

C₆₀, fullerenes, giant fullerenes and soot

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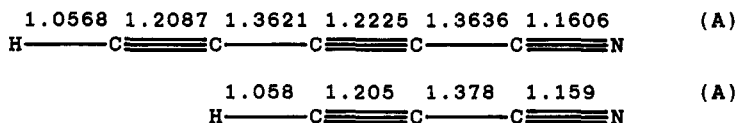
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Abstract - During a series of experiments in which the nucleation of carbon vapour was studied in order to explore carbon chain and particle formation in stars the highly stable C₆₀ molecule was detected. The properties of this molecule are in almost perfect accord with the proposal that the molecule has the closed cage buckminsterfullerene structure in which all 60 atoms are equivalent and lie at the corners of a truncated icosahedron, a shape familiar to many today in the form of the modern foot- or soccerball. This molecule is expected to be stabilised by geodesic and aromatic factors. The most important aspect of this discovery lies in the fact that such a symmetric object can form spontaneously from a chaotic, hot, carbon plasma. This novel conjecture is consistent with a wide range of observations on carbonaceous materials. The emphasis in this article is on those aspects of the C₆₀ saga which pertain to non-planar organic chemistry both on earth and in space.

INTRODUCTION

The procedures required to produce, characterise and probe the properties of a new compound obviously depend very much on the compound's stability, a property which is often not a simple one to define. For instance the species HCO⁺, which can be considered to be protonated CO, is very abundant and stable in the space between the stars where collisions are few and far between. On the other hand it is destroyed essentially on every collision in a gas phase discharge and so specialised techniques must be used to produce and detect this species in the laboratory. There are many molecules however that show a stability intermediate between that of ions or free radicals and the numerous well-known compounds which can be kept in a bottle. With guile it is often possible to produce, detect, identify and probe species with intermediate stability with equipment designed for the study of stable compounds. Molecules with multiple bonds often fall into this category as they show varying degrees of stability. At Sussex various spectroscopic techniques have been exploited to produce a wide range of new compounds (ref. 1): The detection of free thioacetaldehyde CH₃CH=S led to the detection of other thioaldehydes, thioketenes and thioketones including: CH₂=CH-CH=S, CH₂=C=S, (CH₃)₂C=S; seleno-acetaldehyde, CH₃CH=Se, as well as the new sulphidoborons: XB=S (X= Me, Hal) and the selenoboron, ClBSe. This led on to the production with John Nixon of the first phospho-alkenes (molecules with carbon-phosphorus double bonds): including CH₂=PX (X = H, F, Cl, Br, CN etc). The new phosphoalkynes XC≡P (X= F, Cl, Ph, CN, C≡CH, C≡C-CN etc) were produced when previously only HC≡P had been known. This led the development of C≡P and C≡P as ligands in metal complexes and the development of new synthetic routes. In many cases the species have been probed by microwave, as well as photoelectron and infrared spectroscopy used in synergistic combination. In these new molecules with multiple bonds involving second and third row atoms the instability arises from a less favourable p-p overlap than occurs in the C=C and C≡N cases. The methods developed for handling such species enabled us also to study polyynes (refs. 2,3,1) which under normal conditions may be explosive. At Sussex a programme aimed at studying free polyynes was initiated with David Walton who had developed techniques for synthesising such species (refs. 4,5). The polyynes are unique molecules as they are the only ones which consist of linear chains and so present one of the simplest systems for testing many quantum phenomena in detail. In particular we wished to investigate the effects of delocalisation and various

aspects of molecular dynamics. Together with Anthony Alexander we were indeed able to produce and characterise the first free polyyne by microwave spectroscopy and so obtain accurate bondlengths (ref. 2)



This result was most satisfying as it indicated that there were delocalisation effects in carbon chains as the C=C bonds were longer and the C-C bonds shorter than usual; almost a text book example of the way delocalisation should affect bonding in such a system. The dynamics involved when a long flexible chain rotates and vibrates was also investigated (ref. 6). During this period advances were being made in the detection of new molecules in the interstellar medium by radioastronomy, in many cases by astronomers and microwave spectroscopists working together. Working with Takeshi Oka, Lorne Avery, Norm Broten and John MacLeod we used these laboratory microwave measurements (ref. 2) to detect HC₅N in a giant molecular cloud complex near the centre of the Galaxy using the Algonquin Radiotelescope in Canada (ref. 7). This exciting discovery prompted further synthetic/microwave work at Sussex with Colin Kirby (ref. 3) which enabled us to detect HC₇N in the interstellar medium (ref. 8). Soon after that we detected HC₉N (ref. 9) and since then HC₁₁N has been detected by Bell et al (ref. 10).

