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Systematics of Fullerenes and Related Clusters [and Discussion]

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Systematics of fullerenes and related clusters

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Qualitative theoretical treatments of the fullerene family of molecules can be used to count possible isomers and predict their geometric shapes, point groups, electronic structures, vibrational and NMR spectroscopic signatures. Isomers are generated by the ring-spiral algorithm due to D. E. Manolopoulos. Geometrically based magic number rules devised by the present author account for all electronically closed π shells within the Hückel approximation and these 'leapfrog' and 'cylinder' rules apply to the wider class of 'fulleroid' structures constructed with rings of other sizes. Extrapolations from the theory of carbon clusters are described for doped fullerenes, metallocarbohedrenes, fully substituted boron–nitrogen heterofullerenes and decorated-fullerene models for water clusters.

1. Introduction

The fullerenes offer a challenge to theoretical chemistry. They are large molecules and, even with modern computational methods, it would be expensive and often uninformative to perform full *ab initio* calculations on them cage by cage. In the first steps towards understanding these new materials a more qualitative approach is necessary and desirable. Methods based on little more than topology and elementary valence theory can provide information on isomerism, geometric and electronic structure, spectroscopic signatures, stability and selection rules for interconversion. This paper touches on developments in these areas but, in line with the 'post-buckminsterfullerene' theme of the meeting, concentrates on new ideas in the theory of exotic fullerenes, heterofullerenes and related heteroatom and molecular clusters.

2. Fullerenes: isomers and electronic structure

The discovery of C_{60} (Kroto *et al.* 1985) carried with it the implication of the existence of a whole series of similar molecules. In the original experiments strong C_{60} and C_{70} signals were found in association, and intensity was distributed over a wide range of even-numbered clusters. Theoretical rationalizations of the stability of C_{60} made in that paper and elsewhere postulated a pseudospherical σ and π system which clearly admitted application to other nuclearities (Fowler & Woolrich 1986; Fowler 1986; Schmalz *et al.* 1988). The term 'fullerene' was coined (Kroto 1987) and following the preparation of macroscopic quantities of C_{60} by a startlingly straightforward method (Krätschmer *et al.* 1990), higher members of the fullerene family are now being isolated in chemically tractable amounts. The current section concentrates on the relationship between isomer geometry and electronic structure.

A fullerene is a geometrically closed trivalent polyhedral network in which n carbon atoms are arranged in 12 pentagonal and $(\frac{1}{2}n-10)$ hexagonal rings. Such a

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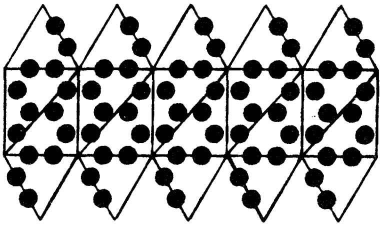

Figure 1. A net for C_{70} composed of five identical strips.

polyhedron can be constructed for all n greater than or equal to 20, with the single exception of 22 (Grünbaum 1967), and in the spherical approximation serves as the basis for a three-dimensional (3D) π system in which each carbon has three σ bonds to its neighbours and donates one electron to a π system of radial p orbitals. The number of isomers compatible with this definition grows rapidly with n.

An initial approach to fullerene enumeration was based on point-group symmetry (Fowler 1986; Fowler *et al.* 1988) and involved an extension of Coxeter's (1971) work on icosahedral tessellations of the sphere and of methods for the classification of virus structures (Caspar & Klug 1962). This approach led to magic numbers in fullerene electronic structure (Fowler & Steer 1987; Fowler 1990) and will be described briefly here.

The construction considers duals rather than the fullerenes themselves. Two polyhedra are dual to each other if the vertices of one coincide with the face centres of the other and vice versa. Each three-coordinate vertex of a fullerene corresponds to a triangular face in the dual, and the centre of each fullerene face to a five- or six-coordinate vertex of the deltahedral dual. The net of an arbitrary fullerene isomer is found by joining points in the infinite plane equilateral triangulated lattice. Twenty master triangles are drawn, joining 22 points of the plane by 19 internal and 22 external edges (figure 1). On folding the net, various vertices (and edges) collapse and a master icosahedron of 12 vertices and 30 edges is formed. The icosahedron is more or less irregular, with a symmetry that follows from the original choice of vertices and is the same as that of the dual fullerene. Its surface area is proportional to the number of small triangles cut from the plane and fixes the fullerene nuclearity. Hence, the enumeration problem reduces to finding all possible nets of given area compatible with a given point group, which in turn reduces to solution of integer equations.

For icosahedral symmetry the solution sets are well known from earlier work: An I or I_h fullerene C_n is possible for all n of the form $20[i^2+ij+j^2]$ (which implies either $n = 60k$ or $n = 60k+20$). The new observation was that electronic and geometric structures of the fullerenes are closely related: closed shells are found for the $60k$ series of which C_{60} is the prototype, but open (G^2) shells for the $60k+20$ series of which C_{20} is the first member (Fowler 1986). Nuclearities for tetrahedral fullerenes (T, T_d and T_h) are $n = 4[i^2+ij+j^2+k^2+kl+l^2+3(il-jk)]$ and for five- and six-fold cylindrical symmetry they are $n = 2p[k^2+kl+l^2+(il-jk)]$ with $p = 5$ and 6 respectively. Two- and three-fold dihedral symmetries were also treated. Details of the limitations on i, j, k, l and comprehensive lists of isomers are available (Fowler *et al.* 1988).

