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Systematics of bonding in non-icosahedral carbon clusters

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General formulas are presented for the vertex numbers, v, of pentagon+hexagon polyhedra of icosahedral, tetrahedral or dihedral symmetries. Criteria for uniqueness of representation, isomer counts and grouping of pentagons are established. All polyhedra with 256 vertices or less and belonging to T, D_5, D_6 or their supergroups are listed. With the addition of C_{3v} to the dihedral and higher groups, at least one pentagon+hexagon cluster is found for all even $v \geq 20$ except for $v = 22$ which is unrealisable in any symmetry, and $v = 46$ (for which a C_3 polyhedron exists). Carbon clusters with closed electronic shells are shown to be generated by a geometrical leapfrog procedure: for all $v = 60 + 6k$ (where k is zero or greater than one) at least one closed shell structure is predicted. In dihedral symmetry closed shells also exist for some other values of v. Separation of the 12 pentagonal faces is not sufficient to ensure a closed electronic shell but appears to be a necessary condition in dihedral or tetrahedral symmetry.

Key words: Carbon clusters — Polyhedra — Electron counts — Point groups

1. Introduction

Carbon clusters are objects of intense theoretical activity at present, sparked off by the discovery in 1985 of a long-lived C_{60} fragment amongst the products of laser vaporisation of graphite [1]-[3]. A truncated icosahedral sixty-carbon cluster, until then simply a theoretical speculation, was proposed as the source of an intense peak at $e/m \approx 720$ in the mass spectrum of the fragmentation products [1]. Calculations at various degrees of sophistication [4]-[10] from simple Hückel to *ab initio* SCF have added plausibility to this proposal, indicating that t-icosahedral C_{60} would have a closed electronic shell with a high delocalisation energy and would occupy a local minimum on the potential energy surface.

Peaks are observed for clusters with even numbers of carbon atoms ranging from a few to over two hundred atoms, and some, such as that at $e/m \approx 840$ (C_{70}), are of an intensity comparable with the C_{60} peak [1]. This pattern has been interpreted as indicating that geometrically closed, pseudospherical clusters C_n may be stable for a range of n, rather than for $n = 60$ alone [3]. Again this suggestion is supported by systematic theoretical studies [11–13] which have found sequences of magic numbers for clusters of this type.

Hückel arguments predict closed electronic shells for an infinite series of icosahedral clusters with $n = 60(a^2 + 3ab + 3b^2)$ (integral $a, b \geq 0$), of which C_{60} is the prototype [12]. High symmetry is only one of several factors conducive to cluster stability [14] and the icosahedral clusters prove to be a subset of a series with $n = 60 + 6k$ ($k = 0$ or $k \geq 2$) where each molecule has a closed shell and again C_{60} is the first member [13]. This latter series is generated by a geometrical "leapfrog" operation [12] to be discussed in detail below.

In the present paper we develop criteria for the existence of clusters with the next highest accessible symmetry, the tetrahedral T, T_d and T_h carbon frameworks, and relate their geometrical and electronic structures. In addition, our method of construction allows us to consider general rules for clusters belonging to some lower symmetry groups (D_n, D_{nd}, D_{nh} with $n = 2, 3, 5$ or 6).

2. Polyhedral carbon frameworks

In looking for possible structures for unsaturated carbon clusters we can restrict attention to polyhedra satisfying certain constraints [3, 10, 12, 14]. They must be 3-connected, to allow each carbon to form σ bonds to its neighbours, and should have a high proportion of hexagonal faces, to maximise the π delocalisation energy. They should also be roughly spherical in shape to minimise angle strain between bonds. These conditions are satisfied by polyhedra with all faces pentagonal or hexagonal; such a polyhedron must in fact have exactly 12 pentagonal faces. They form a subset of the "medial" polyhedra of Goldberg [15, 16] but do not appear to have a specific mathematical name. Kroto [17] has proposed calling the corresponding carbon clusters Buckminsterfullerenes and distinguishing them by vertex number and point-group symmetry, so that for example truncated icosahedral C_{60} would be $(I_h)C_{60}^B$ in his notation.

Polyhedra of this type exist for all even numbers of vertices $v \geq 20$ with the sole exception [18] of $v = 22$: it is impossible to construct a 22-vertex cluster with 12 pentagons and a single hexagon. An odd number of vertices is precluded by the connectivity, since the polyhedron has $e = 3v/2$ edges. As v increases so does the number of combinatorially distinct v-vertex polyhedra, and for a given v clusters of several different point-group symmetries may be possible.

Other things being equal, high symmetry is usually favourable to cluster stability. For the highest possible symmetries, the icosahedral groups I and I_h, the geometric and electronic structures have been systematically studied [11, 12]. The aim of the next section is to extend this work to tetrahedral (T, T_d and T_h) symmetry.

Geometrical factors are considered first. We wish to know for what numbers v is a tetrahedral cluster possible, how many distinct tetrahedral structures correspond to each allowed v, and how each polyhedron may be constructed. The electronic structures of carbon clusters based on these polyhedra are treated later.

3. Tetrahedral clusters

Elementary symmetry arguments can be used to derive some limitations on v by considering the *orbits* [19] of the tetrahedral group. For any point group there is only a finite number of different orbits (types of sets of equivalent points); in the group T_d, for example, there is an orbit of order 1 (an atom at the intersection of *all* symmetry elements), one of order 4 (generated by an atom on a C_3 axis), one of order 6 (two atoms on each C_2 axis), one of order 12 (two atoms in each mirror plane) and one of order 24 (generated by an atom on *no* symmetry element). T, the rotational subgroup of T_d, has orbits of order 1, 4, 6 and 12; T_h, the point group of a centrosymmetric but tetrahedral molecule (e.g. the "octahedral" complex $M(H_2O)_6$ illustrated in Fig. 6.3 of Griffith's book [20]) has orbits of order 1, 6, 8, 12 and 24.

The orbits can be visualised as vertices of polyhedra. For example, the 4-orbit of T and T_d is the set of vertices (*or* face centres) of a regular tetrahedron, the 6-orbit spans a regular octahedron and the 12-orbit a truncated tetrahedon (see Fig. 1).

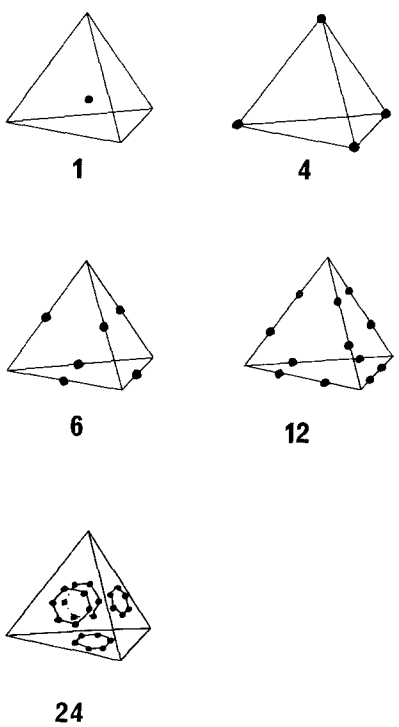

Fig. 1. Orbits of the T_d point group. The five different types of set of equivalent points compatible with T_d symmetry are illustrated

Now, a pseudospherical cluster has no atom at the centre, and a 3-connected cluster can have no atom on a C_2 axis and therefore no set of 6 equivalent atoms. All the other orbits contain a multiple of 4 atoms and thus *v must be a multiple of four* for any tetrahedral pentagon+hexagon cluster. In addition, the number of sets of four equivalent atoms is limited to zero, one or two, since no more than two atoms are allowed on each C_3 axis for a cluster consisting of a single spherical shell. Similarly, the number of sets of 6 equivalent *points* (not atoms) is limited to one.

We can regard any pentagon+hexagon cluster as a pseudosphere on which 12 pentagons lie, with the spaces in-between tiled with hexagons. In tetrahedral symmetry the centres of the pentagons must form a single 12-orbit, i.e. they are all equivalent. (Combinations such as $12=4+4+4$ and $12=6+6$ are ruled out by the pseudospherical topology.) Incidentally, this shows why octahedral (O and O_h) Buckminsterfullerenes are not possible: the 12 equivalent sites would lie on C_2 axes in these groups and this is incompatible with the symmetry of the pentagon. The groups T, T_d and T_h exhaust the allowed cubic groups for Buckminsterfullerenes.

Possible clusters may also be subdivided according to whether the 12 equivalent pentagons are present as 4 fused triples, 6 fused pairs or 12 isolated singles, [14, 17] and further classified according to the orientation of the triples or pairs. Fig. 2 shows the 6 types of cluster for T_d symmetry. By filling in the spaces

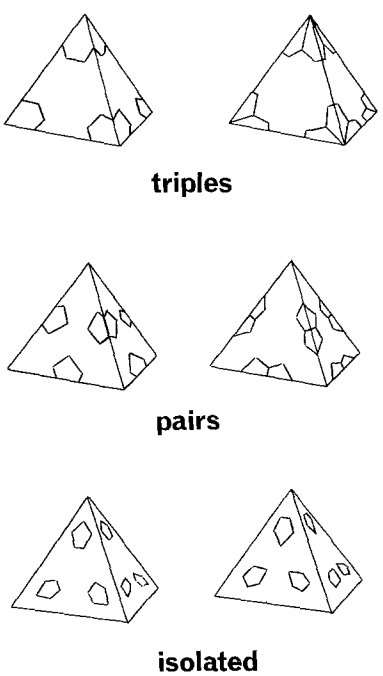

Fig. 2. Disposition of pentagons on the surface of a pseudospherical T_d polyhedron. Six distinct distributions are possible in T_d symmetry, two each involving triples, pairs and isolated pentagons. The spaces between the pentagons are to be filled by hexagons

between pentagons it is possible to build up series of clusters and to derive by induction formulas for their vertex numbers.