These observations were difficult to explain on the basis of the the ion-molecule mechanisms that have successfully explained the presence in space of other, more commonplace species such as NH₃ and H₂CO. As time evolved it seemed that the most promising source of the chains lay in circumstellar processes at high temperatures and pressures (refs 1,11) rather than low temperatures and pressures of the general ISM. The notion became ever more appealing as more and more interesting carbon chain species were being detected, in the amazing red giant carbon star IRC+10216.

The radio discoveries of the long chain polyyne in space stimulated laboratory experiments to simulate the likely chemical processes occurring in such stars. The experiments involved laser vaporisation of graphite to produce carbon clusters in a supersonic beam which did indeed prove that polyyne were produced in these systems (ref. 12,13). It was during these experiments that the remarkable discovery was made that the highly stable C₆₀ molecule forms spontaneously (refs. 14-16).

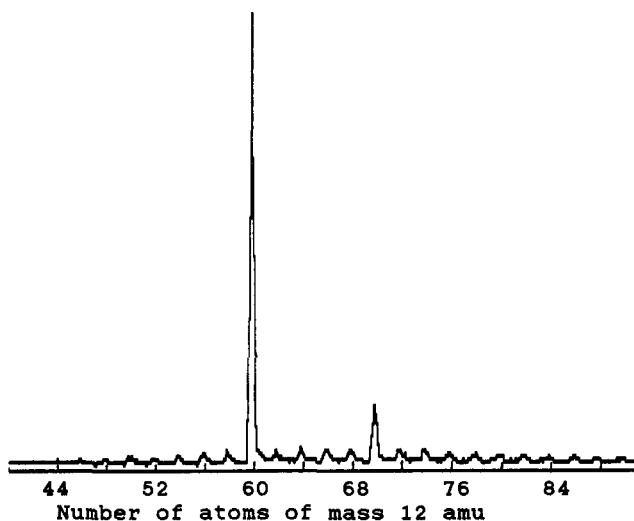
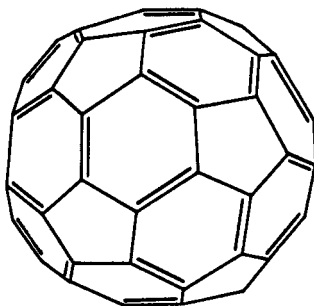


Fig 1 Mass spectrum of laser vapourised carbon showing the dominance of C₆₀. This spectrum is obtained when most of the carbon has nucleated to form carbon particles with masses too great to be detectable. C₆₀ however is left behind because it cannot accrete more carbon under these conditions.

The stability of C₆₀ has been rationalised on the basis of a closed cage buckminsterfullerene structure in which the C atoms lie at the intersections of the seams of a modern football.

