

- Society* (Wiley, New York, 1971), p. 262. Generalization of successional-climax paradigm with overshoot: E. P. Odum, *Science* **164**, 262 (1969).
9. E. T. Rabinowitch, *Photosynthesis* (Interscience, New York, 1946), vols. I and II; J. H. Connell and R. O. Slatyer, *Am. Nat.* **111**, 1119 (1977); J. H. Connell, *Science* **199**, 1302 (1978); S. Rinaldi, *IEEE Trans. Autom. Control* **15** (no. 6), 671 (1970); F. H. Bormann and G. E. Likens, *Pattern and Process in a Forested Ecosystem* (Springer-Verlag, New York, 1979).
 10. Fractal designs result when something is divided into fractions and then divided again and again and again. B. Mandelbrot, *Fractals* (Freeman, London, 1977).
 11. From 1967 to 1984 the names "energy cost" and "embodied energy" were used, and they proved ambiguous. In revising terminology, the author acknowledges collaboration with D. Scienceman of Bathurst, Australia, visiting research associate in Ecological Economics Program in Gainesville, 1983 to 1986, the name EMERGY ("energy memory" and "emergent property of energy use") and its unit the "emjoule" for our embodied energy concept, EMERGY-defined "emdollar" for foreign trade, and "empower" for rate of EMERGY use. See D. Scienceman, in *Environmental Economics*, G. Pillet and T. Murota, Eds. (Leimgruber, Geneva, Switzerland, 1987), pp. 257–276. Editor N. Polunin suggested a different spelling "enmergy" used by H. T. Odum, in *Ecosystem Theory and Application*, N. Polunin, Ed. (Wiley, New York, 1986), pp. 337–369.
 12. Our derivation showed an optimum efficiency for maximum power in transforming energy in systems selected for maximum power to be about half of the reversible efficiency. H. T. Odum and R. C. Pinkerton, *Am. Sci.* **43**, 321 (1955), confirmed independently by many authors as discussed elsewhere, H. T. Odum, *Ecol. Model.* **20**, 71 (1983). In most transformations there is also a step up in hierarchical level, which reduces efficiency as available energy goes into concentrating or otherwise upgrading energy quality. Most real transformations have more than one EMERGY input, each of different transformity.
 13. The phrase "energy transformation ratio" was used in my lecture at the award of the prize of the Institute de La Vie, Paris, in 1975. [Published version: H. T. Odum, *Trop. Ecol.* **16** (no. 1), 1 (1976).] The term "transformity" was substituted in 1984. Solar transformity of a flow or storage is now designated in units: solar emjoules per joule (sej/J) (11): One sej/J = 1 sek/kcal where sek is solar emkilocalories.
 14. Heat flow data from J. G. Sclater, G. Taupart, I. D. Galson, *Rev. Geophys. Space Phys.* **18**, 269 (1980). The solar transformity of the deep heat is inferred from Fig. 7 as the total global solar energy absorbed per year divided by the deep heat it contributes through the sedimentary cycle. The annual solar EMERGY budget of the two main sources together is 8.0 E24 sej/year. The tidal energy is another independent but smaller source. If one adds to this the solar EMERGY of current use of previously stored world fuels (1985 U.N. statistics: 2.78 E20 terajoules coal equivalents/year $\times 4 \text{ E4 sej/J} = 11 \text{ E24 sej/year}$), the world's budget expressed in solar EMERGY is temporarily higher (19 E24 sej/year).
 15. H. T. Odum and E. C. Odum, Eds., *Energy Analysis Overview of Nations* (International Institute of Applied Systems Analysis, Laxenburg, Austria, working paper WP-83-82, 1983) pp. 1–467; G. Pillet and H. T. Odum, *Z. Volkswirtschaft. Stat.* **3**, 409 (1984).
 16. H. T. Odum and E. C. Odum, *Ecology and Economics: EMERGY Analysis of the Texas System* (Special Report of the Lyndon B. Johnson School of Public Affairs and the Texas State Department of Agriculture, Austin, 1987), 184 pp. EMERGY analysis of other commodities were given in H. T. Odum, *Energy and Agriculture*, G. Stanhill, Ed. (Springer-Verlag, Berlin, 1984), pp. 24–51.
 17. A general introduction to principles may be found in H. T. Odum et al., *Energy, Environment, and Public Policy—A Guide to the Analysis of Systems*, United Nations Environment Programme (UNEP) Regional Seas Reports and Studies No. 95, (UNEP, Nairobi, Kenya, 1988), 109 pp.; H. T. Odum et al., *Environmental Systems and Public Policy*, Center for Wetlands, Phelps Laboratory (University of Florida, Gainesville, FL, 1987), 227 pp., with a Florida Supplement: *Florida Systems and Environment* (1986), 83 pp., that includes the details of the Florida EMERGY analysis. Some systems of energy accounting, such as input-output techniques, divide the incoming energies among the pathways of a web. However, solar EMERGY accounting is defined with different rules. In energy webs like Fig. 2, the solar EMERGY of any pathway is the total solar EMERGY required. By-product flows have the same EMERGY due to their common source and should not be added. Before adding the solar EMERGY of inputs, it is necessary to examine a larger system to determine if the sources are really independent. The EMERGY flow of a return feedback loop, as in Fig. 1c, is not added into the production process that it stimulates, since that would result in double counting.
 18. M. Tribus and E. C. McIrvine, *Sci. Am.* **225**, 179 (September 1971).
 19. See (2), p. 558. Meteorological and geological hierarchies are given in (2), chap. 26.
 20. H. T. Odum, in *Economic-Ecological Modeling, Studies in Regional Science and Urban Economics*, L. C. Braat and W. F. J. Lierop, Eds. (Elsevier, New York, 1987), vol. 16, chap. 13, pp. 203–251.
 21. H. T. Odum and E. C. Odum, *Energy Basis for Man and Nature* (McGraw-Hill, New York, ed. 2, 1982); unpublished manuscript.
 22. U.S. Bureau of the Census, *Statistical Abstract of the United States* (U.S. Government Printing Office, Washington, DC, 1987), pp. 120–138.
 23. I acknowledge my associates and students who have shared a lifetime mission to develop general systems theory of the ecosystem.