4. Systematic construction: icosahedral clusters

However, a much more powerful approach is possible, one that gives a unified derivation for all allowed v from which the subtypes emerge as special cases. This is an extension of the method described by Coxeter for icosahedral clusters [21]. To set our results for tetrahedral structures in context, we must first give a summary of the approach as it applies to icosahedral symmetry.

Coxeter's method is best explained by considering not the spherical pentagon+hexagon cluster but its face dual (often simply called the dual). The dual of a polyhedron $\mathscr{P}$ is found by replacing each face-centre of $\mathscr{P}$ by a vertex, and each vertex of $\mathscr{P}$ by a face-centre. The dual of any 3-connected polyhedron with 12 pentagonal and f_6 hexagonal faces is a deltahedron $\mathscr{D}$ (=a polyhedron having only triangular faces) with 12 five-coordinate and f_6 six-coordinate vertices. A polyhedron and its dual have the same point-group symmetry.

For icosahedral symmetry the Coxeter construction runs as follows. The twelve 5-coordinate vertices of $\mathscr{D}$ are all equivalent in icosahedral symmetry and they can be connected together to form a master icosahedron whose surface can then be subdivided into small triangles—the faces of $\mathscr{D}$. Take a planar lattice of equilateral triangles of unit side and draw the net of the master icosahedron onto this plane in the following way. From one vertex (A) move along b edges, then turn through 60° and move along c edges (Fig. 3). b and c are integers satisfying $b \geq c \geq 0$. This defines the second vertex (B). Repeat the sequence to reach vertex C and then return to A. This gives one large triangle ABC. Twenty such triangles make up the net of a spherical icosahedron, and the small triangles contained within it are the faces of the deltahedron of icosahedral symmetry. The area of ABC is $\sqrt{3}/4(b^2+bc+c^2)$ and each small triangle has an area $\sqrt{3}/4$. Therefore the total number of faces in the deltahedron $\mathscr{D}$ is $20(b^2+bc+c^2)$; the number of *vertices* in the pentagon+hexagon cluster $\mathscr{P}$ is also $20(b^2+bc+c^2)$. The vertices A, B, C, ... of the master icosahedron correspond to centres of pentagonal faces in the final 3-connected cluster.

The multiples of 20 which are represented by $20(b^2+bc+c^2)$, and which therefore occur as the vertex number of an icosahedral cluster, are those of the form

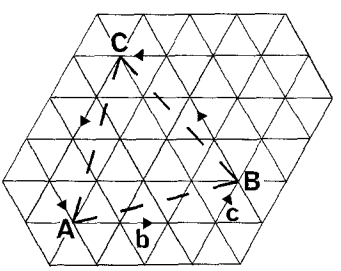

Fig. 3. The Coxeter construction for an icosahedral polyhedron. The equilateral triangle ABC has side $(b^2+bc+c^2)^{1/2}$ and is one of 20 making up the net of the master icosahedron

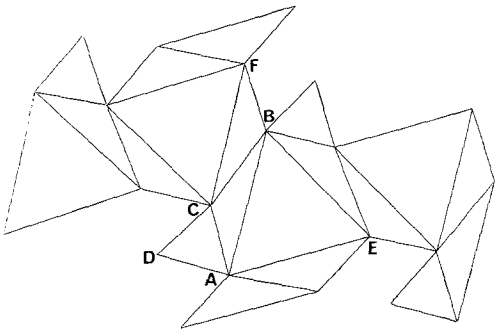

Fig. 4. Net of the twisted truncated tetrahedron, the general polyhedron of tetrahedral symmetry

$v = 20M^2N$ where none of the prime factors of N are of the form $3k+2$: just 40% of the multiples of 20 under 1000 occur.

5. Systematic construction: tetrahedral clusters

The previous section constitutes a general derivation of the vertex-number of an icosahedral (I or I_h) of the Buckminsterfullerene type. Symmetry aspects of this formula and its relation to bonding are discussed in [12]. To extend it to tetrahedral clusters we must generalise the net. The net of the dual deltahedron $\mathscr{D}$ of *any* 3-connected pentagon+hexagon polyhedron $\mathscr{P}$ can be superimposed on the triangulated lattice. The most general tetrahedral polyhedron with 12 vertices $ABC \ldots JKL$ is a twisted truncated tetrahedron and its net consists of 4 large equilateral triangles, 4 small equilateral and 12 scalene triangles as shown in Fig. 4. Each vertex $A \ldots L$ corresponds to a pentagonal face in the final dual polyhedron. To determine the area covered by the net it is sufficient to consider a scalene triangle ABC superimposed on the triangulated plane as in Fig. 5. Taking A as the origin, the vertex B is specified by a pair of integers (i, j), and the vertex C by the pair (k, l). Thus B is reached by taking i steps along the direction $\boldsymbol{e}_1$ followed by j steps along $\boldsymbol{e}_2$. Given these vertices, equilateral triangles ACD and ABE (Fig. 4) are erected on the sides of ABC, the parallelogram is completed by a similar scalene triangle BCF, and so on until the whole net is drawn. The area of ABC is $\sqrt{3}/4(il-jk)$, ACD covers $\sqrt{3}/4(k^2+kl+l^2)$ and ABE has an area $\sqrt{3}/4(i^2+ij+j^2)$. The total area of the net is thus equivalent to $4[i^2+ij+j^2+k^2+kl+l^2+3(il-jk)]$ small triangles. The general pentagon+hexagon cluster of tetrahedral symmetry has therefore

$$v = 4[i^2+ij+j^2+k^2+kl+l^2+3(il-jk)] \tag{1}$$

vertices. By construction the quantities i, j, k and l are integers such that $il-jk>0$ and $i>0$, $j \geq 0$.

This equation for v can be used to give a complete description of all tetrahedral clusters if several important points are noted. If the formula is to count each distinct cluster once and only once, further restrictions must be imposed on i, j, k and l. Detailed consideration of the transformation of these integers under rotations in the plane yields the following additional conditions for uniqueness

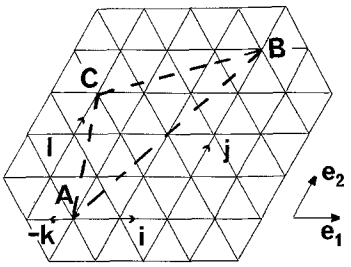

Fig. 5. The Coxeter construction for a general polyhedron of tetrahedral symmetry. *ABC* is a scalene triangle from the net in Fig. 4

(see Appendix for detail):

$$i^2+ij+j^2 \geq k^2+kl+l^2 \tag{2a}$$

$$x \geq y \geq 0, \tag{2b}$$

where

$$x = l(i-j)-k(i+2j)+3(k^2+kl+l^2)$$

and

$$y = l(i+2j)-k(2i+j).$$

Also,

$$\text{If} \quad y=j=0 \quad \text{then} \quad 2k+l \geq 0. \tag{2c}$$

If the two sides in (2a) are equal then $(k+l, -l, i+j, -j)$ represents the same cluster as (i, j, k, l).

A more compact representation of the formula (1) can be obtained in terms of two complex parameters, instead of four integers, as follows. Let ω be the complex number $\exp(2\pi i/6) = \frac{1}{2}(1+\sqrt{-3})$; then the point with triangular coordinates (b, c) on the net can be described by the single complex number $\alpha = b + c\omega$ in the Argand diagram. Note that $|\alpha|^2 = \alpha\bar{\alpha} = b^2+bc+c^2$ is the square of the distance of this point from the origin. The vertex number v of an icosahedral cluster with Coxeter parameters b, c can now be expressed as $v = 20\alpha\bar{\alpha}$ where $\alpha = b + c\omega$; in the tetrahedral case setting $\alpha = i + j\omega$, $\beta = k + l\omega$ gives

$$v = v(\alpha, \beta) = 4[\alpha\bar{\alpha} + \beta\bar{\beta} + \sqrt{-3}(\alpha\bar{\beta} - \beta\bar{\alpha})]. \tag{3}$$

The condition $il - jk > 0$ becomes $\text{Im}(\beta/\alpha) > 0$. The restrictions (2) can be recast in terms of the magnitudes and directions of the vectors α, β in the complex plane. Algebraic properties of the set of allowed v are most easily proved using this complex representation.

6. Assignment to point groups

Tetrahedral clusters must belong to one of three point groups T, T_d and T_h or, if additional elements of symmetry are present, to the higher group I or I_h. A particular cluster can be assigned to one of the five groups from the orientation and shape of its net, *ABC*... *JKL*, or equivalently by inspection of (α, β).

6.1. Case (a) Centrosymmetric icosahedral (I_h)

The triangle ABC is *equilateral* and AB is either horizontal (parallel to e_1) or at 30° to the horizontal. The first condition implies $\beta = \alpha\omega$ and the orientation condition is $\alpha = i$ or $\alpha = i(1+\omega)$. In this case $v(\alpha, \beta)$ reduces to

$$v = 20(i^2 + ij + j^2) \tag{4}$$

with $j = 0$ or $i = j$.

6.2. Case (b) Handed icosahedral (I)

The triangle ABC is equilateral but AB lies at a general angle to the horizontal. Then $|\alpha| = |\beta|$ and $\beta = \alpha\omega$ but α is unrestricted; $v(\alpha, \beta)$ reduces to (4) without the condition on i and j.

