

Most Fullerenes Have No Centrosymmetric Labelling

Patrick W. Fowler*

University of Sheffield, Department of Chemistry, Sheffield S3 7HF, UK

P.W.Fowler@sheffield.ac.uk

Wendy Myrvold

University of Victoria, Department of Computer Science, BC, V8W 3P6 Canada

wendym@cs.uvic.ca

(Received July 3, 2013)

Abstract

A fullerene graph is said to be *centrosymmetric* if it has a vertex labelling for which its adjacency matrix is centrosymmetric. A recent conjecture that *all* fullerenes are centrosymmetric is disproved; in fact, it turns out that *most* fullerenes are not centrosymmetric. Necessary and sufficient conditions are stated in terms of the 28 possible fullerene automorphism groups: if the group is C_1 or C_3 the fullerene is not centrosymmetric; for C_{3h} , C_{3v} or C_s the fullerene is centrosymmetric unless some vertex is fixed by a mirror plane; for all other groups, the fullerene is centrosymmetric. Most fullerenes have trivial C_1 symmetry and hence are not centrosymmetric.

A *fullerene* graph is cubic, polyhedral, has 12 faces of size five, and all other faces of size six. [1] It is the skeleton of a member of the family of all-carbon molecules to which the experimentally characterised C_{60} [2] and C_{70} [3] species belong. The $n \times n$ adjacency matrix \mathbf{A} of a graph on n vertices is said to be *centrosymmetric* [4, 5] if its entries obey

$$a_{i,j} = a_{n+1-i,n+1-j} \quad (1)$$

for all $1 \leq i, j \leq n$, which implies

$$a_{i,j} = a_{j,i} = a_{n+1-i,n+1-j} = a_{n+1-j,n+1-i}, \quad (2)$$

as adjacency matrices are symmetric. Centrosymmetric matrices have many applications [4, 5, 7, 8] and in particular have been used to prove properties of special classes of fullerenes. [6]

A recently published conjecture [6] states that every fullerene has a vertex labelling such that its adjacency matrix is centrosymmetric, or, in short, ‘All fullerenes are centrosymmetric’. However, although many fullerenes including the experimental isomers of C_{60} and C_{70} are centrosymmetric in the sense of (2), the conjecture is in fact false. *Most* fullerenes are *not* centrosymmetric.

The disproof of the conjecture is straightforward. Equation (2) amounts to specification of an automorphism of the graph: a graph has a centrosymmetric labelling, if and only if there is a permutation π of the vertex labels such that $i \rightarrow n+1-i$ for all $1 \leq i \leq n$ and π preserves all edges, i.e., π is an automorphism. The list of automorphisms of a fullerene graph can be constructed efficiently, e.g., with a special breadth-first search [9], and once an automorphism satisfying the above conditions is found, a labelling yielding a centrosymmetric adjacency matrix is immediately available. However, it is well known that many (apparently, most) fullerene isomers have only the trivial automorphism group, [11, 12] and hence cannot have a centrosymmetric adjacency matrix. The conjecture is falsified by the existence of small fullerenes with trivial symmetry, starting at $n = 36$.

We can be more precise about the conditions under which a fullerene has a centrosymmetric adjacency matrix. By Mani’s theorem, [10] any polyhedral graph can be embedded in 3D space so that all of its automorphisms correspond to point-group symmetry operations. The automorphism specified by the permutation π is of order two and fixes no vertex. There are therefore three candidates for the corresponding symmetry operation: it may be the inversion (i) (which fixes no vertex of a polyhedron), a two-fold rotation (C_2) (which fixes no vertex of odd degree), or a reflection (σ) in a plane that contains no vertices. The necessary and sufficient condition for a fullerene to have a centrosymmetric adjacency matrix is that its point group contains at least one of the three specified operations. Extension to other polyhedra is straightforward, if we note that when there is an odd number of vertices the automorphism implied by a centrosymmetric adjacency matrix fixes exactly one vertex and is therefore either a C_2 rotation or a σ reflection.