Space, Stars, C₆₀, and Soot

HAROLD KROTO

Although carbon has been subjected to far more study than all other elements put together, the buckminsterfullerene hollow-cage structure, recently proposed to account for the exceptional stability of the C₆₀ cluster, has shed a totally new and revealing light on several important aspects of carbon's chemical and physical properties that were quite unsuspected and others that were not previously well understood. Most significant is the discovery that C₆₀ appears to form spontaneously, and this has particularly important implications for particle formation in combustion and in space as well as for the

chemistry of polyaromatic compounds. The intriguing revelation that 12 pentagonal "defects" convert a planar hexagonal array of any size into a quasi-icosahedral cage explains why some intrinsically planar materials form quasi-crystalline particles, as appears to occur in the case of soot. Although the novel structural proposal has still to be unequivocally confirmed, this article pays particular attention to the way in which it provides convincing explanations of puzzling observations in several fields, so lending credence to the structure proposed for C₆₀.

IN THIS ARTICLE SOME EXCITING NEW AVENUES IN THE chemistry of one element, carbon, which are a consequence of the premise that the C₆₀ molecule has the high symmetry of a truncated icosahedron, are explored. We shall see that this novel proposal allows many pieces of the carbon chemistry jigsaw puzzle to fall neatly into place.

When David Walton, some years ago, introduced me to some polyyne ($\cdots\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}\cdots$) chain molecules that

he and his colleagues had made (1, 2), they called to mind the problems that a microscopic baton twirler would have in catching a baton that was flexing wildly as it spun in the air. To study this process quantum mechanically we, with Anthony Alexander, made $\text{H}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$ (HC₅N) and measured its microwave rota-

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tional frequencies (3). These measurements, which coincided with advances in the detection of molecules in space by radio astronomy pioneered by Townes and co-workers (4), led to a successful search for HC_5N in space with Takeshi Oka, Lorne Avery, Norman Broten, and John MacLeod (5). This detection was surprising at the time and it instigated further work, with Colin Kirby, on HC_7N (6) (Fig. 1a), which led to the even more surprising radio detection of it (Fig. 1b) (7) as well as the even longer HC_9N (8) and HC_{11}N (9). Many molecules appear to form in the cold interstellar medium by ion-molecule reactions as discussed by Herbst and Klemperer (10) and Dalgarno and Black (11). The chains were, however, peculiar, as

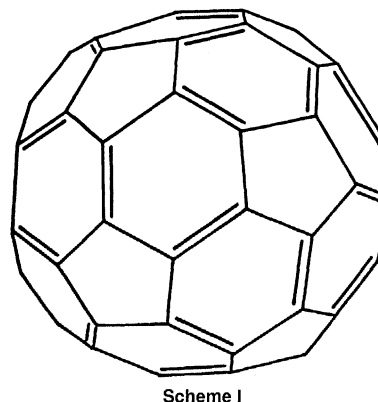
cool, carbon-rich, red giant stars, which are constantly puffing out copious quantities of dust, seemed more plausible sources (12). In such stars the possibility that some symbiotic chain/dust chemistry, perhaps related to soot formation (13), seemed worth considering and also susceptible to study on the basis of work by Hintenberger, Franzen, and Schuy (14) who had detected 33-atom species in carbon arcs in the 1960s. The possibility of detecting 33-atom polyynes chains in space seemed a wildly exciting prospect.

In a meeting with Robert Curl and Richard Smalley the possibility of simulating carbon star chemistry was proposed. Smalley and co-workers (15) had developed a powerful technique in which a laser vaporizes atoms of a refractory material, such as a metal, in a carrier gas (usually helium) where they reaggregate forming clusters which are then cooled by supersonic expansion, skimmed into a beam, and detected by laser photoionization mass spectrometry. The technique seemed ideal for the study of carbon cluster reactions and spectroscopy. The first carbon cluster-beam study was carried out by Rohlffing, Cox, and Kaldor who found clusters much larger than C_{33} but, most curiously, with only even numbers of atoms (16). Our project, to simulate carbon-star chemistry, was initiated some time later with graduate students Jim Heath and Sean O'Brien, and fascinating new results poured out from day one. Many details are given by Curl and Smalley (17) though in the interests of a self-consistent narrative and an insight into this author's perspective there is some overlap.

Carbon Cluster Results

Initially, cluster reactions were probed which showed that C_n ($n < 30$) clusters did indeed react with H and N to form polyynes, such as HC_7N and HC_9N (Fig. 1c) (18, 19), which had been detected in space, a result satisfyingly consistent with the idea of a stellar source of interstellar chains. The larger clusters were totally inert, and as the experiments progressed it became impossible to ignore the antics of the C_{60} peak which varied from relative insignificance to total dominance depending on the clustering conditions (Fig. 2, a through d).

After much discussion we conjectured that the bizarre behavior, particularly the dominance of C_{60} in Fig. 2c, could be the result of stabilization by closure of a graphitic net into a hollow chicken-wire cage similar to the geodesic domes of Buckminster Fuller (20) [Fig. 3 (21)]. Such closure would eliminate all 20 or so reactive edge bonds of a 60-atom flat sheet. This led to the realization that there was a most elegant and, at the time, overwhelming solution—the truncated icosahedron cage:



Scheme 1

This structure necessitated the throwing of all caution to the wind (the Greek icosahedron) and it was proposed immediately (22); after all, it was surely too perfect a solution to be wrong. We named C_{60}