6.3. Case (c) Centrosymmetric tetrahedral (T_h)

ABC is isosceles so that the net consists of 8 equilateral triangles of side $|\alpha|$ and 12 isosceles triangles. The condition that the polyhedron must be centrosymmetric implies that $\beta = \bar{\alpha}\omega^n$ where n is an integer ($0 \leq n \leq 5$).

6.4. Case (d) Tetrahedral (T_d)

This separates into two subcases. In case (d') ABC is a right-angled triangle ($\angle BAC = 90°$) with AB lying at 0° or 30° to the horizontal. Then $\mathrm{Re}\,(\alpha/\beta) = 0$ and $\alpha = i$, $\beta = k(1-2\omega)$ or $\alpha = i(1+\omega)$, $\beta = k(1-\omega)$. So either $j = 0$ and $l = -2k$, giving $v = 4(i^2 - 6ik + 3k^2)$; or $j = i$ and $l = -k$, giving $v = 4(3i^2 - 6ik + k^2)$. The master polyhedron degenerates to a rectangular cuboctahedron. In case (d'') ABC is a scalene triangle with $\angle ABC = 120°$ and AB horizontal or at 30° to the horizontal. Either $\alpha = i$, $\beta = i + l\omega$, so $j = 0$ and $k = i$, giving $v = 4(2i^2 + 4il + l^2)$; or $\alpha = i(1+\omega)$, $\beta = k + (3i - 2k)\omega$, so $j = i$ and $l = 3i - 2k$, giving $v = 12(7i^2 - 6ik + k^2)$. For case (d'') clusters the master polyhedron is a truncated tetrahedron.

6.5. Case (e) Handed tetrahedral (T)

All other combinations give the lower T symmetry: when ABC is a general scalene triangle, or when it is one of the special triangles but the net lies in a general orientation on the triangular grid. In the latter circumstances the master polyhedron is not itself twisted, but the disposition of pentagons at the vertices is chiral.

Reasoning of this kind has been incorporated into a computer program for generating all distinct tetrahedral clusters and classifying them by point group (see Appendix and Table 1).

Table 1. A list of all possible tetrahedral pentagon+hexagon polyhedra, complete to $v=256$ and including the icosahedral supergroups. i, j, k, l are the parameters in Eq. (1). v is the number of vertices and m is the multiplicity—the number of distinct clusters of given v. For I and T symmetries one enantiomer of each pair is given. The column labelled "Pentagons" describes the grouping of the pentagons on the surface of the polyhedron and n_4 is the number of sets of 4 equivalent vertices

v	m	i	j	k	l	Group	Pentagons	n_4
20	1	1	0	0	1	I_h	one patch	0
28	1	1	1	0	1	T_d	one patch	1
40	1	1	1	−1	1	T_d	triples	1
44	1	2	0	0	1	T	triples	2
52	1	2	0	1	1	T	pairs	1
56	1	2	1	0	1	T_d	triples	2
60	1	1	1	−1	2	I_h	isolated	0
68	2	1	2	−1	1	T	triples	2
		1	2	0	2	T_d	pairs	2
76	2	2	0	−1	2	T_d	isolated	1
		3	0	0	1	T	triples	1
80	1	2	0	0	2	I_h	isolated	0
84	1	3	0	1	1	T_d	isolated	0
88	1	1	2	−1	2	T	isolated	1
92	3	2	1	0	2	T	isolated	2
		2	1	1	2	T_h	pairs	2
		3	1	0	1	T_d	triples	2
100	3	2	1	−1	2	T	isolated	1
		2	2	−1	1	T_d	triples	1
		3	0	2	1	T	pairs	1
104	1	1	3	−1	1	T	triples	2
112	1	2	2	0	2	T_d	isolated	1
116	3	1	2	−2	2	T	isolated	2
		1	2	−1	3	T_h	isolated	2
		4	0	0	1	T	triples	2
120	1	3	0	−1	2	T_d	isolated	0
124	3	1	3	−1	2	T	isolated	1
		1	3	0	3	T_d	pairs	1
		3	0	0	2	T	isolated	1
132	1	2	2	−1	2	T	isolated	0
136	2	3	0	1	2	T	isolated	1
		4	1	0	1	T_d	triples	1
140	4	1	2	−2	3	I	isolated	0
		2	3	−1	1	T	triples	2
		3	1	0	2	T	isolated	2
		3	1	1	2	T	isolated	2
148	3	1	4	−1	1	T	triples	1
		3	1	−1	2	T	isolated	1
		3	1	2	2	T	pairs	1
152	2	1	3	−1	3	T	isolated	2
		2	1	−2	3	T_h	isolated	2
156	1	2	2	0	3	T	isolated	0
160	1	2	2	−2	2	T_d	isolated	1
164	4	1	3	−2	2	T	isolated	2
		3	2	0	2	T_d	isolated	2
		4	0	3	1	T	pairs	2
		5	0	0	1	T	triples	2
168	1	1	4	−1	2	T_d	isolated	0

Table 1 (continued)

v	m	i	j	k	l	Group	Pentagons	n_4
172	4	2	2	−1	3	T	isolated	1
		2	3	−1	2	T	isolated	1
		3	0	−1	3	T	isolated	1
		4	0	−1	2	T_d	isolated	1
176	1	4	0	0	2	T	isolated	2
180	1	3	0	0	3	I_h	isolated	0
184	3	2	3	0	3	T_d	isolated	1
		3	2	−1	2	T	isolated	1
		3	3	−1	1	T_d	triples	1
188	5	1	3	−2	3	T	isolated	2
		1	3	−1	4	T_h	isolated	2
		2	4	−1	1	T	triples	2
		4	0	1	2	T	isolated	2
		5	1	0	1	T_d	triples	2
196	6	1	4	−1	3	T	isolated	1
		1	4	0	4	T_d	pairs	1
		2	2	−2	3	T	isolated	1
		3	1	0	3	T	isolated	1
		4	1	0	2	T	isolated	1
		4	1	1	2	T	isolated	1
200	3	1	5	−1	1	T	triples	2
		3	1	−1	3	T	isolated	2
		3	1	1	3	T_h	isolated	2
204	2	4	1	−1	2	T	isolated	0
		4	1	2	2	T_d	isolated	0
208	1	4	0	2	2	T	isolated	1
212	5	2	3	−2	2	T	isolated	2
		2	3	−1	3	T	isolated	2
		3	1	−2	3	T	isolated	2
		3	2	1	3	T	isolated	2
		3	2	2	3	T_h	pairs	2
220	6	1	3	−2	4	T	isolated	1
		1	4	−2	2	T	isolated	1
		2	4	−1	2	T	isolated	1
		3	2	0	3	T	isolated	1
		4	1	3	2	T	pairs	1
		6	0	0	1	T	triples	1
224	1	4	2	0	2	T_d	isolated	2
228	2	2	2	−3	3	T_d	isolated	0
		3	3	−1	2	T	isolated	0
232	3	1	3	−3	3	T	isolated	1
		1	4	−1	4	T	isolated	1
		5	0	−1	2	T_d	isolated	1
236	5	2	3	0	4	T	isolated	2
		3	2	−1	3	T	isolated	2
		3	4	−1	1	T	triples	2
		4	0	−1	3	T	isolated	2
		5	0	0	2	T	isolated	2
240	1	2	2	−2	4	I_h	isolated	0
244	5	1	4	−2	3	T	isolated	1
		2	5	−1	1	T	triples	1
		4	0	0	3	T	isolated	1

Table 1 (continued)

v	m	i	j	k	l	Group	Pentagons	n_4
		4	2	−1	2	T	isolated	1
		5	0	4	1	T	pairs	1
248	3	2	3	−2	3	T	isolated	2
		5	0	1	2	T	isolated	2
		6	1	0	1	T_d	triples	2
252	1	3	3	0	3	T_d	isolated	0

7. Isomeric tetrahedral clusters

Within the restrictions (2) it is still possible for a given v to be generated by two or more different sets (i, j, k, l) but only if the clusters are distinct isomers. Thus for $v=68$ there are two tetrahedral clusters: one with $i=1, j=2, k=0, l=2$ and a second with $i=1, j=2, k=-1, l=1$; the first has pentagons in pairs and has T symmetry, the second has pentagons in triples and belongs to T_d. For $v=92$ there are 3 distinct clusters: one example each of T_h and T_d and a mirror-image pair of T symmetry.

The pentagon groupings within the cluster are easily identified from the net or from (α, β). Vertices joined in the net by lines of unit length represent pentagons in contact in the final polyhedron. When $|\alpha|=1$ or $|\beta|=1$ their respective equilateral triangles correspond to 3-pentagon patches; when $|\alpha-\beta|=1$ the line BC represents a pair of abutting pentagons. C_{20} is the degenerate case $|\alpha|=|\beta|=|\alpha-\beta|=1$ when every pentagon is in contact with five others; C_{28} has $|\beta|=|\alpha-\beta|=1$ and every pentagon touches 3 others. In all larger tetrahedral clusters a pentagon touches at most 2 others and the largest "patches" are groups of at most three pentagons in contact.

Imposing the appropriate restrictions on the general formula for $v(\alpha, \beta)$, it turns out that all tetrahedral clusters with pentagon triples obey

$$v(\text{triple}) = 4(a^2+ab+b^2-2) \tag{5}$$

with $a \geq b \geq 0$, and all clusters with pentagon pairs obey

$$v(\text{pair}) = 8(a^2+3ab+3b^2)-4 \tag{6}$$

with $a, b > 0$. It is straightforward to derive these formulas independently by using Goldberg's result [15] for the number of faces of a medial tetrahedral polyhedron. Tables 2 and 3 list the triple and pair clusters for $v<256$. Note that $v=20$ and $v=28$ are degenerate cases and appear in both lists. Multiple occurrences in a given Table (e.g. $v=188$) indicate distinct isomers with the same type of pentagon patch. Note also that no entry in these tables is a multiple of 3; the significance of this fact will emerge later.

