The Third Allotropic Form of Carbon

By *J. Fraser Stoddart**

From Fiction to Fact. Every so often something happens in science that is extremely simple and immensely satisfying. The harvesting of C_{60} in the late summer of last year by *Krätschmer* and his associates[1] from a rather special brew of soot has vindicated the inspired structural proposal—the celebrated truncated icosahedron with the ultimate symbol (I_h) in point group symmetry that also happens to grace the familiar pattern displayed on regulation soccer balls—advanced away back in the mid-80s by *Kroto* and his collaborators[2] for a compound they dubbed buckminsterfullerene, molecules of which they had clearly observed by time-of-flight mass spectrometry following vaporization of graphite by laser evaporation.

Prior knowledge by most in the field of the autumnal announcement[1] in *Nature* heralded a flurry of activity in numerous research laboratories around the world. Now that sample tube quantities of this new race of carbon compounds are available, this third allotropic form of carbon promises to create chemistry and aid and abet applications around it every bit as rich as those associated with the ubiquitous and rare allotropes—graphite and diamond, with their diversely distinctive properties and distinctly diverse uses.

Harvesting the soot. At present, access to milligram quantities of C_{60}, and its rugby ball counterpart, C_{70} (Fig. 1) depends on perfecting simultaneously two separate arts—firstly, isolating fullerene-rich soot in gram quantities, apparently best achieved when graphite rods of uniform particle size are evaporated by resistive heating under a partial atmosphere of an inert gas like helium[1] or argon[3] and then, secondly, effecting the demanding chromatographic separation of C_{60} from C_{70}, both of which are to be found in boiling benzene extracts of the soot. The top yield reported for this harvest at the onset of winter was a remarkable 14% by *Diederich* and his team at UCLA[4] who have employed a battery of chromatographic and spectroscopic techniques to show that their soot is 85:15, C_{60}:C_{70}. Although chromatography has been executed with modest success using hexane as the eluant on both alumina[3,4] and silica gel,[5] fractional sublimation[1,6] at very high temperatures (ca. 600 °C) under vacuum from an inert atmophere should be amenable to the large scale manufacture of this new product line of carbon. It is surely only a matter of time until both physical and chemical means of isolation are perfected to a point where kilograms of C_{60}, C_{70}, and other homologues, can be stored in bottles. And there is promise[5] of even better things to come—the preparation of C_{60} and C_{70} starting from precursors other than graphite.

Believing is Seeing. Both C_{60} and C_{70} are highly colored crystalline solids that are sparingly soluble in common organic solvents, giving rise to solutions with pinkish-to-red hues to them. The UV-VIS spectra of C_{60} both neat[1] and in solution[3,4] reveal three, if not four, broad bands of considerable intensities in the UV that correspond roughly with the allowed transitions predicted by theory for the molecule.

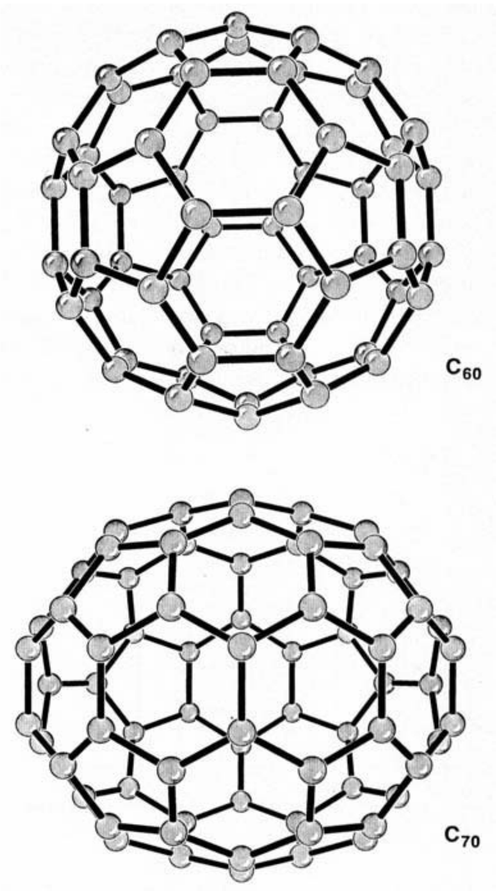

Fig. 1. Drawings of the proposed molecular structures for C_{60} (top) and C_{70} (bottom). Reproduced by permission of Professor *F. Diederich*, Los Angeles.