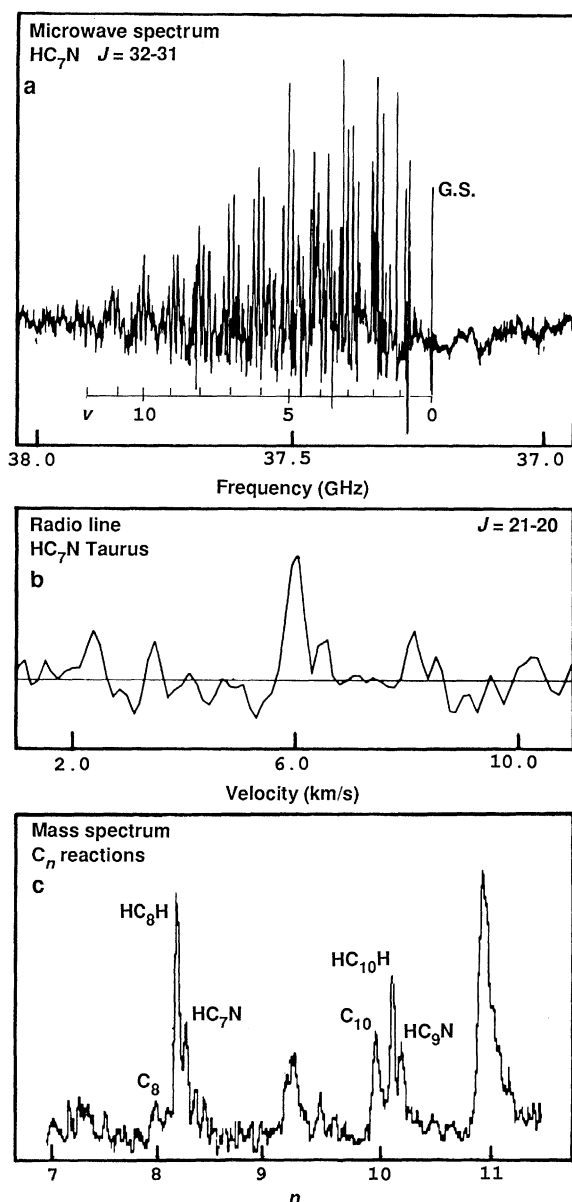


Fig. 1. Data on $\text{H}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{N}$. (a) A microwave rotational transition; J , rotational quantum number; ν , lowest binding vibrational quantum number. The “vibrationless” ground-state line is at the far right, G.S. ($\nu = 0$). Most of the molecules are, however, flexing violently as indicated by the multitude of bending vibrational satellites (all the other lines with $\nu > 0$). This is the quantum picture of the rotation/flexing process. (b) A rotational line detected by radio astronomy from a molecular cloud with a Doppler velocity of 6 km/s in the constellation of Taurus. (c) The mass spectrum of the C/H/N reaction. The bare C_8 and C_{10} peaks (at 8×12 and 10×12 amu positions, respectively) develop satellites at +2 amu for HC_8H and HC_{10}H and at +3 amu for HC_7N and HC_9N , respectively.

(23) after Buckminster Fuller, which has turned out to be a highly appropriate name. Subsequently Martyn Poliakoff, at Nottingham, drew our attention to an idea of David Jones who had, in a delightfully inventive article under the pseudonym of Daedalus in the *New Scientist*, already proposed such cages (24, 25). Jones showed that Euler's network closure requirement,

$$12 = 3n_3 + 2n_4 + 1n_5 + 0n_6 - 1n_7 - 2n_8 - \dots$$

(where n_k is the number of k -sided faces), applies. For carbon only $k = 5$ or 6 are likely (though $k = 7$ should not be overlooked) so 12 pentagonal faces are necessary though the number of hexagonal ones is arbitrary. Jones was influenced by Thompson who had pointed out, in his elegant book (26), that though a sheet of hexagons may

warp and bend, it can never close. In fact C_{60} itself had been predicted, first in 1970 by Osawa and Yoshida (27, 28) and later by Bochvar and Gal'pern (29, 30), Davidson (31), and (coincidentally with our discovery) Haymet (32).

Closed Fullerene Cages

In addition to the basic proviso that only even clusters can close perfectly, some simple physicochemical principles apply to closed 5/6-ring (fullerene) cages (33, 34). They predict stability if (i) curvature-related strain is symmetrically (geodesically) distributed, (ii) there is aromaticity, (iii) the electronic shell is closed, and (iv) pentagons are isolated as much as possible by hexagons to avoid the instability inherent in fused-pentagon configurations. These principles predict unique stability for C_{60} because it is the only 5/6-ring cage for which all atoms are equivalent (so strain is perfectly distributed); has 12,500 resonance forms (35)—slightly more than the archetypal aromatic benzene; should have a closed shell of electrons (36); and is, almost obviously, the smallest fullerene for which all pentagons can be isolated. General consideration of principle (iv) reveals that the next fullerene able to avoid abutting pentagons is, surprisingly, C_{70} (33, 34) (Fig. 4). This result, together with Fig. 2c, offers strong support for closure as a general phenomenon. Generalization of principle (iv) to the feasibility of isolating fused-pentagon multiplets suggests that C_{50} (Fig. 4) is relatively stable as it is the smallest cage that can avoid fused triplets (33, 34). Further analysis indicates that C_{20} is the least stable, C_{22} cannot exist, C_{24} is the first stabilized cage, and C_{28} is the first cage able to avoid directly fused quartets and be geodesically stabilized (Fig. 4). Thus closure predicts the rather unusual magic number sequence: 20, 24, 28, 32, 36, 50, 60, 70, with 22 totally anti-magic (33). This sequence is compellingly consistent with experiment; see, for instance, Fig. 5 (37). This leads to the inescapable conclusion that the whole set are fullerenes, and perhaps also are all the large even clusters in Fig. 2b as well as those off-scale. Note that odd-numbered clusters cannot close perfectly.

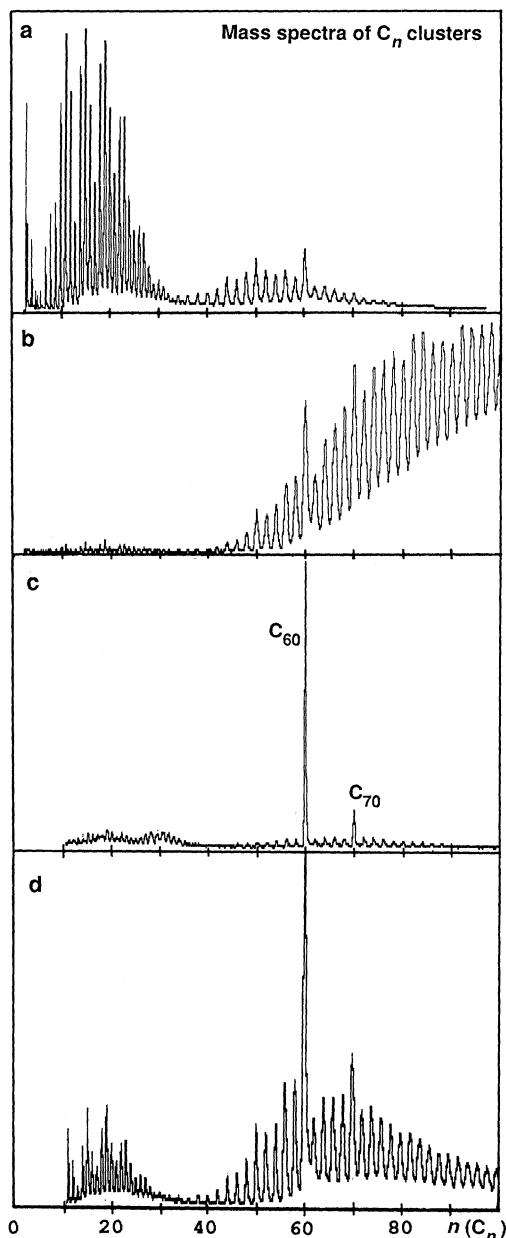


Fig. 2. Mass spectra under various conditions. (a) Moderate clustering: both polyynic chain precursors ($n < 36$) and fullerenes ($n > 20$) observed. (b) Significant clustering: only even clusters (all fullerenes?) detected. (c) Extensive clustering: C_{60} and C_{70} remain and appear to be dominant because the very large clusters are well above the detection range. (d) Clustering similar to (c) but at about 100 times the ionizing laser flux: extensive fragmentation of large clusters (particles) into fullerenes and chain precursors occurs.

