Topological Rotational Strengths as Chirality Descriptors for Fullerenes

André Rassat,*[a] Istvàn Làszló,[b] and Patrick W. Fowler[c]

Abstract: A graph-theoretical procedure is proposed for assigning a chirality descriptor (the topological sign $\tau(+)$ or $\tau(-)$) to each enantiomer of a chiral polyhedron, polyhedral molecule or graph, independently of any vertex labelling scheme. Model Cartesian coordinates and rotational strengths are obtained using only adjacency information; a generalised HOMO–LUMO rotational strength is used to associate a sign with a Schlegel diagram and the corresponding three-dimensional structure, polyhedron or molecule. The topological sign gives an unambiguous way of communicating the identity of an enantiomer. The mean-square topological rotational strength is a possible measure of the *chirality content* of a polyhedral graph or structure.

Keywords: chirality · fullerenes · graph theory · polyhedra · rotational strength

Introduction

Different systems for the assignment of absolute configuration to fullerenes have been proposed, each requiring a standard numbering scheme.[1] Extension of the Cahn–Ingold–Prelog rules[2] to bare carbon cages[3] allows assignment of an *R* or *S* descriptor to each carbon, and if a convention for labelling a specific carbon were added, could give a molecular descriptor by taking the descriptor of this carbon for the fullerene as a whole. However, it seems desirable to have a simpler procedure that is easy, automatic to apply and is based on purely graph-theoretical considerations. The purpose of the present paper is to propose such a procedure, yielding a single configurational descriptor for any chiral fullerene and its corresponding Schlegel diagram.

When a molecular property can be expressed by a (non-zero) single number, there are two possibilities for a chiral molecule: The result of a ideal measurement is either the same for both enantiomers (e.g. a molar absorption coefficient, density) or of opposite sign for each enantiomer (e.g. specific rotatory power, induced twisting power[4]). The first are examples of scalar, the second of pseudo-scalar properties.[5, 6] A scalar is invariant under all transformations of three-dimensional space; a pseudo-scalar is invariant under all proper, but reverses sign under all improper transformations. The assignment of configurational descriptors relies explicitly or implicitly on pseudo-scalars: in the +/− (or *d*/*l*) system[7] the relevant pseudo-scalar, the value of a rotational power, is explicit; in the now superseded D/L system,[8] the pseudo-scalar is implicitly defined by the right or left position of a substituent in a standard planar diagram; in the CIP system,[2] the *R*/*S* labels relate to an ordering of four points in a three-dimensional model, which defines an implicit pseudo-scalar, as in the steering-wheel rule.[2a]

Here we used the physical hint supplied by optical rotatory power[9] and combined it with topological molecular-orbital theory to produce a pseudo-scalar, which will give a sign to each enantiomer of every graph which is capable of representing a chiral fullerene. It is obtained in a fully automatic way from the adjacency matrix **A** of the molecule, without requiring a standard numbering of the atoms. The procedure has two steps. In the first, diagonalisation of **A** affords the "topological" coordinates[10] of one of the two enantiomers. In the second, these coordinates and the eigenvectors of **A** are used to calculate formal rotational strengths[11] R_{ab} of $a \rightarrow b$ transitions within the framework of Hückel theory. The signs of these quantities are uniquely related to the identity of the constructed enantiomer, and we therefore propose to use the sign of a particular rotational strength as an easily calculated chirality descriptor for the molecule. Since this procedure relies only on the adjacency matrix, the result is a *topological*

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chirality descriptor. Hückel theory is used merely as a convenient calculus. The descriptor does not rely on any presumed relation between the formal quantities and experimental rotational strengths.[12] The power of the approach depends on the fact that co-ordinates and model electronic structures can be assigned to such molecules from adjacency information alone.[10] The same approach can also be used to define a measure of the "chirality content" inherent in a given fullerene, or any polyhedral graph or molecule.

Background Definitions

Spheroarenes are all-carbon molecules[13] with molecular graphs (i.e., sets of vertices (atoms) and edges (bonds)) that correspond to cubic polyhedra, that is, trivalent graphs that can be drawn in the plane without edge crossings and require deletion of at least three vertices for disconnection. Fullerenes are carbon cages that obey the additional condition that all faces of the polyhedron are either pentagonal or hexagonal.[14, 15]