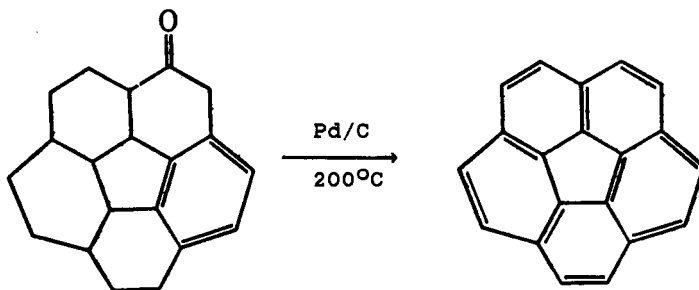


We were subsequently amazed to discover that such a structure had already been contemplated in most imaginative discussions on superaromaticity by Osawa and Yoshida (17,18). There were also later studies by Bochvar and Gal'pern (19) as well as Davidson (20). In their book Yoshida and Osawa (18) discuss the fascinating possibility that this novel molecule might exhibit superaromatic behaviour. This chapter in particular draws attention to the possibility of probing the chemistry of non-flat polyaromatic ring molecules. The initial breakthrough into non-flat aromatic chemistry had been made in the elegant synthetic work of Barth and Lawton (ref. 21) who had synthesised the saucer shaped corannulene molecule. This work appears to have been the stimulus for the idea of C₆₀ (refs 17,18). Numerous important implications follow from the possibility that such a molecule forms spontaneously from a chaotic chemical system and it is most satisfying to note that the assumption that it does has led to neat solutions of several previously vexing problems (ref. 15). This dovetailing of the C₆₀ data with a vast range of well known as well as new data on carbonaceous materials from soot on earth to dust in space makes for a most exciting story.

From an organic chemistry viewpoint it opens up an intriguing new perspective in which a vast range of novel new compounds with unforeseen properties may be envisaged. Although new synthetic strategies need to be developed it may also be worthwhile not to overlook high temperature synthetic approaches, after all our original work on C=S, C=P and C=P etc species involved high temperature routes and C₆₀ itself was discovered as a 10000° plasma cooled. In this article the ramifications of the C₆₀ discovery with particular reference to organic chemistry are discussed.

NON-PLANAR POLYAROMATIC HYDROCARBONS

The most important early work on non-planar aromatic molecules was, as we have seen, that of Barth and Lawton who first synthesised corannulene (ref. 21). The last step in the synthesis is:



and it may be worth quoting what Barth and Lawton say directly about this step (ref. 21, p1738):

" Then, in a rather optimistic experiment, a small sample of the ketone (59) was mixed with an equal amount of 5% palladium on carbon catalyst and the mixture heated gradually, under nitrogen, to 240° over a 2-hr period. After cooling, the product was eluted from the carbon cake with chloroform. Its pmr spectrum showed only one peak, a sharp singlet at 2.19, an indication that all of the protons of the product were aromatic and equivalent and that we had obtained corannulene!"

The use of the term "optimistic" at the beginning and the exclamation mark "!" at the end of this excerpt may well be worthy of note as they pertain to the step in which, most significantly, non-planarity of the aromatic carbon skeleton is achieved and the discussion clearly indicates that the readiness with which this occurred was somewhat unexpected.

It is perhaps worthwhile contemplating that in the ease with which this step occurred there may be an important clue pointing to an unsuspected tendency for carbon polyaromatic networks to propagate as curving/closing sheets rather than flat ones as has traditionally been assumed. The inclusion of a five-membered ring neatly achieves this. It may be that in general this tendency is obscured when network edge dangling bonds are annealed by H atoms in more complex systems. We have proposed that the spontaneous formation of buckminsterfullerene can be readily rationalised if there is a tendency to form closing networks during carbon nucleation in the gas phase (refs. 22,23). Energetic considerations can be invoked to show that a closing carbon network is more stable than a flat one under conditions in which edge dangling bonds are not satisfied. This is almost certainly the case in our experiments with pure carbon where hydrogen is absent. The general gas-phase carbon nucleation scheme which we have proposed provides a highly plausible explanation for the spontaneous production of C₆₀ as a by-product. In this scenario C₆₀ is left behind as the most stable molecular species as all other carbon clusters have grown by accretion into large carbon particles. Our prediction that the nucleation scheme probably also applies to soot formation gains rather strong support from the subsequent detection of C₆₀⁺ in a sooting flame by Gerhardt, Löffler and Homann (ref. 24). The nucleation mechanism in general gives rise to onion-like spiral particles with quasi-icosahedral shells (ref. 23) in excellent agreement with the beautiful scanning electron microscope pictures of spheroidal carbon particle that Iijima produced in 1980 (ref. 25).