The chemical world awaits a detailed single crystal X-ray diffraction analysis of the structure of C_{60} or C_{70}, or more likely perhaps, of a derivative in the first instance. In the meantime, X-ray diffraction studies[1] on micrometer sized hexagonal platelets of C_{60}, with unit cell parameters of 10.02 and 16.36 Å, correspond closely to a simple hexagonal close packing of disordered spherical molecules.[7] These days STM is all the rage for seeing images of molecules very often sitting on a surface of graphite! Late in December two reports appeared in which the imaging of C_{60} and the slightly taller C_{70} with a scanning tunnelling microscope is described.[8]

Seeing is Believing. The weight of the spectroscopic evidence for the structures proposed[2] for C_{60} and C_{70} is overwhelming. There is agreement from at least four camps[1,3,5,9] that the four strongest bands for C_{60} in conventional KBr pellets of soot extracts in various states of purification appear at 1430, 1182, 577, and 527 cm^{-1}. Almost identical spectra were observed[9] from argon and krypton matrices deposited on gold substrates, indicating that the solid state absorptions are close to the gas phase ones.

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The findings[1, 3, 5] of mass spectrometry are equally convincing. Both the EI and FAB methods reveal strong molecular ions at m/z 720 and 840 for C_{60} and C_{70}, respectively. The EIMS shows[5] the expected isotopic distribution patterns with the $[M+1]^{\oplus}$ intensities for C_{60} and C_{70}, 61% and 67%, respectively, of the $M^{\oplus}$ peak. Interestingly, the $C_{60}^{2\oplus}$ ion is detected[5] in appreciable quantities when EI spectra are run at high (70 eV) ionization energies, confirming the amazing stability of the C_{60} carbon cage.

Since C_{60} has I_h symmetry, all its carbon atoms are equivalent. Thus, the ^{13}C NMR spectrum should display one, and only one, signal. It does.[3-6] In a C_6D_6 solution, the single peak is observed at $\delta = 143.2$ (Fig. 2). For C_{70}, with its D_{5h} symmetry, we should observe five signals—two, both with twice the intensities of the other three. Indeed, when a long 20 second pulse delay was used[5] to make allowances for the relatively long T_1 values, the ^{13}C NMR spectrum, also recorded in a C_6D_6 solution (Fig. 2), revealed[5] peaks at $\delta = 150.7$ (a), 147.4 (b), 148.1 (c), 145.4 (d) and 130.9 (e) in the ratio of 10:10:20:20:10 as expected for C_{70}.

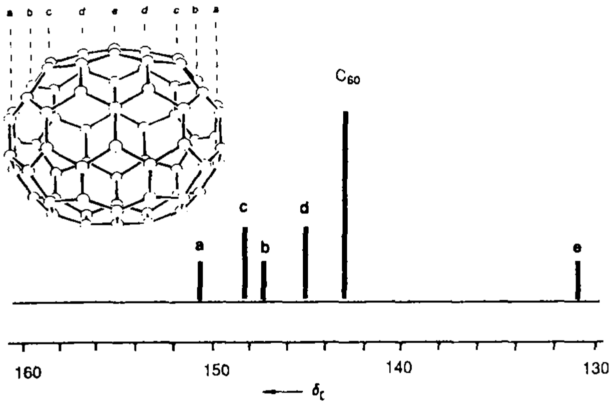

Fig. 2. A ^{13}C NMR line spectrum of a mixture of C_{60} and C_{70}. The five sets (a–e) of identical carbon atoms lie in the vertical planes as indicated on the inset schematic diagram of C_{70}. The assignments are those given in [3]. The schematic diagram is reproduced by permission of Professor *H. W. Kroto*, Brighton.

The Proof of the Pudding is in the Eating. Now that C_{60} and C_{70} exist as authentic crystalline samples, can any chemistry be done with them? The answer is yes according to *Smalley* et al.[9] They have found that C_{60} undergoes a Birch reduction [Eq. (a)] to give a product, which is a mixture of

$$C_{60} \underset{\text{DDQ/Toluene}}{\overset{\text{Li/liquid NH}_3/t\text{BuOH}}{\rightleftharpoons}} C_{60}H_{36} \qquad \text{(a)}$$

isomers with the molecular formula $C_{60}H_{36}$. The fact that treatment of this hydrogenated product with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in toluene produces a substance indistinguishable from authentic buckminsterfullerene demonstrates that the reduction of C_{60} is fully reversible, indicating that no alteration occurs to the carbon skeleton of the molecule during its Birch reduction.