A complete list of the allowed vertex numbers $v<256$ is given in Table 1, together with a list of the isomer counts, point-group symmetries, and classification by

Table 2. Vertex numbers of clusters with 3-pentagon patches, a and b are the parameters in Eq. (5)

b \ a	2	3	4	5	6	7	8
0		28	56	92	136	188	248
1	20	44	76	116	164	220	
2	40	68	104	148	200		
3		100	140	188	244		
4			184	236			

Table 3. Vertex numbers of clusters with 2-pentagon patches. a and b are the parameters in Eq. (6)

b \ a	0	1	2	3	4	5
0			28	68	124	196
1	20	52	100	164	244	
2	92	148	220			
3	212					

pentagon grouping. Each entry for a T (or I) cluster in the Table represents a pair of enantiomers.

Some interesting general points emerge from a consideration of the Tables. First, the tetrahedral clusters are in fact very common. Of the multiples of 4, almost all numbers above 20 admit a tetrahedral cluster. The exceptions are conjectured to be numbers of the form $v = 4 \times 2^N \times 3^M$ where N and M are non-negative integers. This conjecture has yet to be proved but direct enumeration shows it to be true for all v below 10 000. Thus the disallowed v are 24, 32, 36, 48, 64, 72, 96, 108, 128, 144, 192, 216, 256, ... and in the range $20 \leq v \leq 10\,000$ some 98% of the multiples of 4 are allowed.

The multiplicity, i.e. the number of possible isomers at a given v, increases with cluster size but rather slowly and erratically. Examples of T and T_d clusters with the same v are common, e.g. 68, 92, 100 ... and the first example with both icosahedral and tetrahedral isomers is $v = 140$.

8. Multiplication of clusters

A second point illustrated by the Table is that, if v is an allowed tetrahedral number, multiples of v such as $2v$, $3v$, $4v$ ... also occur. In general all multiples of the forms $(p^2+q^2)v$ and $(p^2+pq+q^2)v$ occur; the first missing integer multiple is thus $11v$. Many of these multiplications can be given simple geometrical interpretations.

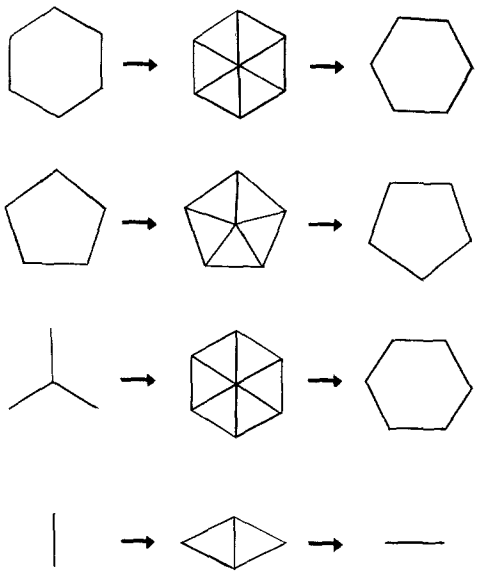

Fig. 6. Effect of the leapfrog operation on the faces, vertices and edges of a 3-connected polyhedron

For example, the transformation $v \to 3v$ can be achieved by scaling all lengths in the net by $\sqrt{3}$ and rotating all position vectors through 90° ($\alpha \to \sqrt{-3}\alpha$, $\beta \to \sqrt{-3}\beta$). In geometrical terms the transformation $v \to 3v$ is the leapfrog operation [12, 13] and applies to any 3-connected pentagon+hexagon polyhedron $\mathscr{P}$ (not necessarily tetrahedral or icosahedral). The leapfrog $\mathscr{L}$ is constructed from $\mathscr{P}$ in two stages. First, the pentagonal and hexagonal faces are capped to produce a deltahedron $\mathscr{D}$. Then the face dual of $\mathscr{D}$ is taken. A simple application of Euler's rule shows that the final polyhedron has three times as many vertices as the original, is still a pentagon+hexagon polyhedron, and retains the symmetry of the original. Fig. 6 shows how the faces and other components of $\mathscr{P}$ change under the leapfrog operation.

Leapfrogging may be repeated and so the numbers v, $3v$, $9v$, $27v$, ... all appear in the list of allowed vertex numbers for a given symmetry. For the particular case of the tetrahedral and icosahedral clusters with vertex numbers $v(\alpha, \beta)$ given by (3) it is possible to show that the cluster is a leapfrog if and only if v is a multiple of 3, so that $v/3$ occurs whenever v is a multiple of 3, and *all* tetrahedral clusters with $3n$ atoms are leapfrogs of smaller clusters. This is not true in all symmetry groups but it explains the observation made earlier that no cluster with $3n$ atoms has pentagons in contact—on leapfrogging every pentagon is surrounded by hexagons. The leapfrog operation is particularly important because, as shown in [13], it is directly connected to the electronic structure of the polyhedral carbon cluster: all leapfrogs have closed electronic shells. The point is taken up in a later section of this paper.

The quadrupling transformation $v \to 4v$, though less important from a bonding standpoint, also has a simple geometrical interpretation and applies to the whole class of 3-connected pentagon+hexagon polyhedra. In terms of the tetrahedral

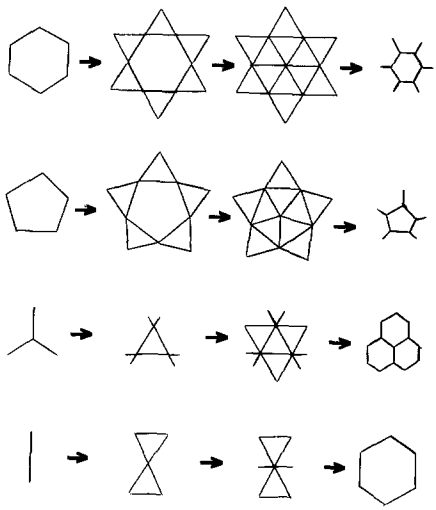

Fig. 7. Effect of the quadrupling operation on the faces, vertices and edges of a 3-connected polyhedron

net it is achieved by the changes $\alpha \to 2\alpha$, $\beta \to 2\beta$, equivalent to doubling all lengths in the net but preserving the orientation. For the more general pentagon + hexagon polyhedron $\mathscr{P}$, the quadruple $\mathscr{Q}$ is found as follows. Form the *edge dual* $\mathscr{E}$ (a polyhedron with edge centres at the vertices of $\mathscr{P}$ and vertices at the centres of the edges of $\mathscr{P}$). Because $\mathscr{P}$ is 3-connected each of its edges meets 4 others and therefore $\mathscr{E}$ is 4-connected with the same number of pentagons and hexagons as $\mathscr{P}$ but with v additional triangular faces. Capping all the pentagonal and hexagonal faces of $\mathscr{E}$ gives a deltahedron $\mathscr{D}'$ whose face dual is the final, quadruple polyhedron $\mathscr{Q}$. $\mathscr{Q}$ is a pentagon + hexagon cluster with the same symmetry $\mathscr{P}$ but with four times as many vertices. Figure 7 shows the effect of the quadrupling operation on components of $\mathscr{P}$ and Fig. 8 illustrates the leapfrog and quadrupling operations for the simplest cluster C_{20}, the regular dodecahedron. Again for the series $v(\alpha, \beta)$ it turns out that whenever v is divisible by 16 then $v/4$ is present so that all tetrahedral and icosahedral clusters with $16n$ vertices are quadruples of smaller clusters.

The doubling transformation $v \to 2v$ is less general than either of these. It does not preserve symmetry for the tetrahedral clusters. It can be shown that transformations $v \to (p^2 + pq + q^2)v$ preserve the T subgroup symmetry but only preserve T_d or T_h symmetry if $p = q$ or $q = 0$; thus for *full* symmetry conservation essentially the only allowed multiplications are $v \to 3v$ and $v \to p^2 v$. Each of these has a simple geometrical interpretation (respectively, leapfrog and p-division of faces of the master deltahedron).

9. Electronic structure of tetrahedral clusters

For every v obeying Eq. (1) there is at least one geometrically closed tetrahedral polyhedron. However, its viability as a stable carbon cluster depends on electronic as well as geometric factors. In the absence of accurate all-electron treatments

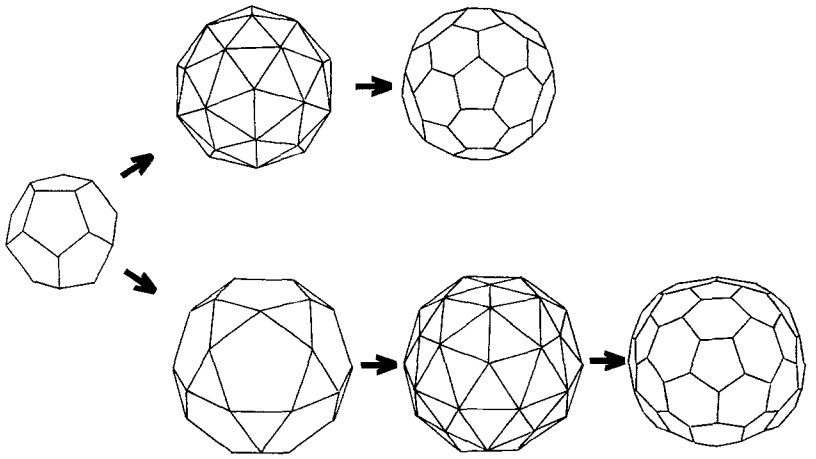

Fig. 8. Effect of the leapfrog (*above*) and quadrupling (*below*) operations on the regular dodecahedron

of large clusters, it is possible to deduce some qualitative features of the electronic structure using simple Hückel theory, assuming well-separated σ and π systems and a single bond integral parameter [4, 5, 9]. Such relatively crude treatments are usually sufficient to predict the number, symmetry and energy-order of bonding MOs (at least near the HOMO-LUMO gap) and to indicate special "aromatic" stability.