An embedding of a graph in three-dimensional space may be built up from its adjacency properties. The elements A_{ij} of the *adjacency* matrix **A** of a molecular graph are equal to 1 if there is a bond connecting atom i to atom j and otherwise they are equal to 0. The atom labels are in principle arbitrary, although standard numbering schemes exist for some fullerenes.[1a–c] In a chemical context, the eigenvalues λ_a of this matrix yield the energies ε_a of the Hückel molecular orbitals ψ_a through $\varepsilon_a = \alpha + \lambda_a\beta$, and the eigenvectors give the coefficients c_{ai} in the expansion of the molecular orbitals (MO) in the atomic basis: $\psi_a = \sum c_{ai}\varphi_i$. In fullerenes (and more generally, in spheroarenes or N-vertex trivalent graphs), the eigenvalues, arranged in non-increasing order, are[16] $+3 = \lambda_1 > \lambda_2 \geq \lambda_3 \geq \lambda_4 \geq \ldots \geq \lambda_N > -3$ ($\lambda_N = -3$ if the graph is bipartite) and the first MO, ψ_1, corresponding to $\lambda_1 = 3$, has $c_{1i} = N^{-1/2}$.

Abstract in French: *On présente un procédé de théorie des graphes pour attribuer un descripteur de chiralité (le signe topologique τ(+) ou τ(−)) à chacun des deux énantiomères d'un polyèdre chiral, d'une molécule polyédrique chirale (sphéroarène) ou encore du graphe correspondant, sans faire appel à un quelconque système de numérotation des sommets. L'information contenue dans la matrice de connectivité fournit à elle seule les ≪coordonnées cartésiennes topologiques≫ et les ≪forces rotationnelles topologiques≫. Le signe de la force rotationnelle topologique associée à la transition HOMO–LUMO, éventuellement généralisée, définit le signe topologique commun à un diagramme de Schlegel et à la structure 3D (molécule ou polyèdre) qui lui correspond, permettant ainsi une définition non ambiguë de l'énantiomère considéré. On considère la possibilité d'utiliser la moyenne quadratique des forces rotationnelles topologiques comme mesure du contenu de chiralité d'un graphe, et du polyèdre ou du sphéroarène qui correspondent à ce graphe.*

The adjacency eigenvectors also supply information about the embedding of the molecular polyhedron in space by furnishing a set of purely graph-theoretically derived coordinates. These topological coordinates[10, 15] are Cartesian coordinates for a particular three-dimensional model and refer to an arbitrarily oriented frame, which we take as right-handed. The models so obtained have the topological symmetry[17] of the molecule, that is, the highest symmetry compatible with the connectivity of the graph. The idea is to identify the three adjacency eigenvectors $\{\psi_x, \psi_y, \psi_z\}$ that have patterns of coefficients on the sphere that are p-like, that is, each composed of a single positive and a single negative lobe, separated by a nodal surface,[10, 18] and to take the coefficients in these vectors as proportional to physical Cartesian coordinates. Figure 1 shows how the positive and negative coefficients of the ψ_x, ψ_y, ψ_z eigenvectors separate in each case for a small spheroarene **1**.

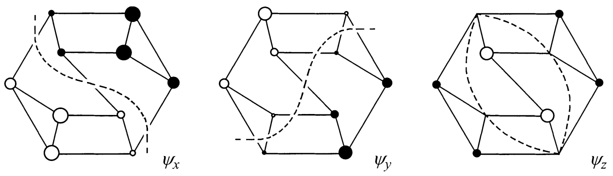


Figure 1. Schematic representation of the three eigenvectors ψ_x, ψ_y, ψ_z of **1**, corresponding to the eigenvalues $\lambda = 2.15$, 1.28, 1, respectively; the diameter of a circle is approximately proportional to the coefficient attached to each atom (vertex); unlabelled vertices correspond to null coefficients; the sign of the coefficient is indicated by white for positive and black for negative. The dotted line in each diagram is the trace of the three-dimensional nodal surface separating the single positive and negative lobes.

The set of three required vectors occur early in the order $\lambda_1 \ldots \lambda_N$, and can often be identified by inspection based on symmetry considerations. In refs. [10, 18], the topological coordinates are scaled in the three directions by a factor depending on the respective eigenvalue; in the present work, we use the pure unscaled eigenvectors in order to retain the simplifications that follow from their orthonormality (see below).