Systematic Hückel calculations on these and other series reveal the connection between geometry and electronic structure that is summarized in two rules. The more general, applying to all symmetries, is the leapfrog rule, which states that at least one isomer C_n with a properly closed π shell exists for all $n = 60+6k$ ($k = 0, 2, 3, \ldots$ but not 1) (Fowler & Steer 1987). In fact, there is one closed-shell C_n for every isomer of $C_{n/3}$, derived from it by the geometrical leapfrog construction. Starting from any fullerene structure, it is possible to construct one with three times as many atoms by first capping the faces and then taking the dual (figure 2). Whatever the starting isomer, the product fullerene always has a properly closed π shell (bonding HOMO, antibonding LUMO) in the simple Hückel approximation; the starting isomer has $20+2k$ ($k \neq 1$) atoms, hence the form of the rule. The fact that a closed shell is produced can be rationalized by considering local bonds and antibonds, spherical parentage of cluster orbitals or Kekulé structures (Fowler 1992), and can be proved by graph theory (Manolopoulos *et al.* 1992). The leapfrog rule subsumes the results for icosahedra, so that C_{60} is the first of an infinite leapfrog family.

The second, more limited, rule is for carbon cylinders. Within the five- and six-fold symmetric families described above, a single π closed shell (but with a non-bonding LUMO) is found for $n = 2p(7+3k)$ (all k). These isomers are expansions of C_{60} and their regular electronic structure follows from the solutions of the Schrödinger equation for the particle on a cylinder (Fowler 1990). C_{70} is the parent of this infinite family, and C_{84} is the first case for which both leapfrog (2) and cylinder (1) closed shells exist. The two rules cover all known cases of closed shells. Both constructions produce fullerenes in which the pentagonal rings are isolated from one another and so all properly closed-shell fullerenes obey the isolated pentagon rule (IPR), as do many open shell.

An independent attack on the enumeration problem was made by Manolopoulos *et al.* (1991) in Nottingham when they devised the spiral algorithm. This is based on the conjecture that any fullerene may be peeled as a coiled strip of pentagons and hexagons, so reducing the 3D structure of C_n to a 1D sequence of 12 pentagons interspersed amongst $(\frac{1}{2}n-10)$ hexagons. Fullerene graph enumeration is then a problem of generating all possible sequences of fixed length, discarding those that do not close to give a fullerene and eliminating the (many) redundant repetitions on the basis of their eigenvalue spectra. A spiral is easily 'inverted' to give the adjacency matrix. Approximate cartesian coordinates can be generated from eigenvectors of the adjacency matrix, (maximal) point group symmetry assigned, IR and NMR signatures of each isomer listed and an approximate electronic structure determined (Manolopoulos & Fowler 1992). Interconversions of isomers by motion of pentagons, and by C_2 intrusion and extrusion, have been mapped and used to explain statistical effects in experimental isomer distributions (Fowler 1992*a*, *b*; Manolopoulos *et al.* 1992*a*, *b*).

The spiral algorithm has been used to confirm that the 'leapfrog' and 'carbon cylinder' isomers are the only properly closed shells in Hückel theory. In turn the leapfrog construction provides informal support for the completeness of the spiral algorithm. In all cases examined, the listing of spirals for C_{3n} includes all the leapfrogs of C_n. The lists of isomers found from the tessellation for the higher point groups are in complete agreement with the symmetry analysis of the spiral lists. One motive for implementing this algorithm for all 28 possible fullerene groups is to give a further check on spiral completeness.

Given the efficient spiral algorithm for generation of isomer lists, many problems in structure and properties of higher fullerenes have been attacked. It is particularly important to have complete lists because it has turned out that possession of a closed

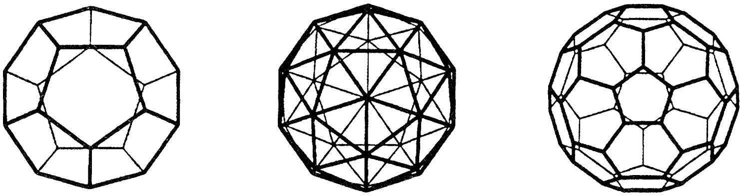

Figure 2. The leapfrog construction. A fullerene polyhedron is omnicapped and dualized to yield a fullerene with three times as many atoms.

shell is not the sole determinant of fullerene stability and electronic and steric factors are in fine balance. The experimental characterization of higher fullerene structures is providing some interesting surprises. All structures found so far are compatible with the IPR, and elimination of pentagon contacts has both steric and electronic advantages. However, local steric criteria such as the uniformity of the pattern of hexagon neighbours also seem important (Raghavachari 1992), and often favour structures of low point-group symmetry. Current beliefs on carbon cluster stability in this range of n can be summarized by a series of filters. First, discard non-fullerene isomers, then those with abutting pentagons, then isomers with disparate hexagon neighbour patterns and those with poor electronic structures. The balancing of the different criteria is not yet an exact science, but the emerging agreement between various qualitative and semi-empirical methods is encouraging. An extended discussion of the isomer problem, comparison with experiment and a catalogue of isomers, steric, electronic and symmetry data is to be published elsewhere (Fowler & Manolopoulos 1993).