The Icospiral Particle Nucleation Scheme

How could we have inadvertently synthesized C_{60} in 100 μ s when Paquette and co-workers had taken somewhat longer to make dodecahedrane, $C_{20}H_{20}$ (38)? How could the entropy factor inherent in the spontaneous creation of so symmetric an object from a chaotic plasma have been overcome? Herein lies the most important aspect of the discovery, and the answer appears to explain many puzzling features of the mysterious process that occurs whenever wood burns to form soot. It also seems to present a plausible mechanism for primordial particle formation in space. In addition to polyynes and particles, a new character, C_{60} , has emerged, whose shadowy role, like that of the Third Man, has only now come to light.

The answer itself is incredibly simple. Although the stability of graphite indicates that carbon must form hexagonal networks rather readily, we also know (now) that such networks cannot close perfectly. A moment's thought, however, suggests that, for a small sheet, energetics should favor closure owing to the bond energy released by eliminating the reactive edge. Indeed, triple (benzyne) bonds will make the edges curl anyway (39). To curve toward closure pentagons are necessary, and from the appearance of C_{60} we conclude that they must occur rather frequently. After all, saucer-shaped corannulene ($C_{20}H_{10}$, a pentagon surrounded by five hexagons) is stable (40) and pentagons are legion in tars (41). The

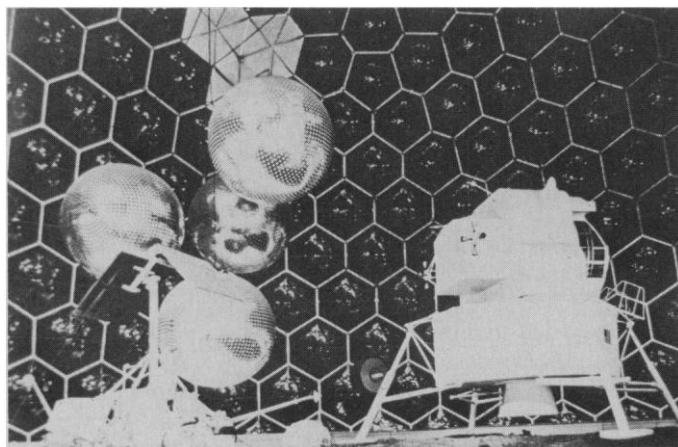


Fig. 3. View inside the U.S. pavilion at Expo 67 in Montreal (21). One pentagon is evident. Note that the hexagons are distorted. [With permission of Graphis Press, Zurich]

original nucleation scheme (42) has been refined by introducing epitaxial control along with the energetic considerations, and this has enabled a study, with Kenneth McKay, of the detailed structures of the resulting particles to be made (43). The initial hypothetical steps involve highly reactive open spiral shell (nautilus-like) embryos (Fig. 6). Smaller accreting carbon fragments are mopped up by adsorption on the surface of such shells and rapidly knit into the advancing edge. Polyene cross-linking is explosive so adsorption is probably rate-limiting, resulting in kinetics proportional to the surface area of the nucleus. Once the trailing edge has been bypassed (Fig. 6c), closure should be impossible (unless annealing takes place) and new network will form under epitaxial control so that the skin lies as closely as possible to 3.4 Å (the graphite interlayer spacing) above the lower layer (Fig. 6d). Now the peculiar 12- and only 12-pentagon closure requirement, together with epitaxy, result in a particle with a fascinating shape and internal structure.

Before describing this, we should recall that the aim of the mechanism was to account for the spontaneous creation of C_{60} . This is readily explained by the occasional, statistical closure during nucleation of a network with the correct disposition of pentagons. On closure C_{60} , along with other fullerenes, is unable to grow and is left behind as the rest "snowball" into giant particles. Ultimately we are left with C_{60} (and C_{70}) as the lone survivors, surrounded by large particles. That large particles are present is demonstrated by the crucial results in Fig. 2d, which show that they can be photofragmented into smaller, detectable species by high-power laser radiation. Probably the less stable fullerenes are attacked and devoured by

a host of voracious carbon particles. This scenario suggests that early C_{60} signals might include contributions from closed isomers that react to form large clusters or rearrange to the ultrastable C_{60} itself.

To predict the structures of the large particles, symmetric giant fullerenes with up to 6000 atoms have been constructed as a preliminary to computer study. This yielded an unexpected result in that, as the fullerenes evolve to ever larger structures, the more or less round shape of the small ones metamorphoses into a more or less icosahedral shape (Fig. 7). The truncation remains, but at microscopic dimensions, forming 12 effective cusps in a smoothly warping single continuous plane of hexagons. The giant fullerenes are essentially the structures of Daedalus (24, 25), but they are not round. A puzzle in the analogy with the geodesic domes was herewith resolved: In the domes the lengths of the struts near the pentagons are very unequal (Fig. 3) (21), and this is necessary to achieve a smooth round shape. Carbon bonds, on the other hand, will not "conveniently" extend and contract and so the bulk of the curvature is focused at the 12 cusps. An intriguing way to consider this surface is as a single sheet of hexagonal graphite with 12 pentagonal defects (only 12, whatever the size) systematically inserted during growth to form an essentially continuous icosahedral monosurface. The growing onion-like particle would have a distorted icosahedral shape, and, as epitaxy causes the cusps to lie more or less above each other, the resulting polyhedral shells will be effectively similar in the geometric sense (43).

This result enabled a further puzzling result to fall neatly into place. Sumio Iijima had drawn our attention to his beautiful electron microscope pictures of carbon particles taken in 1980 (44), which showed concentric graphitic shell internal structure with polyhedral shapes (Fig. 8). The scheme explains such particles as quasi-icosahedral spirals, which are quasi-crystals of graphite composed entirely of sp^2 hybridized carbon. There are 20 pyramidal graphite microcrystallite wedges, the layers of which curve into the layers of those that abut on the three internal faces. C_{60} should not lie at the center of the particle. It is intriguing that the icospiral shell, which does not appear to have been discussed previously, combines the two most biomimetic shapes, the helix and the icosahedron.