FULLERENES AND GIANT FULLERENES

It can also be shown that other closed cages should also show some stability (26,27,15). The set of more stable fullerenes is shown in Fig 2 which seem

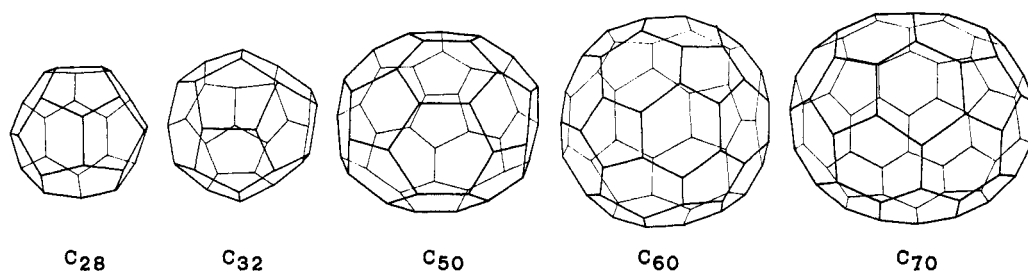


Fig. 2. Five "magic" Fullerenes. C₂₈ is a very interesting tetrahedral molecule with a striking family resemblance to Gomberg's stable free radical triphenylmethyl, ·C(C₆H₅)₃, the first organic free radical and the forerunner of free radical chemistry. C₃₂, here viewed more-or-less along its threefold axis is handed. One of two feasible C₅₀ semi-stable isomers. The one-and-only C₆₀ buckminsterfullerene. C₇₀ is formed by separating two halves of C₆₀ by a ring of 10 extra atoms to form a US football.

to explain the magic numbers observed in carbon cluster experiments by the Exxon Group (ref. 28). In addition we can contemplate much larger cages such as those shown in Fig. 3 which we have shown have quasi-icosahedral shapes (ref. 23). Indeed our experiments show that clusters up to ca 230-240 form which may well be closed. The internal polyhedral structures of graphitic

carbon particles (ref. 25) can thus be explained on the basis of such giant fullerene shapes (ref. 23). Incredible as it may seem the concept of such giant cages also had been made previously. In a highly imaginative article in the New Scientist magazine (ref. 29,30), David Jones (writing under the pseudonym of Daedalus) discusses graphitic balloons in an article in 1966.

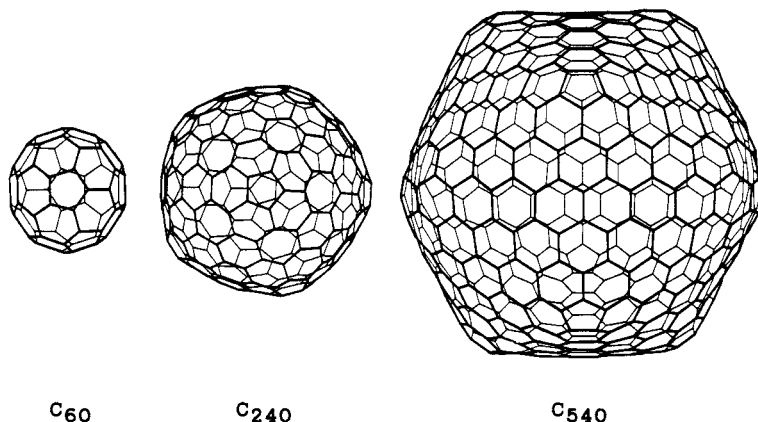


Fig. 3. C₆₀, C₂₄₀ and C₅₄₀ with relative diameters 1:2:3. The rapid shift towards icosahedral shape is dramatic. The objects are really truncated but the truncation remains at microscopic dimensions as the cluster grows to macroscopic size. The surface thus becomes a smoothly curving net with more-or-less flat triangular surfaces between the 12 cusps.

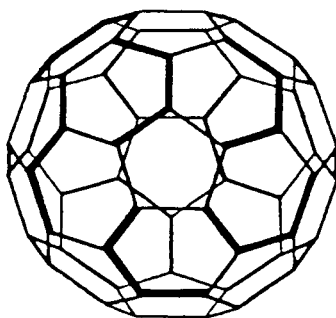
He contemplated the possibility of a modifying the high temperature synthesis of graphite, perhaps by introducing B or N heteroatoms, in order to introduce 5-membered rings into the mainly hexagonal network. He was of course aware that a purely hexagonal network cannot close and that one with 12 five-membered rings and any number of 6-membered ones may. This is a result of Euler's law as is so eloquently discussed by Thompson (31). In fact the pentagonal rings appear to be introduced automatically in pure carbon: The edge of a planar crystal can be considered as a defect which can in the case of a single graphite sheet be eliminated by transporting it as 12 pentagonal defects into the body of the sheet resulting in either partial closure to form an icospiral embryonic microparticle or perfect closure to form a fullerene such as C₆₀ or perhaps even a giant fullerene.

