

# C<sub>60</sub> chemistry expands

Leonard F. Lindoy

NEW milestones in the emerging chemistry of C<sub>60</sub> are described in this issue by H. W. Kroto and coworkers at the University of Sussex (*Nature* 357, 479–481; 1992), and in reports by teams at Sandia National Laboratories and Toyohashi and Mie Universities.

Until recently, the main focuses of C<sub>60</sub> research have been the structural, physical and theoretical aspects of this remarkable molecule. However, following the development of procedures for obtaining usable quantities of pure C<sub>60</sub> increased emphasis is being given to its chemical properties. Chemical studies on the less abundant fullerenes, such as C<sub>70</sub>, are also starting to appear.

The excitement and challenge felt in exploring the emerging chemical reactivity of the fullerenes resembles that which occurred during the development of aromatic chemistry last century, following Kekulé's description of the structure of benzene in 1865. Chemically modified fullerenes open the way to a virtually endless variety of new materials. The potential for the future application of these modified fullerenes is clearly very great when one considers the extraordinary properties (including superconductivity, optical properties and ferromagnetism) of the parent icosahedral cage and its doped derivatives. The likelihood that the properties of a given derivative will be able to be matched precisely to the needs of a particular application via 'chemical tuning' also has far reaching implications.

C<sub>60</sub> is composed of tri-coordinated carbon atoms making up both 5-membered and 6-membered rings on the surface of the cage. The inherent stability of the cage reflects its benzenoid nature. Although all the carbon atoms are equivalent, there are formally two C–C bond types present in C<sub>60</sub>: those that are common to two fused 6-membered rings and those common to a 5-membered ring fused with a 6-membered ring. Further, the  $\pi$ -electron density is not evenly delocalized throughout the cage, because resonance structures incorporating double bonds in the 5-membered rings are unfavourable.

The non-equivalence of bonds throughout C<sub>60</sub> is expected to be reflected in reactivity patterns which differ from classical aromatic compounds. Indeed, clear reactivity differences are emerging as the chemistry of the fullerenes unfolds. Nevertheless, much further work is required to establish fully the reactivity ground rules that apply to the new cages (and their derivatives).

Various derivatives containing atoms

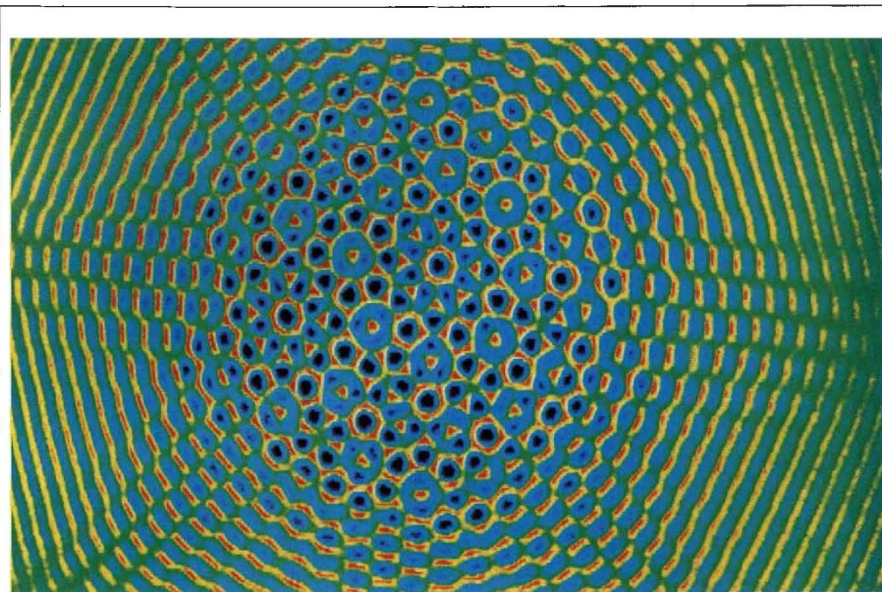
or groups covalently bound to the outside of the C<sub>60</sub> cage have been synthesized but in most cases neither the relative positions of the appended groups nor the isomeric purity of the respective products has been determined. Typical solid products in this category produced in an 'uncontrolled' manner include C<sub>60</sub>H<sub>36</sub>, C<sub>60</sub>F<sub>36</sub>, and C<sub>70</sub>F<sub>34</sub>. Related chlorinated and brominated derivatives have also been obtained. Although the nature of these products has not been fully defined, the integrity of the cage framework appears to be maintained in each compound.