Soot

The scheme predicts C_{60} to be a by-product of soot formation (42), and it is most satisfying that significant support for the C_{60} proposal is provided by the work of Gerhardt, Löffler, and Homann who recently found that C_{60}^+ is indeed a dominant ion in a sooting flame (45). As there is much hydrogen in soot, the question arises as to where it is. The answer may lie in the fact that there is no necessity for pentagons to form stable more or less closed structures in the

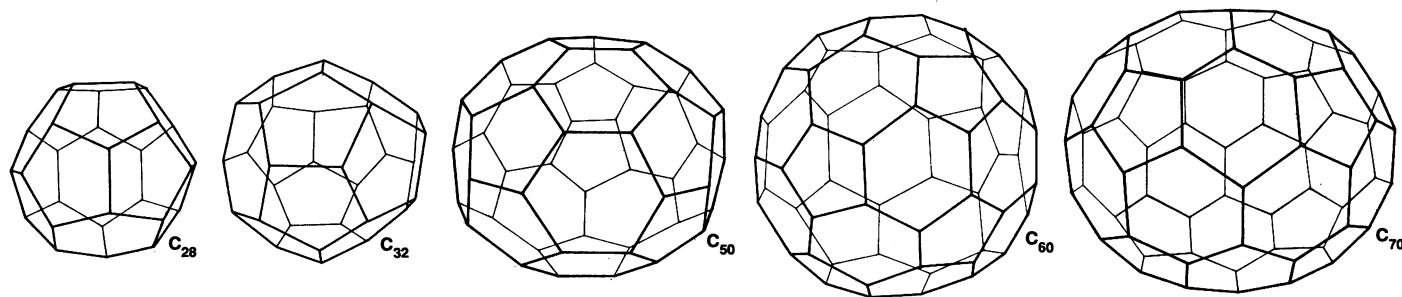
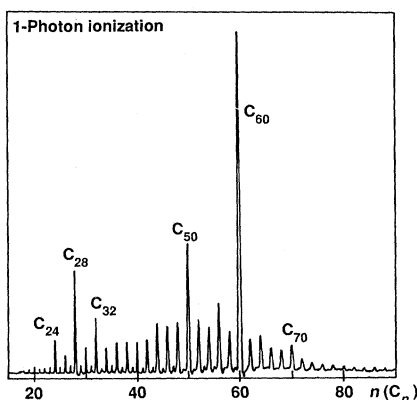


Fig. 4. Five "magic" fullerenes. C_{28} is a very interesting tetrahedral molecule with a striking family resemblance to Gomberg's stable free radical triphenylmethyl, $\cdot C(C_6H_5)_3$, the first organic free radical and the forerunner of free radical chemistry. C_{32} , here viewed more or less along its threefold axis, is handed. One of two feasible C_{50} semistable isomers is shown and the one and only C_{60} buckminsterfullerene. C_{70} is formed by separating two halves of C_{60} by a ring of ten extra atoms to form a U.S. football.

Fig. 5. A particularly interesting spectrum taken from the data of Cox *et al.* (37). The correspondence with the magic fullerene sequence, 24, 28, 32, 50, 60, and 70 (33), is compelling evidence for closure. Note that only C_{60} and C_{70} are ultrastable (Fig. 2c). The sharp cutoff at C_{24} is particularly satisfying as no C_{22} fullerene is possible.



presence of hydrogen (43, 46); stability can be achieved simply with hexagonal nets and internal C–H bonds (Fig. 9). Soot forms under conditions where the balance between the C–C network and C–H bond formation is continually oscillating and thus gaps in the network must occur as an icospiral grows. This will spoil the particle's polyhedral angularity as epitaxial control is lost and gaps—perhaps large ones—are covered over, trapping C–H and dangling bonds in a three-dimensional spiral with a smoother, more spheroidal shape (46).

Cosmic C_{60}

When polyynes and particles form in the laboratory, the fullerenes always turn up as well (Fig. 2). As this must also be true in space, it is worth considering the possible astrophysical consequences of C_{60} , the other fullerenes, and icospiral particles (47–50). It should be

stressed that the consequences are based on the experimental observations and are for the most part totally independent of the structure proposal, which must still be considered circumstantial though it does tie the whole picture together in a most neat and satisfying way.

It seems likely that the cosmic particles associated with polyynes will have basic icospiral structure with varying degrees of hydrogenation. Such species will have infrared signatures similar to those of polyaromatic hydrocarbons (PAH). Indeed, that vital link in planet formation, the primordial solid particle, may well have been carbonaceous and if so it too could have had icospiral structure. The infrared emission from interstellar material near some stars has features consistent with PAH-like material (51, 52) and thus also the particles discussed here. Indeed, the presence of internal C–H bonds such as those in Fig. 9 gives rise to bands that allow an even more satisfactory fit to the interstellar data (53).

Rieu, Winnberg, and Bujarrabal (54) recently found HC_7N outside the Egg Nebula, which is a dust cloud (55) surrounding a star (Fig. 10). This suggests that polyynes are produced by ambient starlight photofragmentation of dust (56). As chains and fullerenes also form during particle nucleation (Fig. 2, a through c) and again during particle photofragmentation (Fig. 2d), we may conclude that C_{60} and other fullerenes are also produced and can survive together with polyynes in the Egg's extended envelope as well as other interstellar regions where chains and dust occur. The results presented in Fig. 2 show that a family of carbon species with 30 to 100 atoms is formed on carbon nucleation and on carbon photofragmentation, suggesting some degree of resilience. The dimensions of these species must be $\sim 8 \pm 2$ Å, a result independent of the structure. This experimental observation ties in intriguingly well (56) with the interesting suggestion by Sellgren that certain interstellar infrared features are consistent with emission from particles with dimensions of ~ 10 Å (57).

Fig. 6. The icospiral nucleation process starts with a reactive saucer-shaped (corannulene) C_{20} (a) and grows by accretion via the half-shell (b) to (c), where edge bypass has occurred, and then on to (d), where the second growth shell is forming under epitaxial control. Statistical closure at stage (c) is proposed as the explanation for fullerene formation.