There are 28 point groups possible for fullerene graphs. [11, 12] Two (C_1 and C_3)

contain no operations of type i , C_2 or σ ; three (C_{3h} , C_{3v} , C_s) contain σ operations but not i or C_2 ; the remaining 23 (I_h , I , T_h , T_d , T , D_{6h} , D_{6d} , D_6 , D_{5h} , D_{5d} , D_5 , D_{3h} , D_{3d} , D_3 , D_{2h} , D_{2d} , D_2 , C_{2h} , C_{2v} , C_2 , S_6 , S_4 , C_i) contain at least one of i and C_2 . Hence there are three cases: (i) if the group is C_1 or C_3 the fullerene is *not centrosymmetric*; (ii) if the group is C_{3h} , C_{3v} or C_s the fullerene is *not centrosymmetric* if there is a vertex is fixed by a mirror plane, but *centrosymmetric* otherwise; (iii) for *any* other fullerene group, the fullerene is *centrosymmetric*. As more fullerenes belong to C_1 than to all other groups taken together, a centrosymmetric adjacency matrix is guaranteed for the majority of fullerene point groups, but is ruled out for the majority of fullerene graphs.

In principle, there is an ‘experimental’ fingerprint of adjacency matrix centrosymmetry for a fullerene in the tricky middle case, where vertices may or may not be fixed by reflection plane. In ideal circumstances, the ^{13}C NMR spectrum of a fullerene consists of a number of distinct peaks, one for each set of symmetry-equivalent nuclei (orbit of vertices), with intensities proportional to the set size. [1] Vertices of a fullerene graph have site symmetries (orbit sizes) C_{3v} ($|\mathcal{G}|/6$), C_3 ($|\mathcal{G}|/3$), C_s ($|\mathcal{G}|/2$), or C_1 ($|\mathcal{G}|$), where $|\mathcal{G}|$ is the order of the fullerene point group. C_{3v} and C_3 orbits are mutually exclusive. [1] For point groups C_{3h} , C_{3v} and C_s , the only orbits *without* vertices fixed by a reflection plane are those with the trivial C_1 site symmetry. Such orbits are present for all fullerenes in these groups, but if vertices fixed by reflection, orbits of other sizes will also be present. Thus, if a fullerene is already known to belong to one of the three groups C_{3h} , C_{3v} or C_s , presence of more than one peak height in the idealised spectrum implies that it is non-centrosymmetric.

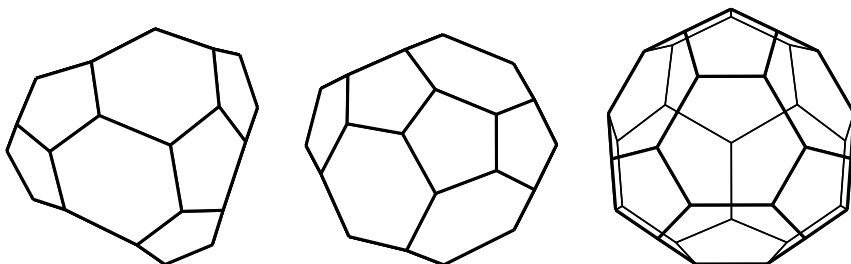


Figure 1: The three smallest non-centrosymmetric fullerenes, all with $n = 34$, drawn as 3D structures to display their respective C_s , C_s and C_{3v} symmetries.

Tables of NMR signatures [1] or programs that embody calculations of site symmetry (e.g., FuiGui [13] and Fullerene [14]) can therefore be used to compile the list of non-centrosymmetric fullerenes. Inspection of point groups shows that all fullerenes with 20 to 32 vertices are centrosymmetric. The first non-centrosymmetric fullerene isomers have 34 vertices: of the six fullerene isomers with $n = 34$, three ($34 : 2(\mathcal{C}_s)$, $34 : 3(\mathcal{C}_s)$ and $34 : 6(\mathcal{C}_{3v})$ in spiral ordering [1]) are non-centrosymmetric (Figure 1). Examples of non-centrosymmetric fullerenes continue with \mathcal{C}_{36} ($2 \times \mathcal{C}_s$, $2 \times \mathcal{C}_1$), \mathcal{C}_{38} ($1 \times \mathcal{C}_{3v}$, $7 \times \mathcal{C}_1$), \mathcal{C}_{40} ($1 \times \mathcal{C}_{3v}$, $1 \times \mathcal{C}_3$, $7 \times \mathcal{C}_s$, $8 \times \mathcal{C}_1$) and reach a majority of isomers by \mathcal{C}_{42} ($6 \times \mathcal{C}_s$, $23 \times \mathcal{C}_1$), where 29 out of 45 fullerene isomers are non-centrosymmetric.