In the simplest picture of a 3-connected carbon cluster each atom is supposed to contribute 3 sp^2 hybrids and 3 valence electrons to the electron-precise σ edge bonding, and one radial p orbital with the remaining valence electron to the "π" system. The spherical harmonics and their derivatives may be used to classify the resulting MOs and to estimate their bonding/antibonding characteristics [9].

If fewer than $N/2$ of the π orbitals of an N-atomic cluster are bonding the cluster is unlikely to exist as a neutral species. However, if at least $N/2$ π MOs are bonding we can distinguish three cases of interest. The cluster may have exactly $N/2$ bonding orbitals and thus a *closed* electronic shell. Or, the cluster may have more than $N/2$ bonding MOs but with a part-filled degenerate HOMO and thus an *open* shell; it is then susceptible to Jahn-Teller distortion to a lower symmetry. Finally, the cluster may have more than $N/2$ bonding MOs of which the lowest $N/2$ are doubly occupied: a closed shell with low-lying empty bonding orbitals (a *pseudo-closed* shell). The predictions of simple Hückel theory are less clearcut in this case but structures with such small HOMO-LUMO gaps are unlikely to be equilibrium geometries—they may rearrange to reduce the number of bonding orbitals to $N/2$ and thereby gain stabilisation energy.

All tetrahedral clusters with $v \leq 100$ are classified in Table 4 according to the results of simple Hückel calculations. In the Table every example of a cluster with 3-pentagon patches or with pentagon pairs has either an open or a pseudo-closed shell. Of the clusters with isolated pentagons only for $v = 60$ and $v = 84$ are true closed shells found.

Table 4. Electronic structure of tetrahedral carbon clusters with up to 100 atoms. O stands for an open shell, PC for a closed shell with low-lying empty bonding orbitals and C for a true closed shell. These are results of Hückel calculations with a single β parameter

Pentagons	v	Group	Electronic structure
Triples	20	I_h	O
	28	T_d	O
	40	T_d	O
	44	T	PC
	56	T_d	PC
	68	T	PC
	76	T	O
	92	T_d	PC
	100	T_d	O
Pairs	52	T	O
	68	T_d	O
	92	T_h	O
	100	T	O
Isolated	60	I_h	C
	76	T_d	O
	84	T_d	C
	88	T	O
	92	T	PC
	100	T	O

The tetrahedral open-shell configurations all have a triply-degenerate HOMO containing two electrons (t^2); in the pseudo-closed shells the bonding LUMO is a triply degenerate set (t^0). For icosahedral open shells the configuration is g^2 [9].

C_{84} and C_{60}, in addition to having the only true closed shells in the list, are the only leapfrog clusters. Explicit calculation shows that leapfrogging any cluster in the list whether closed or open-shell also produces a closed-shell cluster. In fact, the leapfrog of a pentagon+hexagon cluster of any symmetry can be shown to have a closed shell [13].

The argument runs as follows [13]. When a polyhedron $\mathscr{P}$ is converted to its leapfrog $\mathscr{L}$, each edge of $\mathscr{P}$ produces one rotated through 90° in $\mathscr{L}$. Every vertex of $\mathscr{L}$ is contained in just one such derived edge, and remembering that each vertex carries a radial p orbital we can assign one local π bond and one π antibond to each of the $3N/2$ derived edges. Interaction between the local orbitals will produce delocalised MOs and alter their energies but is not expected to change the total numbers of bonding and antibonding combinations. The σ framework is electron-precise simply from the connectivity, so the consequence is that the leapfrog of *any* pentagon+hexagon cluster has a closed shell.

The derivation is not restrictive: all leapfrogs are closed, but non-leapfrogs may or may not have closed shells. This leads to the rule quoted in [13] that for

$v = 60 + 6k$ ($k = 0$ or $k \geq 2$) there is at least one closed-shell structure. In the context of the tetrahedral series this implies that whenever v is divisible by 12 the cluster has a closed shell, since all such clusters are leapfrogs. Thus for

$$v(\text{leapfrog}) = 12[a^2 + 3ab + 3b^2 + c^2 + 3cd + 3d^2 + ad + bc + 3bd] \tag{7}$$

(where a, b, c, d are positive integers) a closed-shell molecule of tetrahedral symmetry exists. By the conjecture stated earlier this should include every multiple of 12 except those of the form $v = 12 \times 2^N \times 3^M$.

A geometrical corollary of this statement is that tetrahedral clusters with no set of 4 equivalent atoms have closed shells. The number of 4-orbits for a cluster $v(i, j, k, l)$ is easily shown to be $2 - x$ where x is the number of multiples of 3 in the pair $(i - j, k - l)$. Incidentally, x itself is the number of 4-orbits in the vertex-set of the corresponding dual deltahedron. The role of the 4-orbit is similar to that of the 20-orbit for icosahedral clusters: a cluster with no 20-orbit is closed-shell and has a vertex number given by

$$v(\text{icos}) = 60[a^2 + 3ab + 3b^2] \tag{8}$$

(where a, b are integers), a special case of both (4) and (7).

Although we have not proved the converse of the leapfrog principle, that no non-leapfrogs have closed shells, it seems a reasonable conjecture that this is so *for tetrahedral clusters* and that (7) generates a complete list of tetrahedral closed shells. It would seem therefore that isolated pentagons are necessary for a closed shell *in tetrahedral symmetry* but not sufficient.

Group theoretical aspects of the leapfrog principle are covered in [13]. It is shown there that the reducible representation spanned by the bonding π MOs of $\mathscr{L}$ coincides with the representation spanned by the edges of $\mathscr{P}$. Thus both the number and the symmetry of the bonding MOs of leapfrog clusters are available without explicit calculation of the Hückel eigenvalues.

10. Systematic construction: dihedral clusters

Clusters with low symmetries are intrinsically less interesting than their cubic and icosahedral counterparts: more parameters enter the simple models of their geometrical and electronic structures and the number of isomers increases rapidly. However some dihedral structures have been proposed for carbon clusters (a D_{6h} structure for C_{72} [3], a D_{5h} structure for C_{70} [2]) and the extended Coxeter construction can give a general formula for their vertex numbers with very little effort. Accordingly we here derive the formulas for D_n, D_{nh} and D_{nd} clusters with $n = 6$, 5, 3, or 2.

For a pentagon + hexagon cluster of D_5 or D_6 symmetry the centres of the 12 pentagons are the vertices of a bicapped twisted prism, either capped by a pentagonal pyramid and having 5-fold rotational symmetry or having a 6-fold axis and a flat hexagonal cap (Fig. 9). In both cases the net of the polyhedron can be constructed from 10 (D_5) or 12 (D_6) identical fragments, each consisting

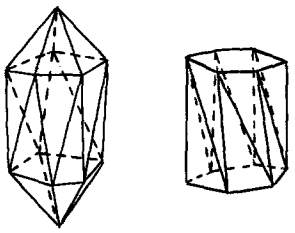

Fig. 9. The general twisted bicapped prisms of D_5 and D_6 symmetry. Each vertex of these polyhedra represents one of the 12 pentagons in a pentagon+hexagon carbon cluster

of an equilateral triangle joined to a scalene triangle. Working through the Coxeter construction for the net superimposed on a triangulated lattice we find, therefore, that clusters belonging to D_5 or one of its supergroups have

$$v(D_5) = 10[k^2 + kl + l^2 + (il - jk)] \tag{9}$$

vertices and for D_6 and its supergroups the formula is the same but with 10 replaced by 12:

$$v(D_6) = 12[k^2 + kl + l^2 + (il - jk)]. \tag{10}$$

As usual $(il - jk) > 0$. Now (9) represents $v = 10n$ for every $n > 1$, so every multiple of 10 except 10 itself gives a D_5 cluster. Similarly every multiple of 12 except 12 itself can be represented by (10) and so gives a D_6 cluster. The special limitations for D_{nh} and D_{nd} symmetry are described in the Appendix.

Table 5 lists all dihedral pentagon+hexagon polyhedra up to a limit of 256 or 300 vertices for five- and six-fold symmetries, respectively. Schmalz el al. [14] generate clusters with $v \leq 84$ by a somewhat different procedure and Table 5 agrees with their list for dihedral clusters in this range. Several of our tetrahedral clusters also appear in [14]. Simple Hückel calculations on dihedral carbon clusters ($v \leq 100$) are summarised in Table 6. As with tetrahedral clusters, the only clusters with true closed shells have isolated pentagons. The closed-shell C_{90} and C_{72} clusters are leapfrogs, as is of course icosahedral C_{60}: closed shells also occur for C_{70}, C_{84} and C_{100}. In all three of the latter cases the cluster has one or more empty nonbonding orbitals whereas the leapfrog clusters have no nonbonding orbital. As noted in [13] the D_{5d} 120-vertex clusters (5, −4, 1, 1) and (3, −4, 2, 0) are leapfrogs of the D_{5d} C_{40} clusters and have closed shells; the D_{5h} and other five-fold C_{120} clusters have open shells. The dihedral leapfrog clusters C_{60}, C_{72}, C_{90}, C_{108}, C_{120}... are accommodated by the $60+6k$ rule and it is tempting to speculate that the numbers 70, 100, ... and 84, 120, ... belong to two further infinite series of closed shells with $v = 10(7 + nm)$ or $12(7 + nm)$ for some m. We note that all clusters with sixfold dihedral symmetry and $v \geq 48$ have the same number of vertices as leapfrog clusters but not all are leapfrogs and not all have closed shells.