In the case of an *intrinsically* chiral polyhedron (i.e., one that, when embedded in three dimensions using its topological coordinates, has only proper elements of symmetry), the topological coordinates represent one enantiomer only, but since the adjacency matrix is the same for both, the identity of that enantiomer is a random consequence of the diagonalisation procedure. However, it is precisely related through a well defined flattening process to a two-dimensional object, the Schlegel diagram. A practical way[1a,b,d, 3] of obtaining this diagram is to place a ball-and-stick molecular model on a plane and to flatten the whole object into the plane so that the bottom face expands to contain the rest. This flattening procedure corresponds to one of several definitions for Schlegel diagrams,[20] and the choice of top and bottom faces is in principle arbitrary although standard conventions are available for fullerenes.[1a,b]

The flattening process may be used to establish a one-to-one correspondence between a three-dimensional model of a given enantiomer and a specific Schlegel diagram, either by visual examination, or by the following automatic procedure. First, labels I, J and K are applied to a set of three (non-collinear) atoms on two adjacent bonds, chosen in a way that the plane defined by these atoms does not contain O, the origin of coordinates. The construction of the Schlegel diagram may then be performed: flattening the polyhedron while insisting that all angles and edge lengths of the tetrahedron OIJK remain constant. The pseudo-scalar triple product

$$P_{\mathrm{IJK}} = \mathbf{OI} \cdot (\mathbf{OJ} \times \mathbf{OK}) \tag{1}$$

is then conserved, and thus can be used to ensure that the same enantiomer is treated throughout. In terms of the topological coordinates, with $\mathbf{r}_\mathrm{I} = \{x_\mathrm{I}, y_\mathrm{I}, z_\mathrm{I}\}$,

$$P_{\mathrm{IJK}} = \mathbf{r}_\mathrm{I} \cdot (\mathbf{r}_\mathrm{J} \times \mathbf{r}_\mathrm{K}) \tag{2}$$

In the coordinate system OXYZ defined by

$$X_\mathrm{I} = Y_\mathrm{I} = 0,\ Z_\mathrm{I} = Z > 0,\ X_\mathrm{J} = 0,\ Y_\mathrm{J} = 0,\ Z_\mathrm{J} = Z,\ X_\mathrm{K} \neq 0,\ Y_\mathrm{K} > 0,\ Z_\mathrm{K} = Z \tag{3}$$

where Z is the distance from O to the ABC plane, this triple product is

$$P_{\mathrm{IJK}} = -ZY_\mathrm{J}X_\mathrm{K} \tag{4}$$

and P_{IJK} and X_K have opposite sign.

The sign of P_{IJK} is directly related to the sense of the arc I → J → K viewed from the outside of the polyhedron: it is positive when motion along the arc would be anticlockwise and negative when it would be clockwise. (It is important to note that in the Schlegel diagram as constructed above, all faces except the bottom face are seen from the outside of the polyhedron, and preserve the same orientation in the diagram and on the polyhedron itself. The face at the bottom is viewed from the inside of the polyhedron and so has a reversal of orientation.)

Hence, the sign of the triple product can be used to determine whether or not a given Schlegel diagram corresponds to the flattened version of a given three-dimensional enantiomer—it is necessary only to compare the computed sense of the arc with its sense on the diagram. This simple idea can be used with any set of three-dimensional coordinates, whether topological, calculated or experimental, to correlate the polyhedral object with the appropriate Schlegel diagram.

The observation that a suitable triple of vertices defines an enantiomer is at the heart of the proposal for $^{\mathrm{f}}C$ and $^{\mathrm{f}}A$ fullerene descriptors.[1d, 19, 21] The prescribed triple in this convention has I, J, K as the first three labels in the standard fullerene numbering system. As these three vertices lie on the top face of the polyhedron, they appear in the central region of the Schlegel diagram. $^{\mathrm{f}}C$ and $^{\mathrm{f}}A$ descriptors are fixed by the sense of motion 1 → 2 → 3, and hence in effect by the sign of P_{123}. This purely automatic procedure is more convenient than the IUPAC C/A system[1a,b] where it is necessary to construct the three-dimensional model and check alignment of specific structural features.

Rotational Strengths

According to the theory of optical activity,[11, 22] a transition from one $|a\rangle$ to another state $|b\rangle$ contributes to the optical rotatory power and to the circular dichroism of a molecule through the rotational strength of the transition, which for a single electron moving in the field of the nuclei is (in atomic units),

$$R_{\mathrm{ab}} = -\langle a|\mathbf{r}|b\rangle \cdot \langle b|\mathbf{r}\times\nabla|a\rangle \tag{5}$$

where $\mathbf{r}$ and ∇ are the position and derivative operators in Cartesian coordinates. These coordinates are attached to the molecule,[23] the origin being taken at the centre of mass. For a one-electron model, the states are orbitals, that is $|a\rangle = \psi_\mathrm{a}$, $|b\rangle = \psi_\mathrm{b}$ and using the LCAO expansion, $|a\rangle = \sum_\mathrm{i} a_\mathrm{i}\varphi_\mathrm{i}$ and $|b\rangle = \sum_\mathrm{i} b_\mathrm{j}\varphi_\mathrm{j}$, the matrix elements in R_{ab} become