Thus there is some fairly convincing evidence for large carbon cages which might in the future be used to contain material in a graphite-like sheath as was envisaged originally by David Jones (ref. 29,30). Indeed such structures may occasionally occur in soots - containing of course carbon. How often perfect closure occurs in this case is however an open and most intriguing question.

SOOT

Various aspects of the mechanism proposed for the formation of spheroidal carbonaceous particles have been mentioned above and the detailed process has been described previously (22,23,15). It readily explains the polyhedral structures observed by Iijima (ref. 25) and the close relationship between these particles and soot particles (ref 32) suggests most strongly that the same mechanism or one very closely related, applies in the combustion case. Soot particles are however round and not obviously polyhedral and we have found a plausible explanation of this (ref. 33). On the basis of some most interesting observations on the relative efficiencies with which various organic feedstocks form solid carbon in thermolysis reactions it was noted that the compound EtPh produces significantly more carbonaceous residue in the form of spheroidal microparticles than other related compounds, such as benzene. This has resulted in the refinement of the basic nucleation process by introducing a plausible reaction mechanism into what has heretofore been primarily a structural scheme. There is evidence that EtPh fragments under thermolysis conditions to form mainly C₄ species which are ideal primary

agents of network propagation. It is for instance fairly straightforward to construct C_{60} out of C_4 components in the pure carbon case:



The main process invoked is of course cycloaddition. It seems not unreasonable to invoke an analogous scenario involving partially hydrogenated C_4H_m radicals as intermediates in combustion and pyrolysis schemes where hydrogen is present. That related nucleation schemes operate in both cases is implied by the similarity of the resulting microparticles, i.e. the onion-like graphitic layer internal structures of soot and pure carbon. In addition the fact that we were able, from our pure carbon studies, to predict the presence of C_{60} in a sooting flame (as was subsequently confirmed (ref. 24)) gives significant further support to the icospiral nucleation mechanism as occurring during soot formation. It seems almost inconceivable that two totally different nucleation mechanisms producing such closely related structures are operating under these conditions.

It should be noted that pentagons are not really needed for closure in the presence of hydrogen. As a curving network grows holes in the shell should develop (33,15). This modification of network growth/wrapping results in a smoother rounder particle consistent with the spherical particles observed. Such a mechanism essentially indicates that the soot formation process involves adsorption of carbon fragments to the surface of the polyaromatic sheet followed by surface catalysed cycloaddition and integration into existing sheet as smoothly as possible forming further new surface for further network propagation.

This predicts a formation rate proportional to the particle's surface area as adsorption should be the rate-limiting step. In this scenario with such rapid network formation one might expect multiple growth sites which will rapidly spread across the surface causing imperfections in the basic spiral and including many local defects. As the spiral grows C-H and dangling bonds should be trapped as successive shells form. This seems quite reasonable as soot forms under conditions where the balance between C-C network and C-H bond formation is continually oscillating and thus such gaps in the network must occur as the icospiral grows.

A most intriguing aspect of the cage proposal is the possibility that species might be trapped inside. We have been able to produce a range of extremely stable monometallic carbon complexes whose properties are completely consistent with a metallofullerene structure. In particular such species as $C_{60}X$ ($X = La, K, Ca, Sr, Ba$) have been produced (ref. 34). This aspect leads on to a possibly important point with regard to the dissemination of radioactive nucleides in the atmosphere. In for instance, the Chernobyl disaster the fire must have resulted in an aerosol of soot-like microparticles which are extremely difficult to precipitate out. What we can note is the ready formation of alkali and alkaline earth complexes either completely caged fullerenes or essentially intercalated within the onion-like layers. This, allied to the lightness of the particles and the lack of reactivity of the graphite-like carbon mantles results in a dangerously mobile airborne transporter of radioactive elements such as ^{90}Sr . The itinerary of such a particle in the ecosphere is not difficult to imagine as it covers vast distances through the upper atmosphere finally to be ingested directly into the lung or perhaps carried to earth (and thus into the food chain) in a rain or snow drop for which it has formed the original nucleation site (ref. 1j).