For D_3 symmetry the net consists of four kinds of triangles (see Appendix), and we obtain the following expression for the vertex number:

$$v(D_3) = 2\Delta_1 + 6(\Delta_2 + \Delta_3 + \Delta_4), \tag{11}$$

Table 5. A list of all possible pentagon+hexagon polyhedra with five or six-fold principal axes, complete to $v = 256$ for fivefold and $v = 300$ for six-fold symmetry. The icosahedral super-groups of D_5 are included. v_5 and v_6 are the numbers of vertices of the five-fold and six-fold polyhedra, m is the multiplicity and i, j, k, l are the parameters of Eqs. (9) and (10). The types of pentagon patch in the polyhedron are: two caps (either one pentagon surrounded by five others or a hexagon surrounded by six pentagons); one ring (10 or 12 pentagons encircling the equator); five or six pairs; 12 isolated pentagons

Vertices							Group		Pentagon
v_5	v_6	m	i	j	k	l	D_5	D_6	patches
20	24	1	1	−1	1	0	I_h	D_{6d}	one ring
30	36	1	1	−2	1	0	D_{5h}	D_{6h}	two caps
40	48	2	2	−3	1	0	D_{5d}	D_{6d}	two caps
			1	0	1	1	D_{5d}	D_{6d}	one ring
50	60	2	2	−4	1	0	D_{5h}	D_{6h}	two caps
			1	−1	1	1	D_{5h}	D_{6h}	pairs
60	72	3	3	−5	1	0	D_{5d}	D_{6d}	two caps
			2	−1	1	1	I_h	D_{6d}	isolated
			1	−1	2	0	D_5	D_6	pairs
70	84	2	3	−6	1	0	D_{5h}	D_{6h}	two caps
			2	−2	1	1	D_{5h}	D_{6h}	isolated
80	96	5	4	−7	1	0	D_{5d}	D_{6d}	two caps
			3	−2	1	1	D_{5d}	D_{6d}	isolated
			2	−2	2	0	I_h	D_{6d}	isolated
			1	−2	2	0	D_{5h}	D_{6h}	isolated
			1	0	2	1	D_{5h}	D_{6h}	pairs
90	108	3	4	−8	1	0	D_{5h}	D_{6h}	two caps
			3	−3	1	1	D_{5h}	D_{6h}	isolated
			1	0	1	2	D_5	D_6	pairs
100	120	4	5	−9	1	0	D_{5d}	D_{6d}	two caps
			4	−3	1	1	D_{5d}	D_{6d}	isolated
			2	−3	2	0	D_5	D_6	isolated
			1	−1	2	1	D_5	D_6	pairs
110	132	3	5	−10	1	0	D_{5h}	D_{6h}	two caps
			4	−4	1	1	D_{5h}	D_{6h}	isolated
			2	−1	2	1	D_5	D_6	isolated
120	144	7	6	−11	1	0	D_{5d}	D_{6d}	two caps
			5	−4	1	1	D_{5d}	D_{6d}	isolated
			2	−1	1	2	D_5	D_6	isolated
			2	−4	2	0	D_{5h}	D_{6h}	isolated
			3	−4	2	0	D_{5d}	D_{6d}	isolated
			1	−1	3	0	D_5	D_6	pairs
			2	−1	3	0	D_{5d}	D_{6d}	isolated
130	156	3	6	−12	1	0	D_{5h}	D_{6h}	two caps
			5	−5	1	1	D_{5h}	D_{6h}	isolated
			2	−2	2	1	D_5	D_6	isolated
140	168	6	7	−13	1	0	D_{5d}	D_{6d}	two caps
			6	−5	1	1	D_{5d}	D_{6d}	isolated
			3	−1	1	2	I	D_6	isolated
			3	−5	2	0	D_5	D_6	isolated
			1	0	2	2	D_5	D_6	pairs
			1	0	3	1	D_5	D_6	pairs
150	180	6	7	−14	1	0	D_{5h}	D_{6h}	two caps
			6	−6	1	1	D_{5h}	D_{6h}	isolated

Table 5 (continued)

Vertices							Group		Pentagon
v_5	v_6	m	i	j	k	l	D_5	D_6	patches
			3	−2	1	2	D_5	D_6	isolated
			1	1	1	3	D_{5h}	D_{6h}	isolated
			1	−2	3	0	D_{5h}	D_{6h}	isolated
			2	−2	3	0	D_5	D_6	isolated
160	192	8	8	−15	1	0	D_{5d}	D_{6d}	two caps
			7	−6	1	1	D_{5d}	D_{6d}	isolated
			1	0	1	3	D_5	D_6	pairs
			4	−6	2	0	D_{5d}	D_{6d}	isolated
			3	−6	2	0	D_{5h}	D_{6h}	isolated
			3	−3	2	1	D_5	D_6	isolated
			2	0	2	2	D_{5d}	D_{6d}	isolated
			1	−1	2	2	D_{5h}	D_{6h}	pairs
170	204	4	8	−16	1	0	D_{5h}	D_{6h}	two caps
			7	−7	1	1	D_{5h}	D_{6h}	isolated
			4	−2	1	2	D_5	D_6	isolated
			1	−1	3	1	D_5	D_6	pairs
180	216	8	9	−17	1	0	D_{5d}	D_{6d}	two caps
			8	−7	1	1	D_{5d}	D_{6d}	isolated
			4	−3	1	2	D_5	D_6	isolated
			4	−7	2	0	D_5	D_6	isolated
			2	−1	2	2	D_5	D_6	isolated
			3	−3	3	0	I_h	D_{6d}	isolated
			2	−3	3	0	D_5	D_6	isolated
			2	−1	3	1	D_5	D_6	isolated
190	228	4	9	−18	1	0	D_{5h}	D_{6h}	two caps
			8	−8	1	1	D_{5h}	D_{6h}	isolated
			2	0	1	3	D_5	D_6	isolated
			4	−4	2	1	D_5	D_6	isolated
200	240	11	10	−19	1	0	D_{5d}	D_{6d}	two caps
			9	−8	1	1	D_{5d}	D_{6d}	isolated
			5	−3	1	2	D_5	D_6	isolated
			2	−1	1	3	D_5	D_6	isolated
			4	−8	2	0	D_{5h}	D_{6h}	isolated
			5	−8	2	0	D_{5d}	D_{6d}	isolated
			2	−2	2	2	D_{5h}	D_{6h}	isolated
			3	−1	2	2	D_{5d}	D_{6d}	isolated
			1	1	2	3	D_5	D_6	isolated
			1	−1	4	0	D_5	D_6	pairs
			2	1	4	0	D_5	D_6	isolated
210	252	7	10	−20	1	0	D_{5h}	D_{6h}	two caps
			9	−9	1	1	D_{5h}	D_{6h}	isolated
			5	−4	1	2	D_5	D_6	isolated
			3	−4	3	0	D_5	D_6	isolated
			2	−4	3	0	D_{5h}	D_{6h}	isolated
			2	−2	3	1	D_5	D_6	isolated
			1	0	3	2	D_{5h}	D_{6h}	pairs
220	264	8	11	−21	1	0	D_{5d}	D_{6d}	two caps
			10	−9	1	1	D_{5d}	D_{6d}	isolated
			5	−9	2	0	D_5	D_6	isolated
			5	−5	2	1	D_5	D_6	isolated

Table 5 (continued)

Vertices							Group		Pentagon
v_5	v_6	m	i	j	k	l	D_5	D_6	patches
			3	−2	2	2	D_5	D_6	isolated
			1	0	2	3	D_5	D_6	pairs
			3	−2	3	1	D_5	D_6	isolated
			1	0	4	1	D_5	D_6	pairs
230	276	6	11	−22	1	0	D_{5h}	D_{6h}	two caps
			10	−10	1	1	D_{5h}	D_{6h}	isolated
			6	−4	1	2	D_5	D_6	isolated
			3	−1	1	3	D_5	D_6	isolated
			2	0	3	2	D_5	D_6	isolated
			2	0	4	1	D_5	D_6	isolated
240	288	15	12	−23	1	0	D_{5d}	D_{6d}	two caps
			11	−10	1	1	D_{5d}	D_{6d}	isolated
			3	−2	1	3	D_5	D_6	isolated
			1	1	1	4	D_{5h}	D_{6h}	isolated
			6	−10	2	0	D_{5d}	D_{6d}	isolated
			5	−10	2	0	D_{5h}	D_{6h}	isolated
			5	−6	2	1	D_5	D_6	isolated
			4	−2	2	2	I_h	D_{6d}	isolated
			3	−3	2	2	D_{5h}	D_{6h}	isolated
			3	−5	3	0	D_5	D_6	isolated
			4	−5	3	0	D_{5d}	D_{6d}	isolated
			1	−1	3	2	D_5	D_6	pairs
			1	−2	4	0	D_{5h}	D_{6h}	isolated
			2	−2	4	0	D_5	D_6	isolated
			3	−2	4	0	D_{5d}	D_{6d}	isolated
250	300	6	12	−24	1	0	D_{5h}	D_{6h}	two caps
			11	−11	1	1	D_{5h}	D_{6h}	isolated
			1	0	1	4	D_5	D_6	pairs
			6	−6	2	1	D_5	D_6	isolated
			2	0	2	3	D_5	D_6	isolated
			3	−3	3	1	D_5	D_6	isolated

where

$$\Delta_1 = i^2 + ij + j^2,$$

$$\Delta_2 = jk - il,$$

$$\Delta_3 = k^2 + kl + l^2 - ik - il - jl,$$

and

$$\Delta_4 = m(j+k) + n(k+l-i).$$

The six parameters i, j, k, l, m and n are subject to the following restrictions: $\Delta_1 > 0$, $\Delta_2 \geq 0$ (but $(k, l) \neq (0, 0)$ or (i, j)), $\Delta_3 \geq 0$, and $\Delta_4 \geq 0$ (but $(m, n) \neq (0, 0)$ or $(k+l-i, -j-k)$). The numbers represented by (11) are (see Appendix) $v = 6N$ for $N = 4$ and $N \geq 6$, and $v = 6N + 2$ for $N \geq 3$; numbers of the form $6N + 4$ are not possible.