In the work of Kroto and colleagues, the new brominated species C<sub>60</sub>Br<sub>6</sub> and C<sub>60</sub>Br<sub>8</sub> have been prepared and the sites of bromination precisely determined using X-ray diffraction (see pages 480 and 481). These products were obtained under closely defined conditions by the reaction of solutions of C<sub>60</sub> with bromine. A third product, C<sub>60</sub>Br<sub>24</sub> was also isolated from the reaction of C<sub>60</sub> with bromine in the absence of solvent. This

latter product was also reported recently by F. N. Tebbe *et al.* (*Science* 256, 822–825; 1992) who determined its X-ray structure. The 24 bromine atoms envelop the carbon core in a symmetrical fashion, shielding the 18 remaining double bonds from further addition. Because halogenated C<sub>60</sub> species have been demonstrated to act as synthetic intermediates, the availability of the new, well characterized and isomerically pure derivatives represents a significant advance — especially in promoting the development of the systematic chemistry of the fullerenes.

The tendency for six or eight groups (or a larger number of groups which are low multiples of these values) to add to C<sub>60</sub> is now documented for a number of different reaction types. Such a realization provides a starting point for unravelling the interplay of electronic influences that clearly underwrite the chemistry of this cage.

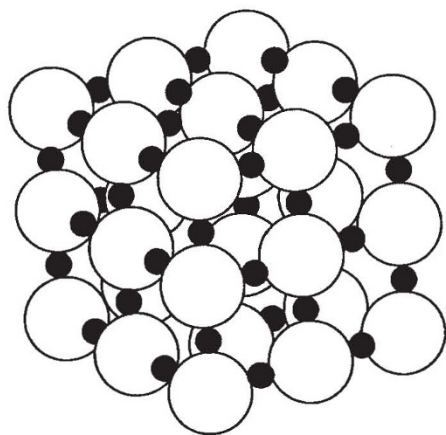
Following reports that C<sub>60</sub> readily reacts with benzylic radicals to form polybenzylated fullerenes, A. D. Loy and R. A. Assink at Sandia used the related diradical from xylylene in the synthesis of a C<sub>60</sub>-*p*-xylylene copolymer in which individual C<sub>60</sub> molecules are



THE surface of liquid ethanol is an unlikely place to look for insights into two-dimensional crystals. But B. Christlansen *et al.* (*Phys. Rev. Lett.* 68, 2157–2160; 1992) have shown that the ripples generated by simply shaking a shallow trough of the liquid can adopt a wide range of ordered patterns.

The patterns are the result of interactions between standing capillary waves (surface waves controlled by surface tension). Christlansen *et al.* generate relatively long-wavelength capillary waves by vertical vibration of a cylindrical container, 8.4 cm in diameter. Trans-

itions from one pattern to another can be induced by changing either the frequency or the amplitude of vibration. When three standing waves interact, the pattern has hexagonal (honeycomb) symmetry; increasing the amplitude creates a square pattern from two standing waves. At lower frequencies, this pattern develops dislocations and ultimately breaks down into a triangular pattern without long-range order. The quasicrystalline pattern shown above is the result of interactions between four standing waves, and appears spontaneously from a largely disordered state. P.B.



The structure proposed by Nagashima *et al.* for the three-dimensional polymer,  $(C_{60}Pd_3)_n$ . The large open spheres each represent a  $C_{60}$  group, the palladium atoms are represented by black spheres.

covalently linked (*J. Am. chem. Soc.* **114**, 3978–3980; 1992). The product, which is believed to be extensively cross-linked, represents the first example of a new class of polymeric materials. Unusual properties are expected but no details are yet available.