In CH_2Cl_2 with $n\text{Bu}_4\text{NBF}_4$ as the supporting electrolyte, C_{60} undergoes electrochemical reduction in two waves at − 610 mV and − 1000 mV relative to the normal hydrogen electrode [Eq. (b)]. This electrochemical behavior[10] suggests that stable salts based on C_{60} as either an anion or dianion might be on the cards.

$$C_{60} \underset{-\,e}{\overset{+\,e}{\rightleftharpoons}} C_{60}^{\ominus} \underset{-\,e}{\overset{+\,e}{\rightleftharpoons}} C_{60}^{2\ominus} \qquad \text{(b)}$$

The photophysical properties of C_{60} have also been studied recently. It is a potential generator of singlet oxygen.[11]

From Fact to Fiction. Confronted with molecules as pretty and as fascinating as C_{60} and C_{70}, the human imagination starts to run riot. Will they behave as the ultimate in lubricants, i.e. as molecular ball-bearings? The materials science of carbon is on the move again.

Then, smaller molecules and ions, which can no doubt be trapped inside the carbon cages, are expected to have a rather unique chemistry. One can also envisage the introduction of holes and even trap doors into the surfaces of the carbon cages, leading to the possibility of dialysis at the molecular level or the controlled slow release of bioactive molecules. The pharmaceutical and agrochemical industries should not be disinterested in the post-Columbus chemistry of carbon.

And then, there is the prospect of doing outer and inner sphere chemistry, particularly with transition metals. To what extent can chemical species that are imprisoned, not only covalently but also mechanically inside fullerenes, influence their optical and redox properties? Can much larger fullerenes,[12] like C_{540}, be made and can one be assembled onion-like inside another? Surely the scientists who are fortunate enough to find themselves bang in the middle of this bonanza will be limited only by their imaginations for some considerable time to come.

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[1] W. Krätschmer, L. D. Lamb, K. Fostiropoulos, D. R. Huffman, *Nature (London) 347* (1990) 354.

[2] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, R. E. Smalley, *Nature (London)* 318 (1985) 162. It should be noted that C_{60} was first predicted by *E. Osawa (Kagaku (Kyoto) 25* (1970) 85 (In Japanese)).

[3] R. Taylor, J. P. Hare, A. K. Abdul-Sada, H. W. Kroto, *J. Chem. Soc. Chem. Commun. 1990*, 1423. Chromatography on alumina using a 8 × 60 cm column with hexane/toluene (98:5 for C_{60} and 80:20 for C_{70}) as eluant is the very best method, according to *F. Diederich* (personal communication). In this way, 400 mg of the C_{60}/C_{70} mixture can be separated. See also [4].

[4] P.-M. Allemand, A. Koch, F. Wudl, Y. Rubin, F. Diederich, M. M. Alvarez, S. J. Anz, R. L. Whetten, *J. Am. Chem. Soc. 113* (1991), im Druck.

[5] H. Ajie, M. M. Alvarez, S. J. Anz, R. D. Beck, F. Diederich, K. Fostiropoulos, D. R. Huffman, W. Krätschmer, Y. Rubin, K. E. Schriver, D. Sensharma, R. L. Whetten, *J. Phys. Chem. 94* (1990) 8630.

[6] R. D. Johnson, G. Meijer, D. S. Bethune, *J. Am. Chem. Soc. 112* (1990) 8983.

[7] According to *F. Diederich* (personal communication), pure C_{60} crystallizes in a cubic f-centered close packing. The hexagonal packing is preferred by pure C_{70} as well as by the conglomerate.

[8] R. J. Wilson, G. Meijer, D. S. Bethune, R. D. Johnson, D. D. Chambliss, M. S. de Vries, H. E. Hunziker, H. R. Wendt, *Nature (London) 348* (1990) 621; J. L. Wragg, J. E. Chamberlain, H. W. White, W. Krätschmer, D. R. Huffman, *ibid. 348* (1990) 623.

[9] R. E. Haufler, J. Conceicao, L. P. F. Chibante, Y. Chai, N. E. Byrne, S. Flanagan, M. M. Haley, S. C. O'Brien, C. Pan, Z. Xiao, W. E. Billups, M. A. Ciufolini, R. H. Hauge, J. L. Margrave, L. J. Wilson, R. F. Curl, R. E. Smalley, *J. Phys. Chem. 94* (1990) 8634.

[10] *Three* observable reversible reductions have been identified in CH_2Cl_2 by *F. Diederich* et al. [4]. C_{70} exhibits the same cyclic volammetry behavior as C_{60}.

[11] J. W. Arbogast, A. P. Darmanyan, C. S. Foote, F. Diederich, R. L. Whetten, Y. Rubin, *J. Phys. Chem. 95* (1991), in press. **Warning**: In a letter to *Chem. Eng. News* (December 17, 1990 issue, page 2) *C. S. Foote* et al. warn researchers to take precautions against skin contact and breathing of the dusts, at least until the physiological properties of the material have been better characterized.

[12] H. W. Kroto, *Science (Washington D.C.) 242* (1988) 1139.