3. Fullerenes and fulleroids

The fullerene structural pattern can be regarded as a minimal departure from the graphite template. Twelve pentagons introduce geometric closure, but otherwise all faces remain hexagonal. It seems at least feasible that other structures might have comparable stability, and in particular structures with just a few of their hexagons enlarged to heptagons might be worth theoretical investigation. Heptagons and octagons figure in the infinite lattices of the hypothetical graphite foams (Mackay & Terrones 1991; Lenosky *et al.* 1992), and heptagonal defects may account for the negative curvature observed in electron micrographs of carbon tubules (Iijima *et al.* 1992). Generation and motion of heptagonal defects have been studied by Saito *et al.* (1992). Large, negatively curved assemblies of carbon atoms have been proposed as building blocks for giant 'hyperfullerene' molecules (Scuseria 1992).

Staying close to the fullerene pattern, we have used qualitative molecular orbital theory to study clusters are similar to cylindrical fullerenes but with a p-gonal ring at each pole ($p = 7, 8, 9, \ldots$) and an extra $(2p-12)$ pentagonal faces (Fowler & Morvan 1992). The tessellation construction described earlier also applies to these 'fulleroid' cylinders, and so there is a seven-fold, eight-fold, ..., axially symmetric cage for every five- (and six-) fold symmetric fullerene. One strip repeated p times gives a net that wraps to form the three-dimensional pseudocylinder. For example, the same strip is used five times to give icosahedral C_{60}, six times to give D_{6d} C_{72}, seven times to give D_{7d} C_{84}, and so on. Corresponding to each five- or six-fold cylindrical isolated-pentagon fullerene is an isolated-p-gon fulleroid in which all defects are surrounded by hexagons.

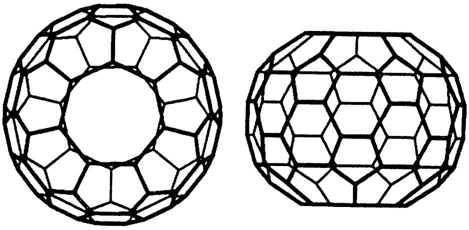

Figure 3. Two views of a hypothetical D_{7d} fulleroid isomer of C_{84}.

The electronic structure of the hypothetical fulleroids also parallels that of the fullerenes in several significant respects. Properly closed π shells are found within the Hückel approximation only for isolated *p*-gon isomers, and then only when the structure is either (*a*) leapfrogged from a smaller fulleroid of the same symmetry, or (*b*) a *p*-fold analogue of one of the fullerene 'carbon cylinder' series (Fowler 1990). D_{7d} C_{84} is the smallest fulleroid with a properly closed shell (figure 3).

Explicit calculation shows that leapfrogging of cages in this particular series produces a closed shell, but in fact leapfrogging of any trivalent cage with at least one pentagonal face will do the same (Manolopoulos *et al.* 1992). If the fulleroid class is defined as comprising those trivalent polyhedra with five or more atoms per face, then all leapfrog fulleroids have closed shells and the $60+6k$ magic number rule is extended accordingly.

The carbon-cylinder analogues obey a slightly more complicated rule. For fullerenes one closed shell below a non-bonding LUMO was found for nuclearities $n = 70+30k$ (five-fold symmetry) and $84+36k$ (six-fold symmetry). This generalizes to $n = 2p(7+3k)$ for the fulleroid cylinders, but analysis of the behaviour of the frontier orbital energies with ring size shows that, whereas k can take values $0, 1, 2, \ldots$ for $p = 5$ and 6, its range is restricted to the strictly positive integers for the higher values of p.

A measure of the electronic stability of the fulleroids is the π delocalization energy per atom. This energy is an increasing function of n for closed-shell cages, flattening off with large n (see fig. 3 in Fowler & Morvan 1992). As might be expected, the loss of hexagons leads to lower stability than for a closed-shell fullerene with an equal number of carbon atoms, but as the cluster size increases the π energy per atom tends to the graphite limit. The steric factor in overall stability is less easy to quantify, but unless the cluster is very large indeed there is likely to be considerable local strain around the heptagonal defects. MNDO calculations on D_{7d} C_{84} by Raghavachari & Rohlfing (1991) found it to be highly strained in spite of a large band gap. Prospects for fulleroid microfibres are brighter than for single-shell clusters.