$$\langle a|\mathbf{r}|b\rangle = \sum_\mathrm{i}\sum_\mathrm{j} a_\mathrm{i}^* b_\mathrm{j} \langle\varphi_\mathrm{i}|\mathbf{r}|\varphi_\mathrm{j}\rangle \tag{6}$$

and

$$\langle b|\mathbf{r}\times\nabla|a\rangle = \sum_\mathrm{k}\sum_\mathrm{l} b_\mathrm{k}^* a_\mathrm{l} \langle\varphi_\mathrm{k}|\mathbf{r}\times\nabla|\varphi_\mathrm{l}\rangle \tag{7}$$

The calculations may be simplified by taking real MOs made up of Gaussian s-type functions to simulate the radially directed hybrid orbitals of the fullerene π system that is

$$\varphi_i = K\exp[-w(\mathbf{r}-\mathbf{r}_\mathrm{i})^2], \tag{8}$$

from which

$$\langle a|\mathbf{r}|b\rangle = \sum_\mathrm{i} a_\mathrm{i}\, b_\mathrm{i}\, \mathbf{r}_\mathrm{i} + \frac{1}{2}\sum_{\mathrm{i<j}} (a_\mathrm{i}b_\mathrm{j} + a_\mathrm{j}b_\mathrm{i})\, S_{\mathrm{ij}}\, (\mathbf{r}_\mathrm{i} + \mathbf{r}_\mathrm{j}), \tag{9}$$

where $S_{\mathrm{ij}} = \langle\varphi_\mathrm{i}|\varphi_\mathrm{j}\rangle$, and

$$\langle b|\mathbf{r}\times\nabla|a\rangle = w\sum_\mathrm{k}\sum_\mathrm{l} S_{\mathrm{kl}} b_\mathrm{k} a_\mathrm{l} \mathbf{r}_\mathrm{k} \times \mathbf{r}_\mathrm{l} \tag{10}$$

To retain only the leading non-zero terms, we can simplify (9) by taking $S_{\mathrm{ij}} = \delta_{\mathrm{ij}}$ in the spirit of the Hückel theory; however, in Equation (10) we must take $S_{\mathrm{kl}} = A_{\mathrm{kl}}S$. Hence, setting $wS = 1$

$$R_{\mathrm{ab}} = \left(\sum_\mathrm{i} a_\mathrm{i} b_\mathrm{i} \mathbf{r}_\mathrm{i}\right) \cdot \left[\sum_\mathrm{k}\sum_\mathrm{l} A_{\mathrm{kl}} a_\mathrm{k} b_\mathrm{l} \mathbf{r}_\mathrm{k} \times \mathbf{r}_\mathrm{l}\right] \tag{11}$$

or

$$\begin{aligned} R_{\mathrm{ab}} &= \sum_\mathrm{i}\sum_\mathrm{k}\sum_\mathrm{l} A_{\mathrm{kl}} a_\mathrm{i} b_\mathrm{i} a_\mathrm{k} b_\mathrm{l} \mathbf{r}_\mathrm{i} \cdot (\mathbf{r}_\mathrm{k} \times \mathbf{r}_\mathrm{l}) \\ &= \sum_\mathrm{i}\sum_{\mathrm{k<l}} A_{\mathrm{kl}} a_\mathrm{i} b_\mathrm{i} (a_\mathrm{k} b_\mathrm{l} - a_\mathrm{l} b_\mathrm{k}) \mathbf{r}_\mathrm{i} \cdot (\mathbf{r}_\mathrm{k} \times \mathbf{r}_\mathrm{l}) \end{aligned} \tag{12}$$

The result of this derivation, R_{ab}, is a purely topological quantity which behaves like a rotational strength and will be called a topological rotational strength.

It has a number of easily derived properties:

a′) From its form as a product of sums over atoms and bonds, the value of R_{ab} is independent of any particular scheme for numbering the vertices of the graph. As a consequence, it is possible to assign a descriptor to any new chiral fullerene, whether or not a convenient standard numbering has been devised.

b′) The terms contributing to R_{ab} are entirely determined by the adjacency matrix: they are matrix elements A_{ij}, coefficients a_i, b_i associated with vertex i in the molecular orbitals a and b, or entries x_i, y_i, z_i in the special vectors ψ_x, ψ_y and ψ_z that determine the topological coordinates.

c′) Each R_{ab} is a pseudo-scalar by construction, with opposite sign for opposite enantiomers. Therefore it changes the sign if all x_i, y_i, z_i are simultaneously reversed. R_{ab} is the trace of a 3×3 tensor.[24]

d′) By the completeness of the Hückel eigenvectors, R_{ab} obeys the Condon sum rule[11a,b]

$$\sum_{b} R_{ab} = 0 \tag{13}$$

e′) As seen from Equation (12), each R_{ab} is invariant to permutation of indices k and l, as under the switch $k \rightleftharpoons l$, both the term $(a_k b_l - a_l b_k)$ and the mixed triple product of position vectors change sign.