In the class of general cubic polyhedra, non-centrosymmetric examples also occur early: the cubic polyhedra with $n = 4$ (1 isomer), $n = 6$ (1), $n = 8$ (2) are all centrosymmetric, but at $n = 10$ two (both \mathcal{C}_{3v}) of the five isomers are non-centrosymmetric, at $n = 12$ six ($4 \times \mathcal{C}_s$, $2 \times \mathcal{C}_s$) of the 14 isomers are non-centrosymmetric, and by $n = 16$, \mathcal{C}_1 isomers are already in the majority. [15] The two smallest non-centrosymmetric cubic polyhedra are shown in Figure 2.

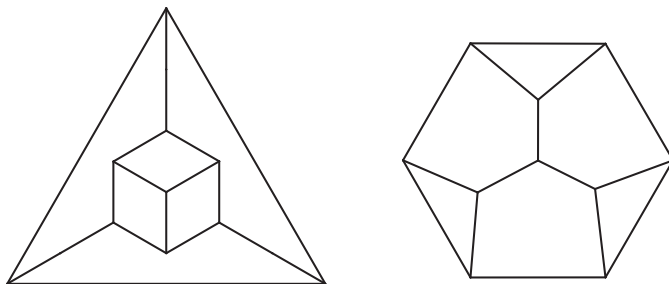


Figure 2: The two smallest non-centrosymmetric cubic polyhedra both have with $n = 10$ and are drawn here as Schlegel diagrams to display their \mathcal{C}_{3v} symmetry.

References

- [1] P. W. Fowler, D. E. Manolopoulos, *An Atlas of Fullerenes*, Oxford Univ. Press, Oxford 1995, Dover, New York 2006.
- [2] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, R. E. Smalley, \mathcal{C}_{60} : Buckminsterfullerene, *Nature* **318** (1985) 162–163.

- [3] R. Taylor, J. P. Hare, A. K. Abdul-Sada, H. W. Kroto, Isolation, separation and characterisation of the fullerenes C_{60} and C_{70} : The third form of carbon, *J. Chem. Soc. Chem. Comm.* (1990) 1423–1425.
- [4] J. Weaver, Centrosymmetric (cross-symmetric) matrices, their basic properties, eigenvalues, and eigenvectors, *Amer. Math. Monthly* **92** (1985) 711–717.
- [5] A. Cantoni, P. Butler, Eigenvalues and eigenvectors of symmetric centrosymmetric matrices, *Lin. Algeb. Appl.* **13** (1976) 275–288.
- [6] A. Graovac, O. Ori, M. Faghani, A. R. Ashrafi, Distance property of fullerenes, *Iranian J. Math. Chem.* **2** (2011) 99–107.
- [7] Z. Y. Liu, Some properties of centrosymmetric matrices, *Appl. Math. Comput.* **141** (2003) 297–306.
- [8] O. Rojo, H. Rojo, Some results on symmetric circulant matrices and on symmetric centrosymmetric matrices, *Lin. Algebra Appl.* **392** (2004) 211–233.
- [9] P. W. Fowler, D. Horspool, W. Myrvold, Vertex spirals in fullerenes and their implications for nomenclature of fullerene derivatives, *Chem. A Eur. J.* **13** (2007) 2208–2217.
- [10] P. Mani, Automorphismen von polyedrischen Graphen,? *Math. Ann.* **192** (1971) 279–303.
- [11] P. W. Fowler, D. E. Manolopoulos, D. B. Redmond, R. P. Ryan, Possible symmetries of fullerene structures, *Chem. Phys. Lett.* **202** (1993) 371–378.
- [12] D. Babić, D. J. Klein, C. H. Sah, Symmetry of fullerenes, *Chem. Phys. Lett.* **211** (1993) 235–241.
- [13] W. Myrvold, B. Bultena, S. Daugherty, B. Debroni, S. Girn, M. Minchenko, J. Woodcock, P. W. Fowler, FuiGui: A graphical user interface for investigating conjectures about fullerenes, *MATCH Commun. Math. Comput. Chem.* **58** (2007) 403–422.
- [14] P. Schwerdtfeger, L. Wirz, J. Avery, Program Fullerene: A software package for constructing and analyzing structures of regular fullerenes, *J. Comput. Chem.* **34** (2013) 1508–1526.
- [15] P. W. Fowler, D. Mitchell, A sum rule for symmetries and isomer counts of trivalent polyhedra, *J. Chem. Soc. Faraday Trans.* **92** (1996) 4145–4150.