4. Doped fullerenes and the metallocarbohedrenes

There is mass spectroscopic evidence for clusters $C_{59}B$, $C_{58}B_2, \ldots C_{54}B_6$ in the products of laser ablation of boron nitride/graphite composites (Guo *et al.* 1991). It is proposed that these may be versions of the fullerene cage in which heteroatoms have occupied carbon sites with little disturbance of the framework. This is a plausible hypothesis for low doping ratios, in view of the ability of carbon to substitute for boron in carboranes. Bond-energy considerations suggest that

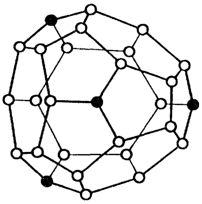

Figure 4. A hypothetical T_d isomer of $C_{24}N_4$ based on the C_{28} fullerene.

heteroatom sites would be well separated to maximize BC and minimise BB contacts, and the fact that each boron site takes up one ammonia molecule in titration experiments bears this out. Moreover, depending on the notional starting fullerene isomer, it is possible to imagine reinforcing or competing steric and electronic effects on isomer stability. Boron atoms would be likely to occupy planar sites (junctions of three hexagons) with low charge in the isoelectronic fullerene cation, whereas nitrogen substituents would be stabilized in pyramidal sites (junctions of three pentagons) with high negative charge in the isoelectronic fulleride anion. For example, substitution of N at the corner sites of C_{28} (figure 4) would give a closed-shell molecule isoelectronic with $C_{28}H_4$ and having four pyramidal nitrogen atoms.

More intricate theoretical issues emerge when we move one step further from the fullerenes to the newly proposed metallocarbohedrenes. Again at the time of writing the evidence is purely mass spectroscopic, but with the C_{60} precedent in mind we can hope for eventual confirmation by other techniques. It appears from laser ablation studies made by Castleman and co-workers using metal surfaces in contact with hydrocarbons that M_8C_{12} (M = Ti, Zr, Hf, V) has special stability, and magic number series M_nC_m have been interpreted in terms of growth of networks of fused dodecahedra (Guo *et al.* 1992*a*, *b*; Wei *et al.* 1992*a*, *b*). These clusters are exciting from the theoretical point of view as a possible embodiment of a substitutional analogue of the Jahn–Teller effect (Ceulemans & Fowler 1992).

The working hypothesis used in the experimental studies for rationalizing the stability of Ti_8C_{12} is that it is a geometrically and electronically closed dodecahedral framework notionally derived from the C_{20} fullerene by isolobal $C \rightarrow Ti$ substitution. Icosahedral C_{20} itself has an open-shell π configuration with two electrons in a fourfold degenerate non-bonding set of orbitals (Fowler & Woolrich 1986), and whereas the dication would have a closed shell, the neutral would be expected to undergo distortion to a geometry of lower symmetry in which double occupation of the lowest component of the symmetry-split frontier orbital set would yield a closed-shell singlet. The epikernel principle (Ceulemans *et al.* 1984) guarantees that the loss of symmetry will be the least possible that achieves the splitting, and for an I_h molecule with an open G shell the two maximal epikernel groups are T_h and D_{3d}.

The substitutional analogue of the Jahn–Teller effect on geometry arises as follows. Instead of geometric distortion lifting the degeneracy of the frontier orbitals, a splitting is induced by changing the chemical nature (and hence energetic parameters) of some of the atoms. This will drive further geometric changes too, as a simple effect of size (just as in the usual case the geometric changes induce changes in bond energetics). The epikernel principle governs the symmetries of effective substitution patterns; and both T_h and D_{3d} support substitution by eight atoms. In T_h the metal atoms occupy the corners of a cube; in D_{3d} they form pyramids capping a puckered C_{12} ring (figure 5).

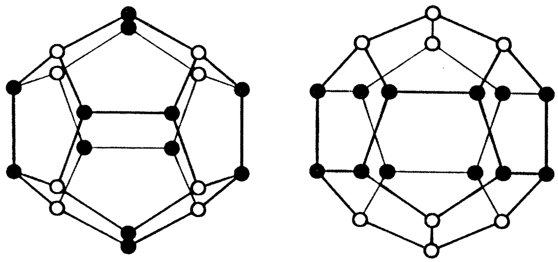

Figure 5. Tetrahedral and trigonal isomers of Ti_8C_{12}.

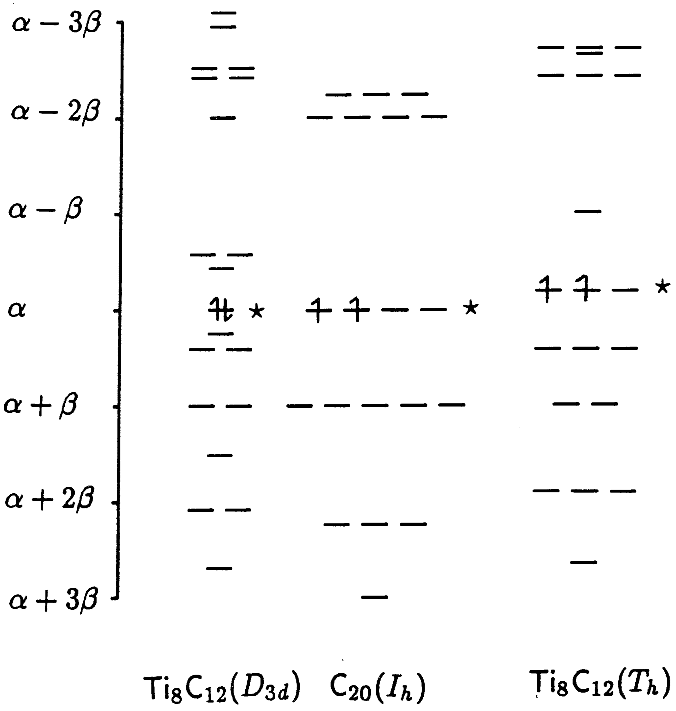

Figure 6. Hückel energy levels for model Ti_8C_{12} and C_{20} clusters. The star marks the HOMO and arrows indicate its occupation.

