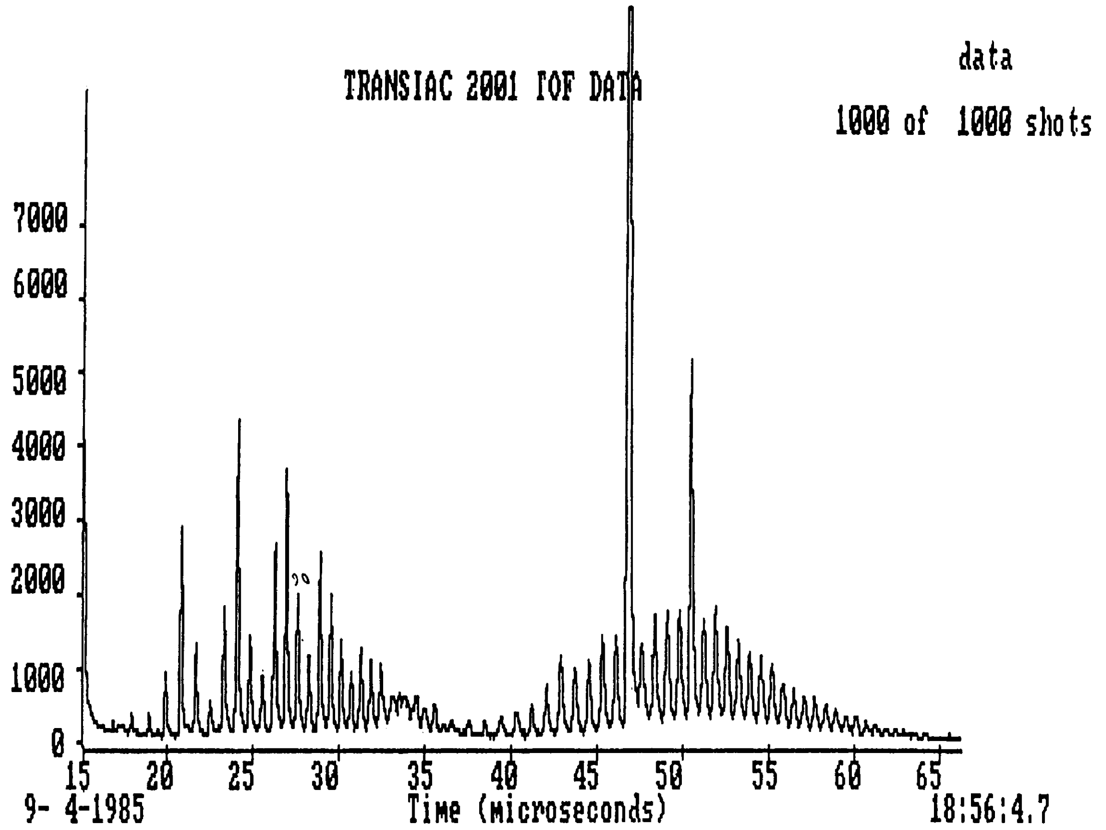

Fig. 2 Time-of-flight mass spectrum of carbon clusters in which the C_{60} and C_{70} species were first noted to display special stability[2]

work[19] on the synthesis of the saucer-shaped corannulene molecule which suggested that they had early evidence that the carbon world might be more round than the pre-buckminsterfullerene horizon suggested. As a consequence one starts to question exactly what graphite is. It is clear that a flat sheet of graphite can never be perfect; the edge must have dangling bonds which would presumably crinkle and deform at the edge. In air of course bonds to impurities such as H and OH groups would form in many cases. Indeed one might also question the structure of diamond near its surface. Suddenly one realises that there can never be a perfect piece of graphite or for that matter a perfect diamond; in practice there would always be edge or surface impurities and edge or surface distortions. More disturbing is the concept of flat graphite. Why exactly is it flat and what is more to the point how flat is an average piece of graphite? Some study of these questions shows that graphite is not always a readily defined material on a macroscopic scale. After diamond and graphite, the fullerenes can be considered the third well defined allotropic form of carbon; other forms such as glassy and amorphous carbons are not well characterised materials.

There are some experiments which suggest that we should be careful about assuming that we know very much about carbon in the 'pure' state. In general it is produced in a most peculiar way. Whereas many solid elements may be crystallised in some way or other (say from a melt), graphite is produced by thermolytic elimination of H and other impurities from some hydrocarbon feedstock. Thus graphite production involves some chaotic network formation process in the solid/fused melts of tarry material. The process is governed by complicated dynamic factors which operate in this condensed-phase situation at the microscopic level. Related energetic factors probably govern the gas-phase formation of C_{60}. However thermolysis in bulk in some cases produces domains which have the basic graphite structure as flattening occurs when there is sufficient energy from interlayer bulk interactions. On a small scale however these factors are almost certainly negligible, hence the facile formation of fullerenes when aggregates of a few tens to hundreds of carbon atoms form and anneal.