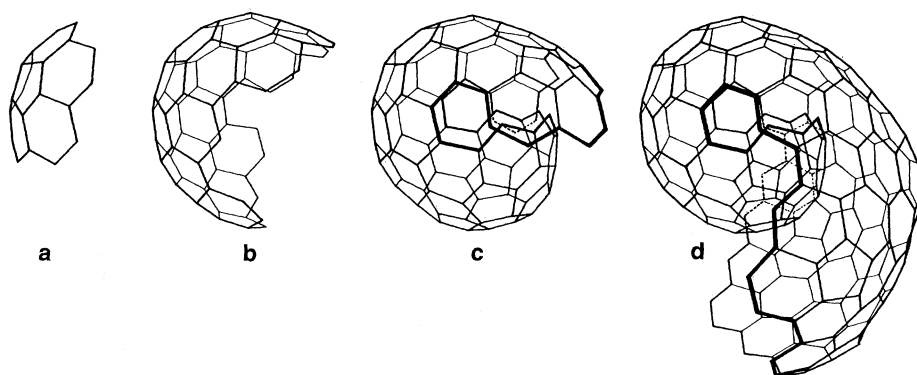
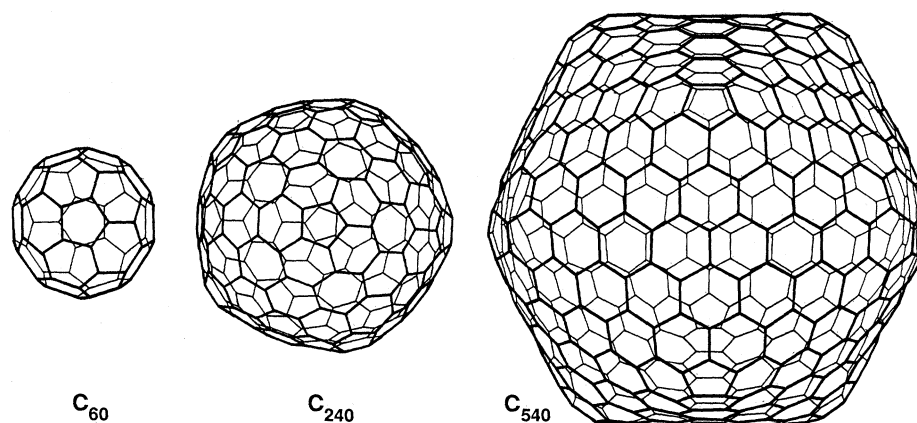


Fig. 7. C_{60} , C_{240} , and C_{540} with relative diameters 1:2:3. The rapid shift toward icosahedral shape is dramatic. The objects are really truncated but the truncation remains at microscopic dimensions as the cluster grows to macroscopic size. The surface thus becomes a smoothly curving net with 20 more or less flat triangular segments connecting the 12 cusps as in an icosahedron.



The ubiquitously distributed molecular material responsible for the Diffuse Interstellar Bands (58) has remained a mystery for decades, and there have been numerous conjectures as to the identity of the carrier. The most important aspect of the problem is that there are not many spectroscopic features, about 40, and so very few carriers can be responsible and they must be very stable to starlight. The carbon nucleation scheme is unique in that it alone offers a scenario for the production of relatively few stable large species from a chaotic interstellar mix. Starlight will ionize much of the interstellar C_{60} present and so C_{60}^+ should be ubiquitously distributed in space, making it a viable candidate for the carrier (47, 49, 50). Again, this is an experimental conclusion quite independent of the structure proposed for C_{60} . Heath *et al.* (59) have detected a weak absorption feature for neutral C_{60} which does not coincide with any known diffuse feature. Similar arguments to the above hold for another puzzling interstellar feature, the 2170 Å band. The ease of formation and the resilience of metallofullerene caged-metal complexes (60) indicate that they also must be abundant in space. Optical spectra of such species as $C_{60}Na$, $C_{60}K$, and $C_{60}Ca$, most probably ionized, are also worthy of consideration (47, 49).

Some interesting isotope anomalies occur in some meteorites (61), and it is possible that the metallofullerenes could play a role (62) in, for instance, the case of the high abundance of ^{22}Ne (63). Clayton has pointed out that as large amounts of ^{22}Na , which decays via β^+ emission to ^{22}Ne with a 2.6-year half-life, are ejected from the helium shells of supernovae and the surface explosions of novae, this element should precipitate in intimate chemical association with any surrounding dust as ejected material expands and rapidly cools (64). Such conditions seem ideal for the formation of C_nNa metallofullerenes in which ^{22}Na decay produces caged ^{22}Ne which cannot escape (62). Such species, occluded in carbonaceous chondrites, offer

support for the suggestion that the ^{22}Ne is an extinct radioactive anomaly bearing witness to the meteorite's presolar origin (64). Alkali and alkaline-earth metals readily intercalate in carbon particles, an observation consistent with the icospiral graphite model. The aggregation of a mix of metallofullerenes and particles with intercalated atoms suggests entrapment sites of at least two kinds for which there is some evidence (61). The icospiral particle might also provide a convenient nucleus for efficient pressure- or shockwave-induced metamorphosis to diamond (62), perhaps bearing on the recent exciting discovery of diamond-like domains in meteorites (65). In this case a third possible trapping site is suggested, as such a scenario leads to diamond zones with significant impurity loads.

Discussion

There is a serious note to the story relating to the Chernobyl disaster. The icospiral is a perfect vehicle for windborne dispersal of

Fig. 9. Hydrofullerenes have hydrogen atoms (open circles) replacing carbon atoms (hatched circles) at the pentagonal cusps.

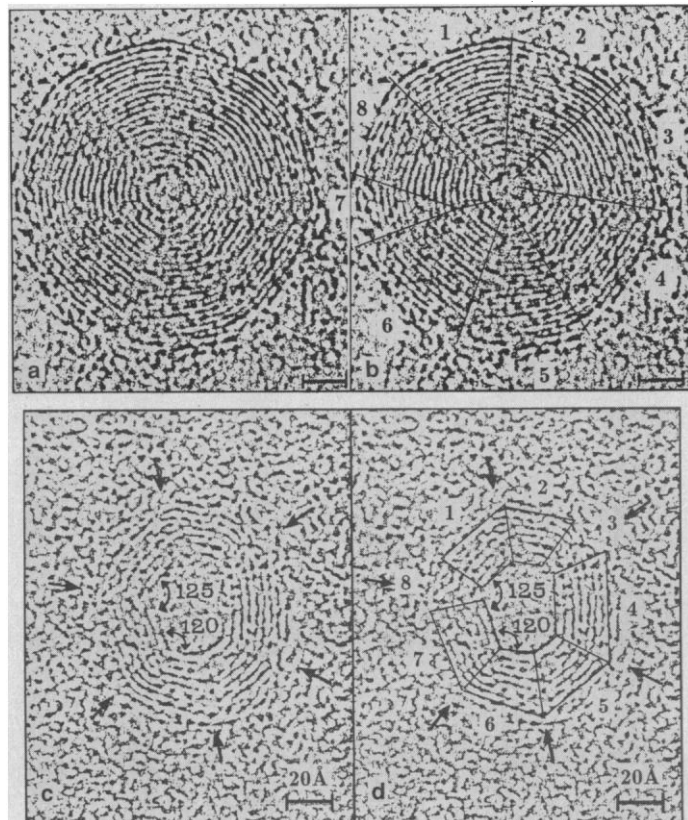
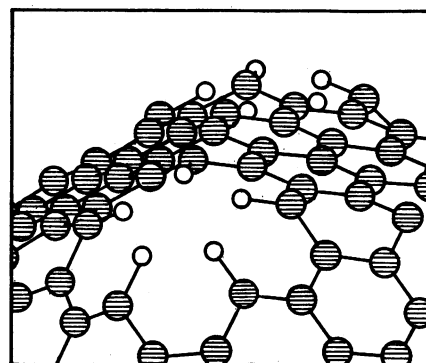


Fig. 8. Particles photographed by Sumio Iijima (44) which show clear evidence of polyhedral concentric shell structure consistent with the icospiral graphite particle model. At the right the contours are delineated.