The induced splitting pattern can be deduced by first-order perturbation theory (Ceulemans & Fowler 1992). In the simple Hückel approximation, the electropositive metal atoms use sd hybrids for π bonding and have smaller negative α parameters. The relation $\alpha_{Ti} \approx \alpha_C - \beta_{CC}$ is suggested by differences in electronegativity, and changes in the β bond parameter have no effect in first order on the energy of the (non-bonding) G_u orbitals. Perturbation theory or explicit diagonalization show that in T_h symmetry the frontier level splits $G_u(4) \rightarrow A_u(1)+T_u(3)$ with the nondegenerate component higher in energy, and in D_{3d} the splitting pattern is $G_u(4) \rightarrow A_{1u}(1)+A_{2u}(1)+E_u(2)$ with the non-degenerate A_{1u} level at the bottom of the stack, at exactly the carbon $2p$ energy (figure 6). Therefore, if Ti_8C_{12} is a closed-shell singlet, it cannot have the T_h symmetry assumed by Castleman and co-workers, and the most symmetrical structure compatible with a closed shell is the D_{3d} cage proposed in our paper. As discussed there, the trigonal cage has a favourable aromatic carbon ring

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around its equator and 12 TiC contacts. The T_h structure has only isolated CC units but 24 TiC bonds. The two epikernel cages represent the extremes of localized (T_h) and delocalized (D_{3d}) electronic structures, and the experimental geometric structure will be a result of competition between the σ and π energies.

The main point illustrated by this over-simplified discussion of the prototype metallocarbohedrene is that a structure and electron count which is unfavourable for carbon may become electronically favoured by substitution of heteroatoms. The 20-electron π system of neutral C_{20} is the smallest of many potential examples of this effect in the fullerene series. An infinite number of icosahedral fullerene isomers with $60k+20$ atoms have the G^2 open-shell configuration as neutrals. Icosahedral C_{80} has a bonding HOMO with energy $\alpha+0.274\beta$ in the simple Hückel approximation. In I_h symmetry its atoms fall into sets of 20 (type 'h', common to three hexagons) and 60 (type 'p', common to two hexagons and a pentagon). In T_h symmetry, these split further into 8(h)+12(h)+12(p)+24(p′)+24(p″) (where p′ atoms are bonded to an atom in 8h, and p″ to an atom in 12(h)). Separate substitution of these sets by electropositive centres and calculation of the π energy levels shows that T_h isomers of $Ti_{12}C_{68}$ (with 12(h) = Ti) and $Ti_{24}C_{56}$ (with 24(p′) or 24(p″) = Ti) would have closed shells with small HOMO–LUMO gaps. For Ti_8C_{72} a D_{3d} isomer would have a closed shell, as in the 20-atom example.

5. Heterofullerenes and cages with isolated pairs of pentagons

Many chemists, familiar since schooldays with the crystal structures of graphite and hexagonal boron nitride must have asked themselves on seeing the C_{60} truncated icosahedron whether a $B_{30}N_{30}$ analogue would be possible (see, for example, Thompson 1992), and quickly rejected the idea because C_{60} is not an alternant. The stability of boron nitride arises from the strength of the heteronuclear BN bond, but it is impossible to alternate B and N around a pentagonal ring. Though pure boron clusters have been produced in laser ablation experiments (La Placa *et al.* 1992), there is no compelling evidence that they adopt fullerene structures, and for B_n a deltahedral shape seems more likely *a priori*. For a skeleton of a $(BN)_{n/2}$ molecule the duals of triangular tessellations of the octahedron (Goldberg 1937) may offer useful prototypes; these polyhedra have solely square and hexagonal faces. However, some variations on the fullerene theme also merit consideration.

The problem with BN occupation of a fullerene framework is not only the homonuclear bond forced in each pentagon, but the fact that the defect spreads into neighbouring rings (figure 7). An isolated-pentagon (BN) heterofullerene has at least 12 homonuclear contacts, but may have many more. If, however, the pentagons are allowed to pair up, the defect is contained, and the structure need only have six homonuclear contacts, one at the waist of each pair. Further aggregation of pentagons introduces more problem bonds, and so the isolated pentagon-pair (IPP) structure is optimal in that it minimizes the number of BB and NN links in a fully substituted fullerene.