Table 6. Electronic structure of dihedral carbon clusters with up to 100 atoms. O stands for an open shell, PC for a closed shell with low-lying empty bonding orbitals and C for a true closed shell. These are results of Hückel calculations with a single β parameter. Clusters are specified by vertex number, symmetry and pentagon grouping. Only for $v=96$ is this ambiguous: the cluster marked * has $(i, j, k, l) = (3, -2, 1, 1)$ and ** has indices $(2, -2, 2, 0)$

Pentagons	v_5	Group	Electronic structure	v_6	Group	Electronic structure
Two caps	20	I_h	O	24	D_{6d}	O
	30	D_{5h}	O	36	D_{6h}	O
	40	D_{5d}	O	48	D_{6d}	O
	50	D_{5h}	O	60	D_{6h}	O
	60	D_{5d}	O	72	D_{6d}	O
	70	D_{5h}	O	84	D_{6h}	O
	80	D_{5d}	O	96	D_{6d}	O
	90	D_{5h}	O			
	100	D_{5d}	O			
Single ring	40	D_{5d}	PC	48	D_{6d}	PC
Pairs	50	D_{5h}	O	60	D_{6h}	PC
	60	D_5	O	72	D_6	PC
	80	D_{5h}	O	96	D_{6h}	PC
	90	D_5	O			
	100	D_5	O			
Isolated	60	I_h	C	72	D_{6d}	C
	70	D_{5h}	C	84	D_{6h}	C
	80	D_{5d}	PC	96	D_{6d}	PC*
		I_h	O		D_{6d}	O**
		D_{5h}	O		D_{6h}	PC
	90	D_{5h}	C			
	100	D_{5d}	C			
		D_5	O			

For D_2 symmetry the net consists of five kinds of triangles and the vertex formula is given by

$$v(D_2) = 4(\Delta_1 + \Delta_2 + \Delta_3 + \Delta_4 + \Delta_5), \tag{12}$$

where

$$\Delta_1 = il - jk,$$

$$\Delta_2 = kn - lm,$$

$$\Delta_3 = mq - np,$$

$$\Delta_4 = p(k-i) - q(i+j-k-l)$$

and

$$\Delta_5 = (k-m)(i+j-k-l-p) - (l-n)(p+q+l-j).$$

Here the eight parameters i, j, k, l, m, n, p and q are subject to some mild restrictions, as in the case of D_3. Every $v \geq 20$ which is a multiple of 4 can be represented by (12), so occurs as the vertex number of a cluster with D_2 symmetry: see Appendix for details.

Several low-symmetry clusters are included in the calculations of Schmalz et al. [14]. Some low-symmetry isomers of C_{60} were considered by Stone and Wales [22] and found to have delocalisation energies comparable with that of the icosahedral form.

11. Conclusions

A geometrical method has been described by which general formulas for the vertex numbers of pentagon+hexagon clusters may be found. Because such clusters may have n-fold rotational symmetry only if n is 1, 2, 3, 5 or 6, the possible point groups are limited to I_h, I, T_d, T_h, T, D_{nh}, D_{nd}, D_n, S_{2n}, C_{nh}, C_{nv}, C_n, C_s and C_i. The possible site-symmetry groups for a 3-connected vertex are C_1, C_s, C_3 and C_{3v}. The results in the present paper cover all dihedral and higher molecular point groups and therefore most cases likely to be of interest.

The only vertex numbers for which at least one cluster of at least dihedral symmetry is not possible have the form $v = 60k+22$, $60k+34$, $60k+46$ or $60k+58$ so that our construction provides possible structures for all but $v = 22$, 34, 46, 58, 82 and 94 in the range $20 \leq v \leq 100$ and of these $v = 22$ is unrealisable in any symmetry.

Consideration of the list of orbits and site symmetries [19] yields some information about vertex numbers for the remaining groups. For S_{2n}, v must be multiple of $2n$, for C_5, C_{5h} and C_{5v}, v is a multiple of 10; for C_6, C_{6h} and C_{6v}, v is a multiple of 12. Thus to fill the gaps in the v sequence it will be necessary to descend to C groups with a principal axis of order 3. In fact, structures of C_{3v}, dihedral or higher symmetry are possible for all even $v \geq 20$ except 22 and 46; for $v = 46$ it is necessary to descend to C_3. With these additional groups we are thus able to exhibit at least one pentagon+hexagon cluster for any even number of vertices $v \geq 24$.

The leapfrog principle gives a relationship between geometrical and electronic structure and the $60+6k$ rule [13] accounts for all tetrahedral and many dihedral closed shells. In the range $20 \leq v \leq 100$ the closed shells found for non-leapfrog clusters are at $v = 70$, 84 and 100. In this range of v all closed-shell clusters found so far have 12 isolated pentagons: as such clusters also tend to minimise geometrical strain they are plausible candidates for stable molecules. Isolation of the pentagons is not however a guarantee of a closed electronic shell.

Finally, it may be noted that the duals of pentagon+hexagon polyhedra are deltahedra with 12 five-coordinate and $v-12$ six-coordinate vertices. They may be useful model skeletons for the hypothetical supraicosahedral *closo*-boranes [23, 24]. A deltahedron has $v = \frac{1}{2}v_3 + 2$ vertices where v_3 is the vertex-number of its 3-connected dual. For example, using (1) we find that deltahedra of tetrahedral or higher symmetry belonging to this restricted class have

$$v = 2[i^2 + ij + j^2 + k^2 + kl + l^2 + 3(il - jk) + 1] \tag{13}$$

vertices. The first few borane cages predicted by Eq. (13) are B_{12} (I_h), B_{16} (T_d), B_{22} (T_d), B_{24} (T), B_{28} (T), B_{30} (T_d) and B_{32} (I_h). Icosahedral $B_{12}H_{12}^{2-}$ is known experimentally and four of the other cages are illustrated by Lipscomb and

co-workers [23, 25]. Group-theoretical arguments [24] suggest that the clusters with 16, 22 and 28 vertices give neutral boron hydrides whereas the 24 and 30-vertex clusters would bear a charge of -2 as hydrides B_nH_n. The charges are related to the number of 4-orbits present in the cage [24] (see above, Sect. 10).

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Appendix

A1. Tetrahedral clusters

Uniqueness of representation: Let $\mathscr{P}(\alpha, \beta)$ denote the tetrahedral cluster determined by the complex parameters $\alpha = i + j\omega$ and $\beta = k + l\omega$ with $ik - jl > 0$ as in Sects. 5–8 above. We seek to determine restrictive conditions on α and β which will guarantee that each distinct cluster is generated once and once only. These restrictions were incorporated into the computer programs which produced the data for the tables. The tables are complete: in Eq. (1) the condition $il - jk > 0$ implies that all four parameters are less than $\sqrt{v/12}$, so that a systematic enumeration of all clusters with up to a given number of vertices is possible. Similar remarks hold for the generation of the tables for the dihedral clusters.

Rotating the net (Fig. 5) through 60° replaces (α, β) by $(\alpha\omega, \beta\omega)$. Thus $\mathscr{P}(\alpha, \beta) = \mathscr{P}(\alpha\omega, \beta\omega)$. We can eliminate these repeats by requiring $i > 0$ and $j \geq 0$, so that $0° \leq \arg(\alpha) < 60°$.

Interchanging the roles of the two types of equilateral triangles in the net has the effect of interchanging α and β. It follows that $\mathscr{P}(\alpha, \beta) = \mathscr{P}(-\beta, \alpha)$, the minus sign being necessary to preserve the orientation condition $\mathrm{Im}(\beta/\alpha) > 0$. By specifying $|\alpha| \geq |\beta|$ we eliminate most of the redundancy here; for the borderline case when $|\alpha| = |\beta|$ we must ensure additionally that the pairs (α, β) and $(\bar{\beta}, \bar{\alpha})$ are not both included.

The mirror-image polyhedron to $\mathscr{P}(\alpha, \beta)$ is $\mathscr{P}(\bar{\beta}, \bar{\alpha})$ or $\mathscr{P}(\bar{\alpha}, -\bar{\beta})$, as the net is obtained by complex conjugation. To eliminate the separate listing of enantiomers one can specify $\mathrm{Re}(\alpha/\beta) \geq 0$. Again, the borderline case where $\mathrm{Re}(\alpha/\beta) = 0$ needs special treatment (see below).