As the topological coordinates are obtained from eigenvectors of the same matrix that determines the MOs, the quantities R_{ab} obey additional identities when pure topological coordinates are employed:

a″) When $|b\rangle \mp \psi_x$, ψ_y or ψ_z, $\langle 1|\mathbf{r}|b\rangle = 0$, from the orthogonality properties of the vectors of a symmetric matrix, and R_{1b} is zero.

b″) When $|b\rangle = \psi_x$, ψ_y or ψ_z, the orthonormality properties give $\langle 1|\mathbf{r}|\psi_z\rangle = k/\sqrt{N}$ where $\mathbf{k}$ is the unit vector on the z axis, and R_{1z} rearranges to

$$R_{1z} = \frac{1}{N}\sum_{k}\sum_{l} A_{kl} z_l (x_k y_l - y_k x_l) \tag{14}$$

with similar expressions for R_{1x} and R_{1y}. As the topological coordinates are eigenvectors of the adjacency matrix, $\sum_{k} A_{kl} x_k = \lambda_x x_l$, so that

$$R_{1x} = \frac{1}{N}(\lambda_y - \lambda_z)\sum_{l} x_l y_l z_l \tag{15.1}$$

$$R_{1y} = \frac{1}{N}(\lambda_z - \lambda_x)\sum_{l} x_l y_l z_l \tag{15.2}$$

$$R_{1z} = \frac{1}{N}(\lambda_x - \lambda_y)\sum_{l} x_l y_l z_l \tag{15.3}$$

Note the xyz product in Equation (15), the simple chiral perturbation used in the first one-electron theory of rotatory power[11a] and in the celebrated octant rule.[25]

c″) As a consequence, the sum $R_{1*} = R_{1x} + R_{1y} + R_{1z}$ is zero.

d″) Further, in case of degeneracy between at least two of the ψ_x, ψ_y or ψ_z vectors, not only the sum R_{1*}, but all three components R_{1x}, R_{1y} and R_{1z} vanish. In the absence of degeneracy (i.e., space groups C_1, C_2 and D_2), all three components are non-zero and distinct.

When one or both of the states a and b belong to degenerate levels, each set of orthonormal degenerate eigenvectors, $\{a_1, \ldots a_\mu, \ldots a_\alpha\}$ and $\{b_1, \ldots b_\nu \ldots b_\beta\}$, is arbitrary to within a unitary transformation. Although the corresponding rotational strengths $R_{a_\mu b_\nu}$ depend on the particular choice of orbitals, the aggregate sum over the two sets,

$$R_{AB} = \sum_{\mu=1}^{\alpha}\sum_{\nu=1}^{\beta} R_{a_\mu b_\nu} \tag{16}$$

is independent of this choice. R_{AB} will be termed the aggregate rotational strength. This term will be taken to include the non-degenerate cases, where $R_{ab} = R_{AB}$ for $\alpha = \beta = 1$.

Recipe for the Descriptor

The full set of aggregate rotational strengths R_{AB} defines a matrix $\mathbf{R}$ of topological invariants for a chiral polyhedral graph. For the purpose of assigning a descriptor (i.e., the sign of a pseudo-scalar) to the graph representing an enantiomer, any non-zero entry R^*_{AB} in $\mathbf{R}$ would be sufficient to define the topological sign. An intuitive and chemically plausible choice for the defining rotational strength R^*_{AB} is to assume that the N-vertex graph represents a neutral molecule, thus defining HOMO and LUMO eigenvalues at $\lambda_{N/2}$ and $\lambda_{(N/2)+1}$ and to take A and B as HOMO and LUMO, respectively. In case of degeneracy, we take the HOMO set to comprise all the MOs with eigenvalue $\lambda_{N/2}$, and the LUMO set to contain all the MOs at the next eigenvalue. If the aggregate rotational strength for the transition between these sets vanishes, then the LUMO is taken as the next available set of unoccupied orbitals, and so on. If this variation in B fails to produce a non-zero R_{AB}, then A, and in the last resort both A and B, can be varied. With this flexibility, we can always find a descriptor, unless *all* R_{AB} are "accidentally" zero, or zero to within computer precision, as in a topological analogue of a chiral molecule with no detectable optical rotatory power (a case of "potential optical activity",[26] "cryptochirality"[27] or "cryptooptical activity"[28, 29]). The hierarchical definition of R_{AB} should avoid the problem of "latent handedness"[30] that may arise for single descriptors.[6]

The explicit recipe for associating a sign with the enantiomer described by a particular Schlegel diagram of a chiral polyhedral graph is therefore as follows.

