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Calculation of the complexity of a chiral C_{140} - fullerene

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Abstract

The use of Group Theory in a calculation on the chiral icosahedral C_{140}-fullerene has allowed the complexity (number of spanning trees) to be determined exactly by hand. Its value is

186933228961206047277453224101263957782657451663 36.

The fullerenes[1,2] constitute a new class of molecule, containing only carbon atoms. Since their discovery in 1985, they have prompted an unparalleled volume of research.[3] Their structure, chemical physics and chemistry has received both experimental and theoretical attention; in addition to work on the limited number of known species, many authors (*e.g.* refs. 2, 4, 5) have considered what further structures might exist. Among their many theoretical properties which have been investigated, the one of interest in this work is the complexity (refs. 6, 7; see also ref. 2); this is the number of spanning trees in the carbon-network treated as a graph.[8] The chemical relevance of complexity has been treated in ref. 6, and relates chiefly to "ring currents" in magnetism and N.M.R.[9] We have recently shown (C. W. Haigh, full papers in preparation) that, by making use of Group Theory, the calculation can be very considerably simplified, and we now present a striking example where the result is an exact fifty-digit integer.

We require the admittance matrix,

$$\mathbf{K} = \mathbf{D} - \mathbf{A}\,, \tag{1}$$

where $\mathbf{D}$ is a diagonal matrix with $D_{ii} = v_i$, the valency of the i'th vertex (3 if the calculation were performed on the fullerene itself), and $\mathbf{A}$ is the adjacency matrix of the

graph[8], showing the connections of the atoms. Now, by a corollary of Kirchhoff's Theorem, the complexity of the graph G is given by[10]

$$t(G) = N^{-1}\prod_k{}' \lambda_k \ , \qquad (2)$$

where N is the number of vertices (or atoms), λ_k are the eigenvalues of **K**, and the prime indicates the omission of the zero eigenvalue (for **K** is always singular). When the graph is planar, *i.e.* it can be drawn on the plane without crossings (as in the present case), it is known[11] that its complexity is the same as that of its dual[8] (a graph where the faces become vertices and the vertices become faces).

We shall calculate the complexity of **1**, shown in Fig. 1. This is nearly the largest fullerene treated in ref. 12, but also the smallest one whose point-group is I (*cf.* ref. 4a). Although it is icosahedral, it does not possess the inversion centre and mirror-planes present in the dodecahedron and in buckminsterfullerene (both of symmetry I_h): accordingly, it is chiral.[13,*] Since its graph is a planar graph, we shall calculate the complexity of the smaller dual, consisting of 12 vertices corresponding to the pentagons (henceforth "5-vertices") and 60 vertices corresponding to the hexagons (henceforth "6-vertices").

The representation of the 5-vertices is given (as in the icosahedron - the dual of the dodecahedron) by the direct sum

$$a + t_1 + t_2 + h \ ,$$

where the g and u subscripts appropriate to the centrosymmetric group I_h have been deleted. Since there are 60 6-vertices, and the group I is of order 60, we immediately have for their representation the direct sum

$$a + 3t_1 + 3t_2 + 4g + 5h \ .$$

We now factorise the **K** matrix of the dual according to these group-theoretical results.

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* For the first experimental data on a chiral fullerene, C_{76}, see ref. 14; for a quantum-mechanical calculation on a chiral fullerene, C_{84}, see ref. 15; see also refs. 2 and 4.

Because of the Jahn-Teller effect, the ground state of the neutral C_{140} should be distorted from exact icosahedral symmetry.[4a] However, this is irrelevant to our graph-theoretical calculation, which is concerned only with the connectivity of the graph.

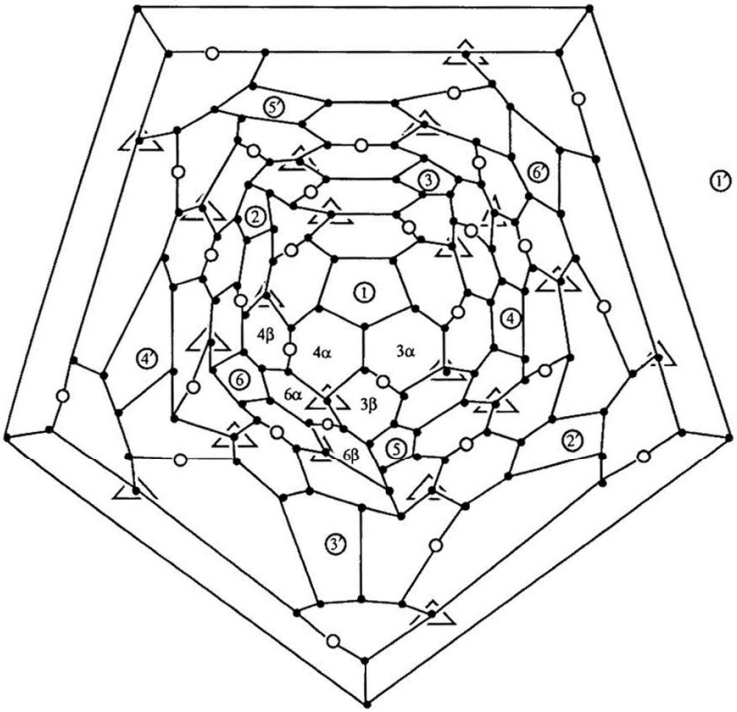

FIG. 1 The C_{140}-fullerene **1**. (This kind of drawing is technically known as a Schlegel diagram.) The twelve pentagonal faces (whose relative positions correspond to those in the dodecahedron) are labelled with circled numbers. The ten threefold rotation axes (triads) are indicated by triangles on the pair of atoms through which each passes. (Each triangle corresponds to one of the twenty hexagonal faces in buckminsterfullerene.) The fifteen twofold rotation axes (diads) are indicated by small circles in the centres of the pair of edges through which each passes. In addition, by way of illustration, the six hexagonal faces surrounding one such triangle are also given labels; this constitutes one "fragment" (see text).