The first organometallic polymers incorporating  $C_{60}$  units bridged by palladium atoms were described recently by Nagashima *et al.* (*J. chem. Soc., Chem. Commun.*, 377–379; 1992). The polymers are of type  $(C_{60}Pd)_n$ ,  $(C_{60}Pd_2)_n$  and  $(C_{60}Pd_3)_n$ . The authors postulate that the products are made up of alternating uncharged palladium atoms and carbon cages in regular arrays, with the palladium atoms serving to link the individual  $C_{60}$  groups in respectively one, two and three dimensions. The palladium appears to act as a bridge by binding to the  $\pi$ -electron density on the surfaces of two  $C_{60}$  molecules; precedence for such bonding already exists in the growing organometallic literature of  $C_{60}$  derivatives. The two-dimensional polymer has not been isolated but is considered to be an intermediate in the formation of the three-dimensional product. The latter (see figure) is clearly the most thermodynamically stable and, for example, may be generated by thermal disproportionation of  $(C_{60}Pd)_n$ .

In the presence of excess palladium, a product was obtained of stoichiometry  $(C_{60}Pd_{3.5})_n$  which is believed to contain the excess palladium deposited on the surface of the polymer. This metal-rich product was observed to catalyse the heterogeneous hydrogenation of diphenylacetylene in cyclohexane — a harbinger for the importance of this class of polymer in the future. □

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## Sex and the male stick insect

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STICK insects are better known for their mimetic ability than for their contribution to our understanding of reproductive biology. During the day they remain immobile on branches, where they generally escape detection because their bodies bear an uncanny resemblance to sticks or leaves (Fig. 1). During the night they slowly move about feeding, and reproducing — often, as a group at the University of Bologna has found<sup>1–4</sup>, in decidedly peculiar ways.

There are many variations on the theme of sexual reproduction. An egg can develop without activation by a sperm (parthenogenesis), or it can eliminate the male pronucleus after fertilization (gynogenesis). The male genetic material, however, is much less versatile and development in the absence of the female pronucleus (androgenesis) has so

(Fig. 2c); thus the hybridogenetic form is a perpetual  $F_1$  hybrid, which can evolve to a full self-sustaining species if it shifts to parthenogenesis. Males of the two hybridogenic strains discovered by Scali and co-workers (*B. rossius-grandii benazzii* and *B. rossius-grandii grandii*) are infertile, whereas females, besides maintaining the hybridogenetic strain, can also reproduce by gynogenesis. Hybridogenesis has often been advocated as a possible mechanism of speciation in fish and amphibians<sup>6</sup>, but no case had yet been found in invertebrates.

The female stick insects had more surprises in store. When a female of *B. rossius-grandii benazzii* is fertilized by a *B. rossius* male, up to 20 per cent of the offspring have the genetic make-up of the father alone (Fig. 2e). This was first demonstrated by use of enzyme elec-



FIG. 1 Female of the stick insect *Bacillus rossius-grandii benazzii*.

far been described only in plants. Since 1887, when the Hertwigs first demonstrated experimental androgenesis in echinoderms<sup>7</sup>, students of animal biology have been taught that this phenomenon occurs only when induced artificially. But now the group at Bologna has discovered natural androgenesis, as well as other unexpected forms of reproduction, in certain species of stick insect.

Using gel electrophoretic separation of alloenzymes and chromosomal analysis to reconstruct the evolutionary history of the stick insect population of Sicily, Scali, Mantovani and Tinti identified two hybridogenetic strains which have arisen naturally from hybridization between *Bacillus rossius* females and *B. grandii* males of different subspecies<sup>1,2</sup>.

Hybridogenesis is a type of reproduction particular to interspecific hybrids, and involves the maintenance of one parental genome in the gametes and the elimination of the other. The discarded genome is provided anew through fertilization by the host fathering species

trophoresis, and has now been confirmed by chromosomal analysis<sup>4</sup>. The genetic material of the mother is eliminated so that her eggs develop entirely under the instruction of paternal chromosomes. The resulting androgenetic males and females are fertile, and diploid through duplication of the active chromosomes, or by fusion of two sperm

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