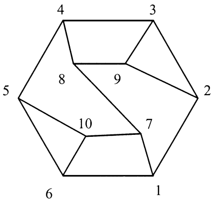
1) *Start* with the Schlegel diagram.
2) *Use* this to determine the adjacency matrix in an arbitrary labelling.
3) *Diagonalise* that matrix and use the eigenvectors to obtain the derived set of topological coordinates and to calculate R^*_{AB}.
4) *Identify* a triple IJK in the Schlegel diagram and calculate P_{IJK} from the topological coordinates.
5) *Compare* the computed sign with the sense of the triple on the diagram.

Either the Schlegel diagram corresponds to the three-dimensional enantiomer, and the sign of the defining R^*_{AB} is the desired descriptor, the topological sign of the Schlegel diagram, *or* the diagram corresponds to the opposite enantiomer, and the topological sign of the diagram is then that of $-R^*_{AB}$.

Graphs and enantiomers with a positive topological sign will be labelled $\tau(+)$ and those with a negative topological sign $\tau(-)$.

Examples

The procedure specified in the previous section was applied to a selection of chiral fullerene and other spheroarene polyhedral graphs. The Schlegel diagrams of the molecules **1**–**10** are given in Figures 2–7. Structures **1**–**4** are the carbon skeletons of spheroalkanes $C_{10}H_{10}$ barettane,[31] $C_{12}H_{12}$, $C_{16}H_{16}$ and $C_{28}H_{28}$.



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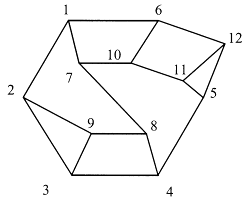

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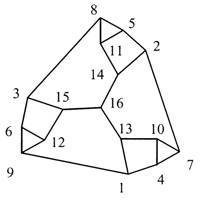

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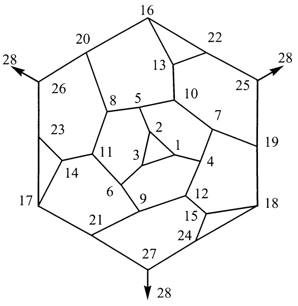

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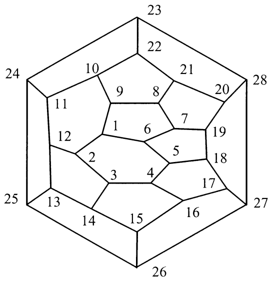

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Figure 2. Schlegel diagrams for: **1**, the $\tau(-)$ enantiomer of a C_2-symmetric C_{10} spheroarene; **2**, the $\tau(-)$ enantiomer of a C_1-symmetric C_{12} spheroarene; **3**, the $\tau(+)$ enantiomer of a C_3-symmetric C_{16} spheroarene; **4**, the $\tau(-)$ enantiomer of a chiral, tetrahedrally symmetric $C_{28}H_{28}$ spheroarene (the smallest spheroarene of *T* symmetry); **5**, the $\tau(-)$ enantiomer of the hypothetical D_2-symmetric C_{28} fullerene.

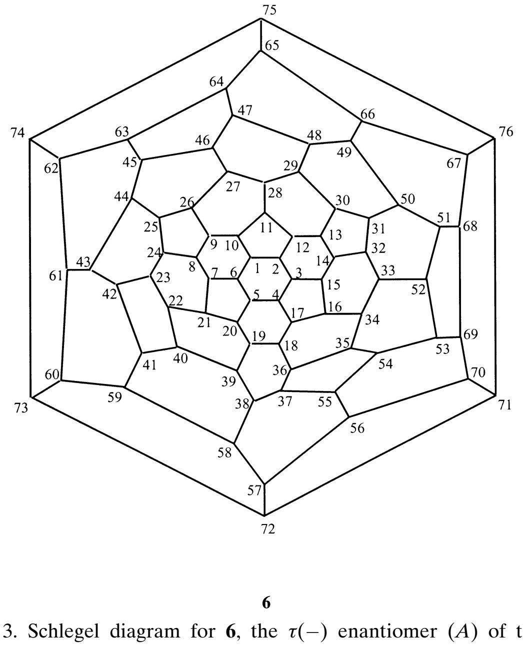

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Figure 3. Schlegel diagram for **6**, the $\tau(-)$ enantiomer (*A*) of the D_2-symmetric C_{76} isolated-pentagon fullerene.