Hypothetical B_xN_y cages based on IPP polyhedra have 6 BB, 3 BB+3 NN, or 6 NN homonuclear bonds, and overall stoichiometries $B_{n/2+2}N_{n/2-2}$, $B_{n/2}N_{n/2}$, $B_{n/2-2}N_{n/2+2}$, with $(n-4)$, n or $(n+4)$ π electrons respectively. This is proved as follows. Associate one third of each atom with each of its three bonds. In the total atom count, homonuclear BB bonds then contribute $\frac{2}{3}$B+0N each, heteronuclear bonds contribute $\frac{1}{3}$B+$\frac{1}{3}$N, etc. Therefore the number of homonuclear bonds of BB type is

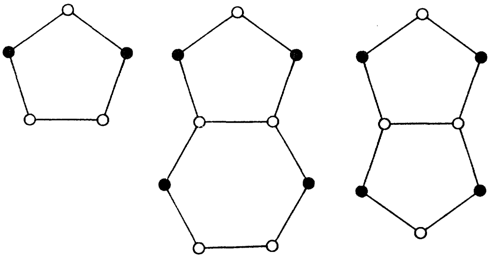

Figure 7. A pentagon has one forced homonuclear contact, which forces a second in a neighbouring hexagon. A pentagon pair has only one forced homonuclear bond which is without effect on neighbouring rings.

0, 3, 6. IPP fullerene polyhedra are labelled even or odd according to the parity of the number of BB links.

An NN contact would presumably provoke elimination of N_2 from the cage, and therefore a secondary stability condition is that all forced homonuclear links should be BB rather than NN. This can only be achieved by having an excess of four B atoms. A $(BN)_{n/2}$ IPP isomer must have three unfavourable NN contacts.

The two constraints define a class of polyhedral structures for which surface π and weakened edge σ bonding are possible. If the BB link is very weak it may be energetically favourable to break it altogether, leading to a true alternant polyhedron. Each pentagon pair would then become a distorted octagon and the structure would have $(\frac{3}{2}n-6)$ heteronuclear contacts, $(\frac{1}{2}n-10)$ hexagonal faces and six octagonal rings. It would also have 12 reactive two-coordinate atoms. In the original structure B forms three edge bonds with sp^2 hybrids and contributes an empty 2p orbital to the π system. With sufficient distortion at the low-coordinate sites, sp^2 hybridization could be retained, but with one hybrid now taking part in the π system and an empty B 2p orbital aligned with the deleted pentagon–pentagon edge. This latter bonding scheme would place an extra 12 electrons in the π system, with eight in non-bonding or nominally antibonding orbitals.

Irrespective of the viability of the bonding schemes outlined above, the mathematical problem of cataloguing the fullerene isomers that obey the starting condition of isolation of pentagon pairs is straightforwardly solved. One method is based on the spectral moments

$$\mu_j = \sum_i^n (\epsilon_i)^j$$

of the eigenvalues of an adjacency matrix (see, for example, Burdett *et al.* 1985). Through the association of each μ_j with closed walks of length j, the moments can be used to count structural components of a fullerene graph. A general fullerene C_n has moments $\mu_0 = n$, $\mu_1 = 0$, $\mu_2 = 3n$, $\mu_3 = 0$, $\mu_4 = 15n$, $\mu_5 = 120$, $\mu_6 = 93n-120$, and $\mu_7 = 1680$ but terms beyond μ_7 depend on the detailed arrangement of pentagons. A pentagon pair introduces an eight-ring and so modifies μ_8. Structures in which all pentagons are either isolated or linked in p pairs can be accommodated by the equations $\mu_8 = 639n-1920+16p$, $\mu_9 = 18360-36p$, $\mu_{10} = 4653n-22680+400p$, $\mu_{11} = 184800-924p$. Any further linking of pentagons into triples, etc., changes μ_9, μ_{10} or μ_{11} and can be excluded on the basis of these moments. Coupling the moment formulas to the Nottingham spiral algorithm (Manolopoulos *et al.* 1990) produces the IPP isomer counts listed in table 1. Six pentagon pairs account for 48 atoms, and it

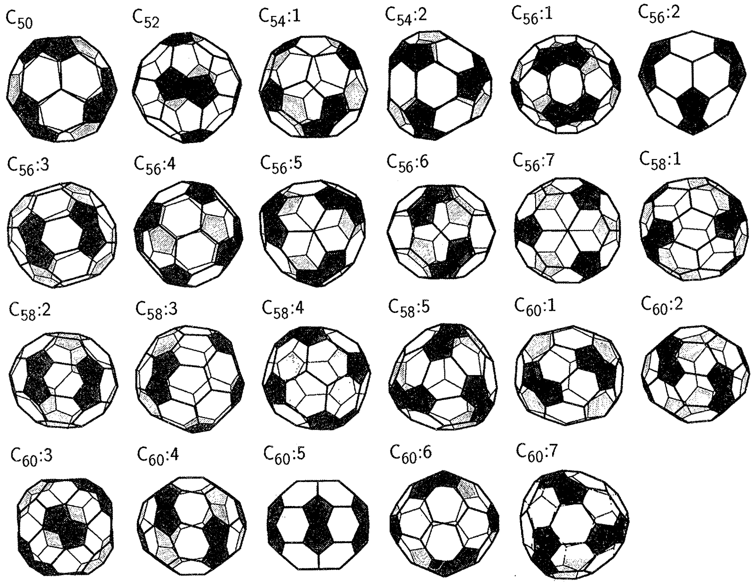

Figure 8. The isomers of C_n ($n \leqslant 60$) with six isolated pairs of pentagons. Symmetries are listed in table 1.