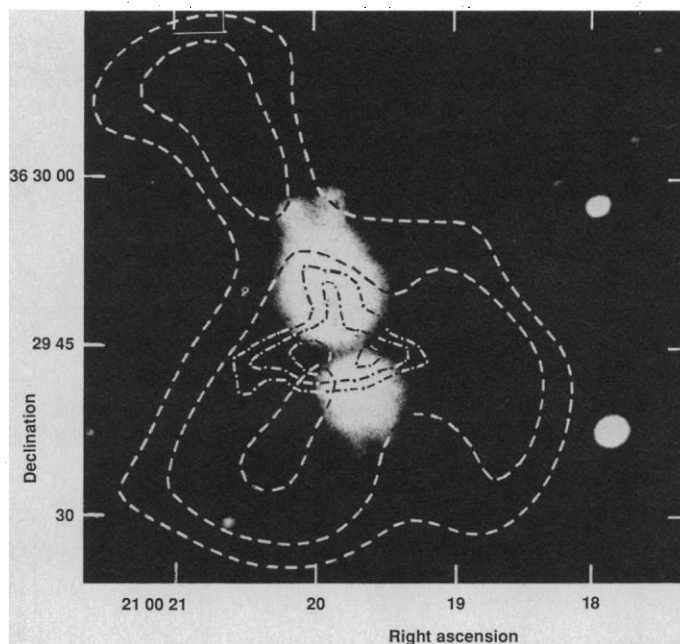


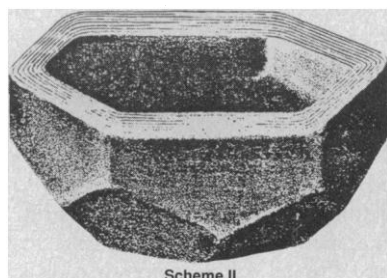
Fig. 10. Map of HC_7N (---) and NH_3 (- · - · -) from Rieu *et al.* (54) superimposed on a photograph of the Egg Nebula scattering (55). The dust emanates in two lobes from a central star. These data suggest that HC_7N results from fragmentation of carbonaceous dust by starlight; compare with Fig. 2d. Laboratory data (Fig. 2) indicate that even carbon clusters, in particular C_{60} (most likely ionized as C_{60}^+), must be present along with chains.

trapped (radioactive) atoms. This recalls the Minotaur imprisoned in a maze designed (coincidentally) by the original Daedalus, the great craftsman of antiquity. Unfortunately in this case the prisoner need not escape to cause havoc.

A rather esoteric interest in quantum molecular dynamics led to the discovery of long chains in space and subsequently the discovery of C_{60} , the icosahedral carbon particle, and the associated nucleation scheme. The associated prediction that C_{60} should be a by-product of combustion and a key to the soot formation process is a prime example of the way in which an interest in fundamental problems for their own intrinsic sake, irrespective of their predicted use, can yield results of applied significance.

If the spontaneous C_{60} formation proposal is correct, and as we have seen all the observations augur well, then a new direction in organic chemistry is presaged. Under the correct conditions, presumably those which favor sp^2 carbon network formation (perhaps under epitaxial control) at the expense of other pathways, puckered nets and closed cages should be susceptible to synthesis. Indeed, there is some evidence in the elegant corannulene synthesis of Barth and Lawton (40) that the step in which saucer shape was achieved may be more favored than some flat-earth chemists might think.

For me the most intriguing revelation of the whole C_{60} story has been the realization that the inclusion of pentagonal, or effectively pentagonal, defects in the propagating front of a growing layer results in cusps; and with but 12 cusps an icosahedral shell results, whatever the size. It seems likely that this is the solution to a wide range of problems such as, for instance, the formation of suspensions of materials that tend to form layers and the microscopic structures of intrinsically layered materials. There does not now seem to be any reason why any molecular or atomic array should grow as a perfectly flat plane unless epitaxially restricted to do so. In fact, energetics at the microscopic level suggests that materials should form under the influence of the mysterious, ubiquitous, and all-powerful icosahedral template. It is thus very intriguing to find



Scheme II

hidden in the carbon literature this schematic drawing by Heydenreich, Hess, and Ban of a graphitized carbon black particle, 500 million pounds of which were produced in the United States in 1968 (66).