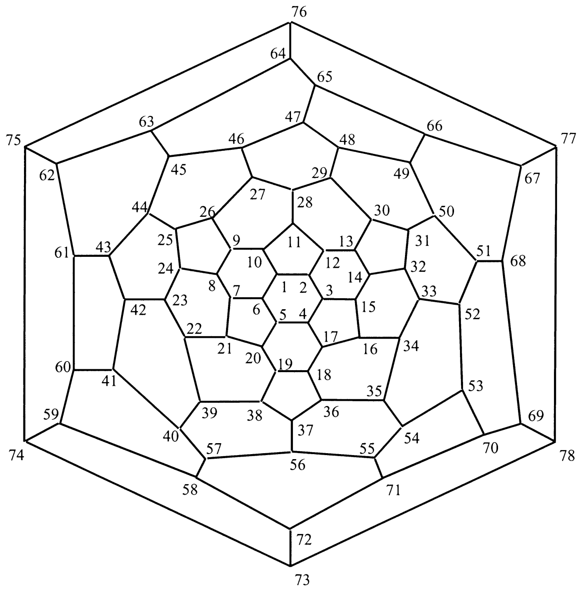

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Figure 4. Schlegel diagram for **7**, the $\tau(+)$ enantiomer (*C*) of the D_3-symmetric C_{78} isolated-pentagon fullerene.

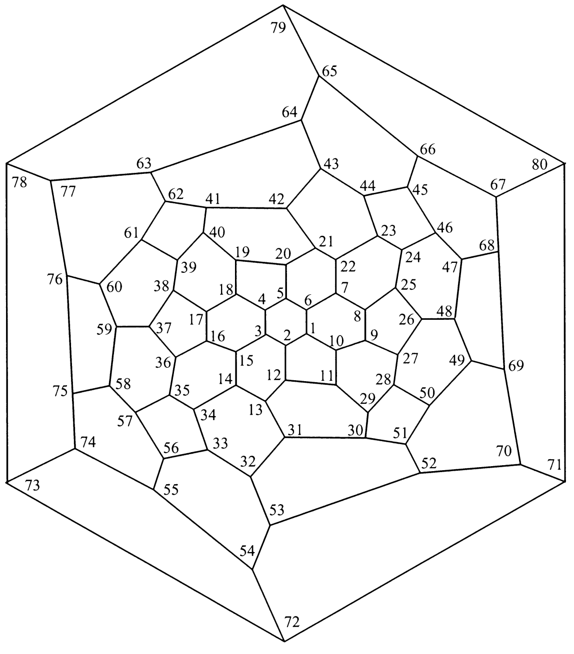

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Figure 5. Schlegel diagram for **8**, the $\tau(-)$ enantiomer of the D_2-symmetric C_{80} isolated-pentagon fullerene.

Structures **5**–**10** are chiral fullerenes, comprising the D_2 isomer of C_{28} (**5**) (the smallest possible intrinsically chiral fullerene), four of the smallest experimentally produced chiral fullerenes (the isolated-pentagon D_2-C_{76} (**6**),[32] D_3-C_{78} (**7**),[33] D_2-C_{80} (**8**)[34] and D_2-C_{84} (**9**)[35] isomers), and the smallest chiral icosahedral fullerene isomer, *I*-C_{140} (**10**). For **6**, **7** and **9** the standard IUPAC numbering scheme[1a,b] is used to label the Schlegel diagram, and for **1**–**5** and **10** the labelling