CARBON IN SPACE

When polyynes and particles form in the laboratory the fullerenes always turn up as well, and this must be true in space also. It also seems likely that the cosmic particles associated with polyynes will be basically hydrogenated icospiral species with infrared signatures similar to polyaromatic hydrocarbons (PAH). Indeed the primordial solid particle may well have been carbon and if so it probably had icospiral structure. There is a set of infrared emission spectral features called the Unidentified Infrared Bands emitted by interstellar chemically bound material near some stars which have many features in common with PAH's (refs. 35,36) and thus also the particles discussed here. It is interesting to note that our curved particles differ from normal PAHs in that the edges are internal rather like those in the molecule kekulene first synthesised by Diederich and Staab (ref. 37). Indeed the internal C-H bonds of kekulene seem to give rise to bands which allow an even more satisfactory fit to the interstellar infrared data (ref. 38) than is provided by flat PAH material. Perhaps the most exciting observation to be made from a comparison of laboratory and astrophysical results is that there is very strong circumstantial evidence that C₆₀, most likely ionised, must be ubiquitously distributed in space (refs 39,15,40).

CONCLUSIONS

Perhaps some of the most intriguing consequences of the C₆₀ proposal concern organic chemistry. Why are polyaromatic systems flat? Indeed Almlöf has shown that pure carbon sheets are not going to be flat because they must have short benzyne bonds at the edge (ref. 41). The results here suggest that under conditions where C-H bonds cannot form and C-C bonds can, non-planar carbon networks may be more stable. Thus in high temperature (combustion/thermolytic) reactions the disparity between the aromatic C=C bond energy and that of the much weaker C-H bond allows simple thermodynamic arguments to dictate the structure of extended carbon aggregates. The number of molecules found in tars that possess five membered rings included in Clar's book (ref. 42) also should give pause for thought and in the present context are to be expected.

Most interestingly Fowler and Steer (43) have discovered an aromaticity rule which is the fullerene analogue of Hückel's $4n+2$ rule. The rule indicates that electronic stability occurs when the number of π electrons is $6n+60$ ($n=0,2,3,4\dots$). Thus it could be that we are entering a new age for just as the pre-columbian assumption that the earth was flat made way for a round world-view, it may be that post buckminsterfullerene, the traditional assumption that polyaromatic organic chemistry is essentially a flat field may also make way for a bright, non-planar future. As far as the smallest fullerene C₂₀ is concerned it must be the least stable member of the family and of course is the fully dehydrogenated analogue of dodecahedrane synthesised by Paquette and co-workers (44).

There has been much discussion about the name of C₆₀ (ref. 45) and of course there are many interesting possibilities. However it seems, as luck would have it, that the one chosen, buckminsterfullerene (ref. 14), though a little long has turned out to be a highly appropriate one. The wonderful geodesic domes of Buckminster Fuller (46) were the key to identifying the likely structure of C₆₀ and as there are many variants in size and shape of these domes, all having 5/6 ring structures, the family name fullerene is highly appropriate.

The work described here originated in a programme aimed at various fundamental aspects of chemistry such as: The stability of CH₃C≡N suggests that CH₃C≡P should also exist, according to simple Mendeleevian principles, though it might be reactive. The techniques developed to produce such unstable species allowed us to make and study the explosive polyynes and the reason to make these was an interest in delocalisation effects and molecular dynamics of flexing/rotating chain molecules. This led to the intriguing discovery of the long carbon chains in the space between the stars and the quest for their origin. It was during experiments which aimed at explaining the origin by simulating the conditions in carbon stars that we stumbled upon C₆₀ and finally turned out attention toward nucleation and soot particle formation.

It is worth noting that this last discovery, which is clearly of applied importance (particularly with regard to particle formation in combustion),

was made as a consequence of intrinsically fundamental research. It is vital to all aspects of science that the part played in discovery by research in which the primary drive is the solution of intellectually intriguing puzzles rather than the strategic significance of the goal is recognised as historically the most important in an overall social as well as economic context.

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