At this time it is possible that we can explain, at least partly, the formation of the fullerenes and also the spheroidal graphite microparticles observed by Iijima[20] in 1980 (Fig. 3). It has been suggested[21] that giant fullerenes[22] also form and recent results[23] confirm this conjecture. The archetypal giant fullerenes have icosahedral symmetry, Fig. 4,[22,24,25] but in general such 'perfect' structures are probably rather rare and quasi-icosahedral cages are likely which still should have 12 cusps but distorted and perhaps elongated shapes. During gas-phase

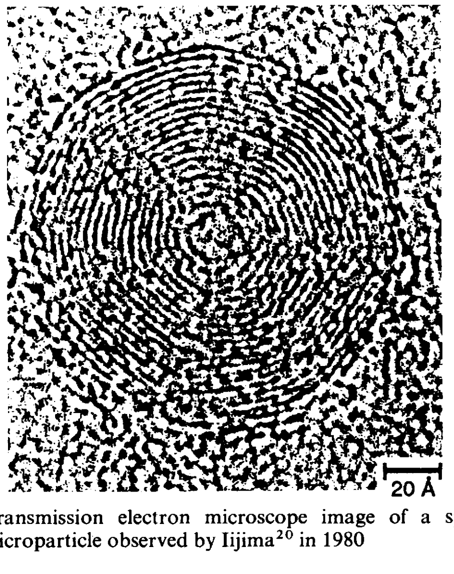

Fig. 3 Transmission electron microscope image of a spheroidal graphite microparticle observed by Iijima[20] in 1980

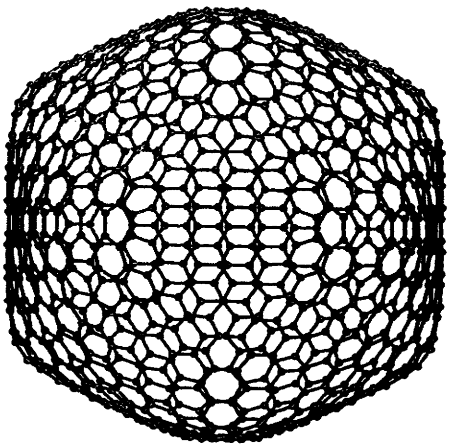

Fig. 4 Computer simulation of the giant fullerene-960[22,24] which has 'perfect' icosahedral symmetry. The structure has been relaxed[25] using molecular dynamics software

nucleation, larger aggregates with from 10^5–10^6 atoms which possess onion-like spiralling, concentric, graphite shell structures, Fig. 3, also form. These microparticles may also be elongated,[20] indeed elongated cages may form readily as carbon microfibres have been observed recently by Iijima[26] and also Endo.[27]

On a larger scale, graphite structure is controlled by the method of production and subject to a mix of epitaxial growth control[22] as well as temperature- and pressure-dependent factors. In a solid/tarry mix, fearsomely complex processes appear to take place involving dehydrogenation/diffusion, radical formation and cyclisation to produce graphite-like networks which are far from flat initially. Indeed when some feedstocks are carbonised, graphitic domains of any significant size do not form; this is the case for the 'so-called' non-graphitisable carbons.

All in all one of the most fascinating aspects of the whole fullerene story is the fact that it has forced us to look at carbon again, graphite in particular. The text-book picture of graphite which is usually (necessarily) a drawing of a small finite array of carbon atoms needs to be reassessed because it may have exerted an influence on our minds far beyond its range of applicability. It might apply to some cases where the edge electrons are tied down by bonds to say hydrogen, but not if they are free to move, into the π cloud for instance. When this sort of delocalisation occurs it may be that out-of-plane strain simply has no meaning.* It may have caused us to believe the world of graphite and aromatic chemistry is a predominantly flat one when all about us there was subtle and also overt evidence that this was not the case. In fact the words of Jones[10,11] in 1966 who wrote 'Daedalus proposes to modify the high-temperature synthesis of graphite' in order to produce a hollow graphite molecule appear quite prophetic today as the fullerene research balloon blows up. Since September 1990 some 450 or more papers have appeared as the New Round World of Post-Buckminsterfullerene Chemistry is being explored.

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* *Note added at proof.* Convincing evidence that the concept of out-of-plane strain requires careful reassessment is provided by the remarkable observation that the saucer-shaped molecule, corannulene, inverts rapidly at room temperature.[28]