REFERENCES AND NOTES

1. R. Eastmond, T. R. Johnson, D. R. M. Walton, *Tetrahedron* **28**, 4601 (1972).
2. B. F. Coles, P. B. Hitchcock, D. R. M. Walton, *J. Chem. Soc. Dalton Trans.* **1975**, 442 (1975).
3. A. J. Alexander, H. W. Kroto, D. R. M. Walton, *J. Mol. Spectrosc.* **62**, 175 (1976).
4. A. C. Cheung, D. M. Rank, C. H. Townes, D. C. Thornton, W. J. Welch, *Phys. Rev. Lett.* **21**, 1701 (1968).
5. L. W. Avery, N. W. Broten, J. M. MacLeod, T. Oka, H. W. Kroto, *Astrophys. J.* **205**, L173 (1976).
6. C. Kirby, H. W. Kroto, D. R. M. Walton, *J. Mol. Spectrosc.* **83**, 26 (1980).
7. H. W. Kroto *et al.*, *Astrophys. J.* **219**, L133 (1978).
8. N. W. Broten, T. Oka, L. W. Avery, J. M. MacLeod, H. W. Kroto, *ibid.* **223**, L105 (1978).
9. M. B. Bell, S. Kwok, P. A. Feldman, H. E. Matthews, *Nature* **295**, 389 (1982).
10. E. Herbst and W. Klemperer, *Astrophys. J.* **185**, 505 (1973).
11. A. Dalgarno and J. H. Black, *Rep. Prog. Phys.* **39**, 573 (1976).
12. H. W. Kroto, *Int. Rev. Phys. Chem.* **1**, 309 (1981).
13. ———, *Chem. Soc. Rev.* **11**, 435 (1982).
14. V. H. Hintenberger, J. Franzen, K. D. Schuy, *Z. Naturforsch. Teil A* **18**, 1236 (1963).
15. J. B. Hopkins, P. R. R. Langridge-Smith, M. D. Morse, R. E. Smalley, *J. Chem. Phys.* **78**, 1627 (1983).
16. E. A. Rohlfing, D. M. Cox, A. Kaldor, *ibid.* **81**, 3322 (1984).
17. R. F. Curl and R. E. Smalley, *Science* **242**, 1017 (1988).
18. J. R. Heath, Q. Zhang, S. C. O'Brien, R. F. Curl, H. W. Kroto, R. E. Smalley, *J. Am. Chem. Soc.* **109**, 359 (1987).
19. H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, R. E. Smalley, *Astrophys. J.* **314**, 352 (1987).
20. R. B. Fuller, *Inventions—The Patented Works of Buckminster Fuller* (St. Martin's Press, New York, 1983).
21. M. Proulx (photographer), *Graphis* **132**, 378 (1967) (Graphis Press, Zurich).
22. H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, R. E. Smalley, *Nature* **318**, 162 (1985).
23. A. Nickon and E. F. Silversmith, *Organic Chemistry—The Name Game: Modern Coined Terms and Their Origins* (Pergamon, New York, 1987).
24. D. E. H. Jones, *New Sci.* (3 November 1966), p. 245.
25. ———, *The Inventions of Daedalus* (Freeman, Oxford, 1982), pp. 118–119.
26. D. W. Thompson, *On Growth and Form* (Cambridge Univ. Press, Cambridge, 1942).
27. E. Osawa, *Kagaku (Kyoto)* **25**, 854 (1970) (in Japanese).
28. Z. Yoshida and E. Osawa, *Aromaticity* (Kagakudojin, Kyoto, 1971) (in Japanese).
29. D. A. Bochvar and E. G. Gal'pern, *Dokl. Akad. Nauk SSSR* **209**, 610 (1973) [English translation, **209**, 239 (1973)].
30. I. V. Stankevich, M. V. Nikerov, D. A. Bochvar, *Russ. Chem. Rev.* **53**, 640 (1984).
31. R. A. Davidson, *Theor. Chim. Acta* **58**, 193 (1981).
32. A. D. J. Haymet, *J. Am. Chem. Soc.* **108**, 319 (1986).
33. H. W. Kroto, *Nature* **329**, 529 (1987).
34. T. G. Schmalz, W. A. Seitz, D. J. Klein, G. E. Hite, *J. Am. Chem. Soc.* **110**, 1113 (1988).
35. D. J. Klein, T. G. Schmalz, G. E. Hite, W. A. Seitz, *ibid.* **108**, 1301 (1986).
36. P. W. Fowler and J. I. Steer, *J. Chem. Soc. Chem. Commun.* **1987**, 1403 (1987).
37. D. M. Cox, K. C. Reichmann, A. Kaldor, *J. Am. Chem. Soc.* **110**, 1588 (1988).
38. L. A. Paquette, R. J. Ternansky, D. W. Balogh, G. Kentgen, *ibid.* **105**, 5446 (1983).
39. J. Almlöf, in *Carbon in the Galaxy*, S. Chang, Ed. (National Aeronautics and Space Administration, Washington, DC, in press).
40. W. E. Barth and R. G. Lawton, *J. Am. Chem. Soc.* **93**, 1730 (1971).
41. E. Clar, *Polycyclic Hydrocarbons* (Academic Press, New York, 1964), vols. 1 and 2.
42. Q. L. Zhang *et al.*, *J. Phys. Chem.* **90**, 525 (1986).
43. H. W. Kroto and K. G. McKay, *Nature* **331**, 328 (1988).
44. S. Iijima, *J. Cryst. Growth* **50**, 675 (1980).
45. P. H. Gerhardt, S. Löffler, K. H. Homann, *Chem. Phys. Lett.* **137**, 306 (1987).
46. H. W. Kroto, K. G. McKay, D. R. M. Walton, S. G. Wood, in preparation.
47. H. W. Kroto, in *Polycyclic Aromatic Hydrocarbons and Astrophysics*, A. Leger *et al.*, Eds. (Reidel, Dordrecht, 1987), p. 197.
48. ———, *Proc. R. Inst. G.B.* **58**, 45 (1986).
49. ———, *Philos. Trans. R. Soc. London Ser. A* **325**, 405 (1988).
50. ———, in *Carbon in the Galaxy*, S. Chang, Ed. (National Aeronautics and Space Administration, Washington, DC, in press).
51. W. W. Duley and D. A. Williams, *Mon. Not. R. Astron. Soc.* **196**, 269 (1981).
52. A. Leger and J. L. Puget, *Astron. Astrophys.* **137**, L5 (1984).
53. H. W. Kroto, in preparation.
54. Nguyen-Q-Rieu, A. Winnberg, V. Bujarrabal, *Astron. Astrophys.* **165**, 204 (1986).
55. E. P. Ney, K. M. Merrill, E. E. Becklin, G. Neugebauer, C. G. Wynn-Williams, *Astrophys. J.* **198**, L129 (1975).
56. H. W. Kroto and M. Jura, in preparation.
57. K. Sellgren, *Astrophys. J.* **277**, 623 (1984).
58. G. H. Herbig, *ibid.* **196**, 129 (1975).
59. J. R. Heath, R. F. Curl, R. E. Smalley, *J. Chem. Phys.* **87**, 4236 (1987).
60. J. R. Heath *et al.*, *J. Am. Chem. Soc.* **107**, 7779 (1985).
61. E. Anders, in *Meteorites and the Early Solar System*, J. F. Kerridge, Ed. (Univ. of Arizona Press, Tucson, 1987), chap. 13.1.
62. K. McKay, L. Dunne, H. W. Kroto, in preparation.
63. D. C. Black and R. O. Pepin, *Earth Planet. Sci. Lett.* **6**, 395 (1969).
64. D. D. Clayton, *Nature* **257**, 36 (1975).
65. R. S. Lewis, T. Ming, J. F. Wacker, E. Anders, E. Steel, *ibid.* **326**, 160 (1987).
66. R. D. Heydenreich, W. M. Hess, L. L. Ban, *J. Appl. Crystallogr.* **1**, 1 (1968).

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