Table 1. *Fullerene isomers* C_n *with six isolated pairs of pentagons*

(Symmetries are listed for isomers in the order in which they are generated by the spiral algorithm. Even cages are marked by a star.)

n	count	point group symmetries
50	1	D_3
52	1	$T*$
54	2	C_2, D_3
56	7	D_2, C_{2v}, C_2, C_2, D_3, D_2, $D_{3\mathrm{d}}$
58	5	C_2, C_2, C_1, C_2, C_3*
60	7	C_2, C_2, $D_{2\mathrm{d}}$, D_2, $D_{6\mathrm{h}}$, D_2, D_3
62	7	C_2, C_2, $D_{3\mathrm{h}}$, C_2, D_3, D_3, D_3
64	11	C_2, C_1, D_2, C_2, C_3*, C_2, C_2, C_1, C_2, C_2, D_2
66	11	C_2, C_1, C_2, C_1, C_1, C_2, C_2, C_2, C_2, C_s, D_3
68	25	C_2, C_2, D_3, C_2, C_1, C_1, C_2, D_3, D_2, C_2, C_1*, C_2, C_2, C_1, C_2, C_2, C_2, C_2, C_2*, S_6*, C_2, D_2, C_3*, D_2, $T_\mathrm{d}*$
70	19	C_2, C_1, C_2, C_1, C_1, C_1, $C_{2\mathrm{V}}$, C_2, C_2, C_2, C_2, C_2, C_3*, C_1, C_2, C_2, C_2, C_2, C_2
72	34	C_2, C_2, C_1, C_2, C_2, C_1, C_1, D_2, C_2, C_2, C_2, C_2, C_2, C_2, C_1, C_2, C_1, C_1, C_2, C_2, C_1, D_3, C_2, C_2, D_6, C_2, C_2, C_1*, C_2, C_2* $C_\mathrm{s}*$, D_2, $C_\mathrm{s}*$, D_3

turns out that the smallest realizable IPP isomer has just two atoms outside pentagons and is a D_3 C_{50}. As with isolated-pentagon fullerenes, the number of IPP isomers grows erratically at first and is non-zero for every even vertex number above a threshold value. The first 23 IPP clusters are illustrated in figure 8.

The second criterion for stability implies that even polyhedra should be preferred to odd ones. One way to check the parity label automatically is to calculate the eigenvectors of the adjacency matrix obtained by deletion of the six pentagon–pentagon links of the original fullerene. Since the cut fullerene is an alternant, it has paired eigenvalues; the lowest non-degenerate vector is fully bonding and has all n coefficients in phase, and its totally antibonding counterpart has a phase change along each remaining edge. If the coefficients in the latter vector are of one sign for all 12 special atoms, then the cage is even.

The D_3 C_{50} cage is odd, as are most clusters examined, but the C_{52} is even and a total of 13 even structures are found amongst the first 130 IPP fullerenes (table 1). Simple Hückel calculations on the 52 vertex $B_{28}N_{24}$ cage with $\alpha_B \approx \alpha_C - \beta_{CC}$ and $\alpha_N \approx \alpha_C + x\beta_{CC}$ ($x = 1$ or $\frac{3}{2}$) show a closed shell at 48 π electrons with a large band gap, indicating stability for the neutral molecule with intact BB bonds. Semi-empirical calculations to determine the electronic structure and steric stabilities of more of these novel clusters are needed, and should give an indication of whether the polyhedra of figure 8 are chemically realistic or merely mathematical curiosities.

6. Decorated fullerenes and hydrogen bonding

The extrapolations from fullerenes described so far are models for chemically bonded frameworks of atoms, but the structural motif of hexagonal and pentagonal rings of linked units has much wider application in chemistry and beyond (Caspar & Klug 1962; Coxeter 1971; Marlin 1984). Given the prevalence of rings of corner-linked tetrahedra in silicates, it seemed logical to propose stability for fullerene-like silicate frameworks such as $Si_n O_{5n/2} H_n$ where each vertex of the fullerene polyhedron is 'decorated' by a tetrahedron composed of a central Si atom joined to three others by Si–O–Si linkages, and carrying an *exo* OH group (Fowler *et al.* 1991).