Finally, the most subtle way in which a polyhedron may have more than one way of being described as a $\mathscr{P}(\alpha, \beta)$ arises from the original claim that $\mathscr{P}$ is a "twisted truncated tetrahedron", from which one could decompose the net into triangles of three types: "large" equilateral triangles of side $|\alpha|$, "small" equilateral triangles of side $|\beta|$, and scalene triangles with sides $|\alpha|$, $|\beta|$ and $|\alpha - \beta|$. It turns out that there is more than one way, in general, of joining the 12 pentagon centres of the polyhedron into such a net. The polyhedron $\mathscr{P} = \mathscr{P}(\alpha, \beta)$ can also be described by parameters (α', β') and (α'', β'') where

$$(\alpha', \beta') = (\omega\alpha + (1+\omega)\beta, \beta)$$

and

$$(\alpha'', \beta'') = (\alpha, \omega\beta - (1+\omega)\alpha),$$

provided that the condition $\mathrm{Im}(\beta/\alpha) > 0$ is preserved. Each transformation has order 6. Our existing conditions on α and β are satisfied by at most one of the six pairs linked by the first transformation, and at most three of the six linked by the second (which has the effect of rotating α/β through 60° about $+\sqrt{-3}$). For uniqueness here we may specify that

$$-90° \leq \arg\left(\frac{\alpha}{\beta} - \sqrt{-3}\right) \leq -60°$$

or equivalently that

$$0° \leq \arg(\gamma) \leq 30°,$$

where $\gamma = (3\beta + \alpha\sqrt{-3})\bar{\beta}$. Writing $\gamma = x + y\omega$ we have

$$x = l(i-j) - k(i+2j) + 3(k^2 + kl + l^2)$$

and

$$y = l(i+2j) + k(2i+j)$$

and the conditions are $x \geq y \geq 0$. Borderline case considerations in the treatment of enantiomers also mean that when $y = j = 0$, we must have $2k + l \geq 0$.

Multiplication of clusters: if $\gamma = p + q\omega$ then the transformation $(\alpha, \beta) \mapsto (\alpha\gamma, \beta\gamma)$ produces a new cluster with tetrahedral symmetry, and $v(\alpha\gamma, \beta\gamma) = \gamma\bar{\gamma} v(\alpha, \beta) = (p^2 + pq + q^2) v(\alpha, \beta)$. This transformation will only preserve T_d or T_h symmetry if $\arg(\gamma)$ is a multiple of 30°; essentially, this means $p = q$ or $q = 0$, giving the restricted multiplications $v \mapsto 3p^2 v$ and $v \mapsto p^2 v$. Leapfrogging is the special case $\gamma = \sqrt{-3}$; quadrupling is the case $\gamma = 2$.

If v is a multiple of 12, then in Eq. (1) the quantity $i^2 + ij + j^2 + k^2 + kl + l^2$ is a multiple of 3. This implies (using modular arithmetic) that both $i^2 + ij + j^2$ and $k^2 + kl + l^2$ are multiples of 3, or equivalently that the complex numbers $\alpha = i + j\omega$ and $\beta = k + l\omega$ are multiples of $\sqrt{-3}$; hence the corresponding cluster is a leapfrog, and $v/3$ also occurs as the vertex number of a tetrahedral cluster.

If p and q are any integers (not both zero) then the transformation

$$(\alpha, \beta) \mapsto (p\alpha + q\beta, -q\alpha + p\beta)$$

transforms the cluster with $v = v(\alpha, \beta)$ vertices into one with $(p^2 + q^2)v$ vertices. In general T symmetry is preserved but the special cases T_d or T_h are not. In particular we may take $p = q = 1$: this gives the doubling $v \mapsto 2v$ via $(\alpha, \beta) \mapsto (\alpha + \beta, -\alpha + \beta)$. Moreover if $v/4$ is even, then again using complex modular arithmetic one can show that $\alpha \pm \beta$ are both divisible by 2, so that $\mathscr{P}(\alpha, \beta)$ is obtained by doubling $\mathscr{P}(\frac{1}{2}(\alpha - \beta), \frac{1}{2}(\alpha + \beta))$ which has $v/2$ vertices.

Combining the above observations we see that if a number $v = 4 \times 2^M \times 3^N \times v_0$ occurs as the vertex number of a tetrahedral cluster $\mathscr{P}$, then $\mathscr{P}$ can be constructed *uniquely* from a cluster $\mathscr{P}_0$ with $4v_0$ vertices by doubling M times and leapfrogging (trebling) N times. Since no cluster exists with 4 vertices it follows that no (tetrahedral) clusters have vertex numbers of the form $v = 4 \times 2^M \times 3^N$.

A2. Dihedral clusters: D_5 and D_6

For both D_5 and D_6 clusters we write $\alpha = k + l\omega$ and $\beta = i + j\omega$ where i, j, k and l are the parameters used in Sect. 10 above. The first normalization condition, as for tetrahedral clusters, is $k > 0$ and $l \geq 0$.

Secondly, changing the alignment of the two rings of pentagons has the effect of replacing β by $\beta \pm \alpha$. It is convenient to normalize here by specifying $0 \leq \mathrm{Re}(\beta/\alpha) \leq 1$. We can also eliminate listing of enantiomers by the further restriction $0 \leq \mathrm{Re}(\beta/\alpha) \leq \frac{1}{2}$, together with an extra check when either equality holds.

Finally if ten (for D_5) or twelve (for D_6) pentagons lie in the equatorial plane there is an ambiguity as to which set of five (or six) belong to which end of the cluster. In terms of the parameters, if $|\alpha| = |\beta - \alpha\omega|$, then we may replace (α, β) by $(\alpha - \beta\bar{\omega}, \alpha - \beta)$ without changing the cluster. So only one of these pairs should be included.

For D_{5d} or D_{6d} symmetry we require that the basic scalene triangle is isosceles, i.e. $|\beta| = |\alpha - \beta|$, and that $\arg(\alpha) = 0°$ or 30°. The first condition is equivalent to $\mathrm{Re}(\beta/\alpha) = \frac{1}{2}$. Similarly, for D_{5h} or D_{6h} symmetry we require the scalene triangle to be right-angled (equivalently $\mathrm{Re}(\beta/\alpha) = 0$) with the same condition on α. One final possibility: when the pentagons lie in the equatorial plane (i.e. when $|\alpha| = |\beta - \alpha\omega|$ as above), then we have D_{5d} or D_{6d} symmetry when $\arg(\alpha) = 0°$ or 30°, and D_{5h} or D_{6h} symmetry when $\arg(\beta) = 0°$ or 30°.

In Eqs. (9) and (10) we may specialize $i = l = 0$, $k = 1$ and $j = 1 - N$ for $N \geq 2$ to obtain $v(D_5) = 10N$ and $v(D_6) = 12N$ respectively.

A3. Dihedral clusters: D_2 and D_3

The net for the master polyhedron of a D_3 cluster consists of two copies of Fig. 10a; thus there are two equilateral triangles and six each of three scalene triangles. Writing $\alpha = i + j\omega$, $\beta = k + l\omega$ and $\gamma = m + n\omega$, these triangles contribute Δ_1, Δ_2, Δ_3 and Δ_4 to the vertex number respectively, where $\Delta_1 = i^2 + ij + j^2$, etc. as in Sect. 10.

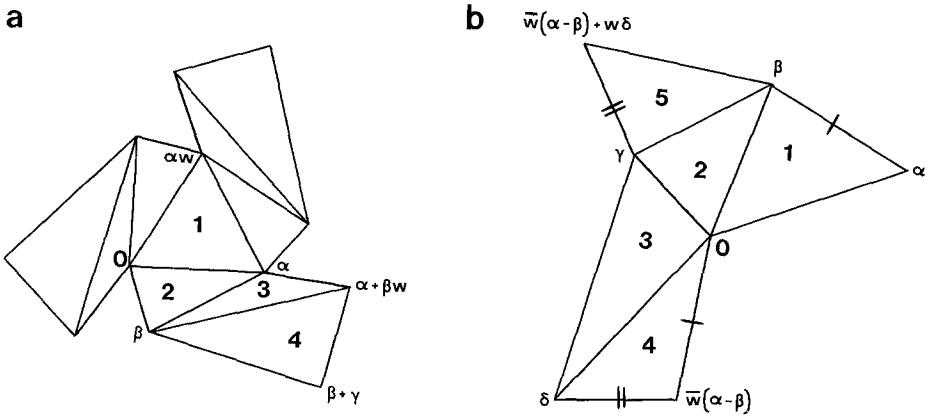

Fig. 10. **a** One half of the net of the general polyhedron of D_3 symmetry. **b** One quarter of the net of the general polyhedron of D_2 symmetry

For $n \geq 1$, Eq. (11) gives $v(0, 1, 1, 0, 0, n) = 6n + 14 = 6N + 2$ for $N = n + 2 \geq 3$; for $m \geq 1$ it gives $v(1, 1, 2, 1, m, -m) = 6m + 30 = 6N$ for $N = m + 5 \geq 6$; and $v(1, 1, 1, 0, 1, 0) = 24$. Vertex numbers $v = 30$ and $v = 6N + 4$ are impossible.

The net for a D_2 cluster consists of four copies of Fig. 10b. Writing $\alpha = i + j\omega$, $\beta = k + l\omega$, $\gamma = m + n\omega$ and $\delta = p + q\omega$, we find that triangles $1, 2, \ldots, 5$ contribute $\Delta_1, \Delta_2, \ldots, \Delta_5$ to the vertex number, where $\Delta_1 = il - jk$ etc. as in Sect. 10. Specializing $\beta = \omega$, $\gamma = \omega^2 = \omega - 1$ and $\delta = \omega^3 = -1$ we obtain $v = 4(3i + j + 2)$. Taking $j = 0, 1, 2$ and $i \geq 1$ we see that all $v = 4N$ for all $N \geq 5$ do occur.

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