The totally symmetrical irreducible representation (henceforth "irrep") a is solved trivially. One basis vector is the sum of all the 5-vertices, the second is the sum of all the 6-vertices. The resulting two-by-two submatrix of **K** has eigenvalues 0 and 6.

For the remainder, we shall make extensive use of the recent results of James[16], who has given an elegant analysis of the group-theoretical bases of the vibrations of buckminsterfullerene. Because we are concerned with point-group I, we shall combine his *gerade* and *ungerade* sets. In order to apply his analysis, we define a "fragment" in **1** to consist of the set of three hexagons surrounding any one triangle in Fig. 1 (the inner set) together with the next three hexagons (the outer set), as illustrated for one case in Fig. 1. We shall use the same terminology for the dual graph (see Fig. 2). In order to obtain basis vectors for our problem, we replace the vectors $\mathbf{a}_{ij}$ of ref. 16 (associated with a particular hexagon there) by the inner set of the corresponding "fragment" here, and replace $\mathbf{b}_{ij}$ by the outer set.

In considering the irrep g, we apply this procedure to the vectors $\mathbf{v}_1$, $\mathbf{v}_2$, $\mathbf{v}_3$ and $\mathbf{v}_4$ of ref. 16: these constitute a satisfactory basis for one row of the irrep. The determinant of the four-by-four **K** submatrix has the value 1006.

For the irrep h, we use as our first basis vector an h_g eigenvector of the icosahedron[17]. We can also use $\mathbf{v}_9$ and $\mathbf{v}_{12}$ of ref. 16, transformed as above. The remaining vectors $\mathbf{v}_5$, $\mathbf{v}_6$ and $\mathbf{v}_7$ of ref. 16 cannot be expressed in terms of $\mathbf{a}_{ij}$ and $\mathbf{b}_{ij}$ and are not therefore suitable here. But we have derived three further basis vectors to produce an orthonormal complete set for one row of this irrep. The determinant of this (quite sparse) six-by-six **K** submatrix is 21972.

The remaining vectors of the X subspace of ref. 16 were not convenient for the present problem. For the t_1 irrep, we first have, for the 5-vertices, an icosahedron eigenvector[17]. Secondly, for the 6-vertices, we make use of a t_{1g} eigenvector of the line-graph[8] of the dodecahedron, a graph with 30 vertices: in it, we replace each vertex by the sum of the corresponding pair of 6-vertices in our dual graph which are joined by an edge with a diad through it, *e.g.* vertices 4α and 4β in Figs. 1 and 2. To these two

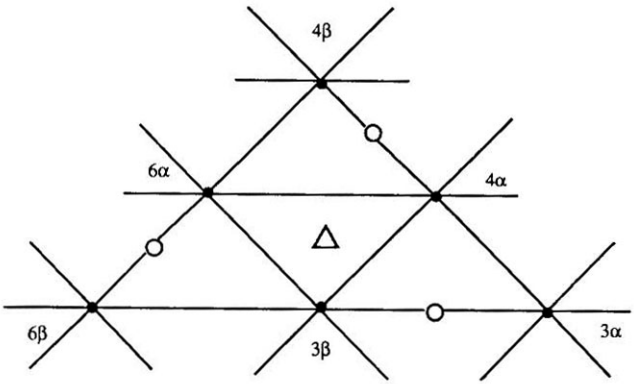

FIG. 2 A "fragment" of the dual of **1**. These vertices correspond to the six faces of the "fragment" indicated in Fig. 1. A triad and three diads are indicated as before.

basis vectors, we adjoin two more basis vectors of 6-vertices, constituting an orthonormal complete set for one row of the irrep. The determinant of this four-by-four **K** submatrix is $\frac{1}{2}(1657 - 519\sqrt{5})$. The corresponding value for the t_2 irrep is $\frac{1}{2}(1657 + 519\sqrt{5})$.

We need only substitute these results in (2). Bearing in mind that the g irrep is fourfold, and the h irrep fivefold degenerate, we obtain the value of the complexity of the dual, and hence of **1** itself, as

$$t = \frac{1}{72} \times 6 \times (1006)^4 \times (21972)^5 \times [\tfrac{1}{2}(1657 - 519\sqrt{5})\,\tfrac{1}{2}(1657 + 519\sqrt{5})]^3 .$$

Thus

$$t = 18,693,322,896,120,604,727,745,322,410,126,395,778,265,745,166,336.$$

This number (about 2×10^{49}) appears to be the largest complexity yet published for a fullerene (the previous largest known to us being *ca.* 2×10^{40} for a C_{120}-fullerene[7d], and indeed perhaps for any graph whatsoever. It has been obtained, exactly, by hand; and, for this 140-atom molecule, the largest determinant used was rather sparse and had dimensions only six-by-six.

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