Another type of decorated fullerene discussed in the same paper has already been detected in experiment. This is the hydrogen-bonded fullerene-like water cluster. Drawing on the classical picture of the water molecule as a tetrahedral oxygen capable of participating in four hydrogen bonds, two as proton-donor and two as acceptor, a finite 2D ice-like network can be constructed on the surface of a hollow sphere. In this decoration each molecule is linked to three neighbours by hydrogen bonds, and the fourth vertex of the tetrahedron is occupied by either H or a lone pair. It can be shown that at least one closed structure $(H_2O)_n$ with $\frac{1}{2}n$ *exo* H atoms and $\frac{1}{2}n$ *exo* lone pairs can be constructed for every isomer of the n-vertex fullerene. The simplest of these is based on the Platonic dodecahedron (i.e. C_{20}). With an embedded (and possibly mobile) proton or hydroxonium ion, this cage had already been proposed as the explanation of $(H_2O)_{20}H^+$ and $(H_2O)_{21}H^+$ clusters observed in mass spectra of water vapour (Kassner & Hagen 1976; Wei *et al.* 1991). Structures equivalent to decorations of the 24-, 26- and tetrahedral 28-vertex fullerenes enclose Cs^+ and $H_2O\ldots Cs^+$ in proposals for gas-phase clathrates made by Selinger & Castleman (1991). Simulation of water clusters by Monte Carlo and other methods produces $(H_2O)_{20}$ and $(H_2O)_{60}$ cage structures topologically equivalent to decorated fullerenes, though with low point group symmetry. For a given fullerene frame, many conformers of similar energy may exist, and internal motion or proton conduction mechanisms are easily envisaged. A clear difference between water clusters and carbon fullerenes is that the interaction between units is σ in character, directed along the edges of the polyhedron. Lacking the π interactions of carbon rings, the faces are not constrained to near planarity and the geometries may depart considerably from the idealised model. The decorated fullerene series does however define a systematic way of generating starting configurations for water clusters, solvation cages and microstructures in liquid water.

7. Conclusion

Once the fullerene concept had been defined, it was inevitable that it would find application in many fields of chemistry. In this paper several real and hypothetical cluster types have presented in order to show how the basic fullerene structure may adapt to the requirements of building blocks other than carbon atoms. Many more analogies of this kind remain to be explored.

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Discussion

R. F. Curl (*Rice University, U.S.A.*). How do the number of isomers grow with the size? That is, is it geometric growth? Do you have a ready answer say for taking all isomers, how that grows with size, and taking only those that satisfy the isolated pentagon rule, and how that number grows with size?

P. Fowler. I do not have a ready answer for what the function is, but if you take the isolated pentagon isomers alone, and you take the general isomers, all that happens is you get the same kind of curve but shifted. You start off with not many isomers, and then it grows enormously. It looks as if it might be exponential, but it has steps in it.

J. N. Murrell (*University of Sussex, U.K.*). You mentioned that there were these conflicting contributions to the energies, the electronic effect and what you call the steric effect. Of course, the steric effect in itself is an electronic effect. What you are really showing is that the total electronic energy can be divided into two parts, as we traditionally do with Hückel theory. But perhaps there does come a point if you are starting to consider other systems, seven-membered rings, etc, where this model would be insufficient, I don't know when that happens. The other possibility is that if, for larger systems, the electronic effects become less important, then even simple models based on molecular mechanics type approaches, where you devise potentials between carbon atoms, and groups of carbon atoms, might turn out to be a perfectly adequate approach.

P. Fowler. There might be a point where s–p separation is not such a good idea, and I think the empirical evidence is that somewhere between C_{76} and C_{84} this seems to be happening. Molecular mechanics hasn't done too well so far. Given the isomers, it can predict an order, but everybody's parametrization gives a slightly different order in detail. I was trying to point out that using ideas and programmes based on the Hückel model does not in fact tell you only the behaviour of the electrons. Maybe the important use for this type of methodology, is in fact, for counting. Quantitative things, like relative energies, are trickier. Semi-empirical methods are now converging on the same answer for C_{84}. Various types, from density functional to parametrized

CNDO and MNDO have been tried. They may give the right answer eventually, but those methods are unattractive because they are parametrized.

R. F. Curl. Do you have any simple relation for the observed material that's isolated higher than C_{70}; that is, why do C_{76}, C_{78}, C_{84} follow the rules?

P. Fowler. Well, more or less. C_{76} doesn't. You should take a loose interpretation of the leap-frog rule, in other words, these are numbers that are going to turn up, but perhaps not with the detailed geometric structures that are predicted. There are two leap-frogs and one cylinder at 84, and unfortunately, not one of them is in the experimental mixture but the reason why 84 is such a good number, does seem to come from electron counting. In detail, the best explanation seems to be that you take all of these 24 isolated pentagon isomers, and look for the ones with a democratic distribution of hexagon neighbour indices. This is Ragavachari's idea about C_{84}, and it holds. If you go to C_{100}, you get something like 46 possibilities that obey his rule, so it doesn't seem very selective. In the early days, it seemed that high symmetry was important, and that very simple force type models might be expected to produce some highly symmetric results, but beyond C_{60}, symmetry seems to be dropping, and the first isolated C_1 higher fullerene must be just around the corner.

J. N. Murrell. This is really taking your speculation down the line, but, I'm struck by what happens with clusters generally. I don't mean water clusters, which we know are hexagonal type rings, rather like carbon. Even if you go to metal clusters, there are two very distinct approaches at the moment in the literature, and it's not quite clear where the right answer lies. One says that sodium clusters are a 'jellium' of electrons, and you count stabilities by counting electrons and getting closed shells; it's really like Hückel theory. The other picture is that you take just the forces between the atoms and end up with an icosahedral structure. In this case you tend not to get magic numbers. In this particular field there is some conflict in the experimental evidence as to whether or not you obtain magic numbers, but I can see the same sort of parallelism. You've got (i) an electronically driven stability, and (ii) a mechanical type stability, and I suspect the answer will depend upon the kind of experiment you are doing. It is rare that you have an equilibrium system.