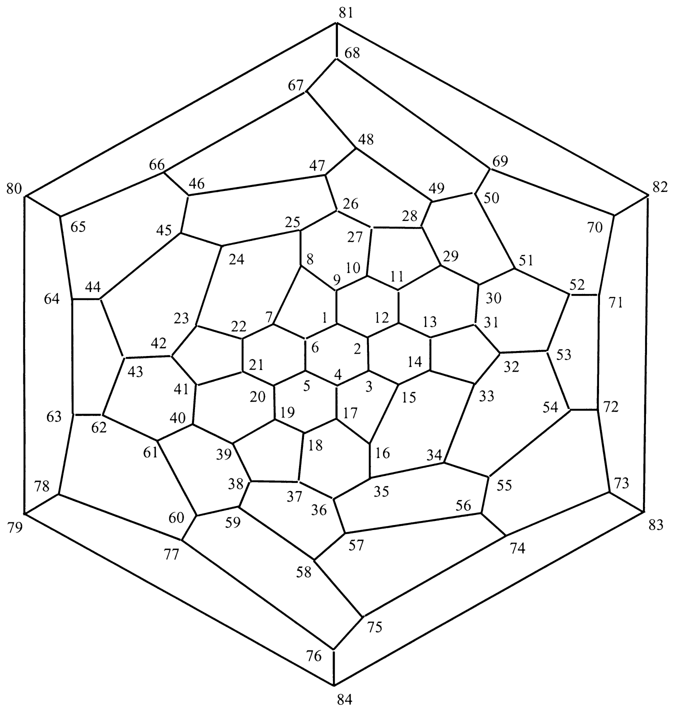

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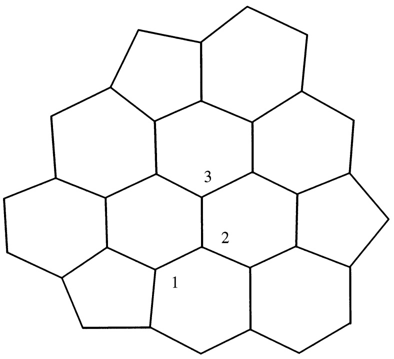
Figure 6. Schlegel diagram for **9**, the $\tau(-)$ enantiomer (A) of the D_2-symmetric C_{84} isolated-pentagon fullerene 84:22 (spiral nomenclature[15]).



10

Figure 7. Central portion of the Schlegel diagram for **10**, the $\tau(-)$ enantiomer of the I-symmetric C_{140} isolated-pentagon fullerene.

is taken from ref. [3]. For **10**, only a small central portion of the Schlegel diagram is shown (for the full version of the diagram of the opposite enantiomer, see ref. [13]).

The procedure described above for assigning a topological sign was applied to each Schlegel diagram **1**–**10**, giving the results listed in Table 1. In all cases it turns out that the topological coordinates are defined by the first three non-isotropic eigenvectors, the vectors $|\lambda_2\rangle$, $|\lambda_3\rangle$, $|\lambda_4\rangle$. As only the sign of any computed property is relevant here, the coordinates were taken directly from the raw eigenvectors ($x_i = c_{2i}$, $y_i = c_{3i}$, $z_i = c_{4i}$).[10, 15] The normalisation of the eigenvectors then implies a scaling of the polyhedron in which the radius of sphere defined by the rms distance of the vertices from the centre of gravity is $\sqrt{3/N}$. If we wish to compare all graphs as objects of similar average size, scaling the coefficients by $\sqrt{N/3}$ gives a unit average sphere. For applications where the coordinates are required to be more geometrically realistic, an isotropic scaling factor of $N\sqrt{3}$ applied to each coordinate would give a polyhedron with the expected $\sqrt{N}$ dependence of the rms radius; the quantities R^{*}_{AB} and P_{IJK} would then be scaled by $3N\sqrt{3N}$ with respect to the values reported in Table 1.

A similar result would be obtained by scaling the raw coefficients to give a desired average bond length for the polyhedron edges, as is often done to obtain a starting point for further optimisation.

As Table 1 shows, the definition of R^{*}_{AB} produces in every case a non-zero result for A including the eigenvalue $\lambda_{N/2}$ and for B defined by the next or next-but-one available eigenvalue. Cage **1** and the fullerenes D_2-C_{28}, D_2-C_{76}, D_3-C_{78}, D_2-C_{80} and D_2-C_{84} all have closed π shells in Hückel theory (though in all cases these are pseudo-closed[36] in that further formally bonding levels are available for occupation) and in all but D_2-C_{84} the HOMO–LUMO transition has non-zero rotational strength; for D_2-C_{84} the HOMO and LUMO symmetries are identical and hence the rotational strength vanishes identically, so that B must be taken as the LUMO+1. Cages **2**–**4** and the icosahedral fullerene I-C_{140} (**10**) have open π shells in simple Hückel theory and A comprises the full set of partially occupied orbitals and B the first set of wholly unoccupied orbitals.

For the purpose of identifying the Schlegel diagram with either the enantiomer corresponding to the particular topo-

Table 1. Derivation of topological signs for the polyhedral graphs **1**–**10**. G is the point group defined by the topological coordinates of the graph. R^{*}_{AB} is the defining topological rotational strength, which involves a product of moments of transitions from orbital set A to orbital set B. P_{IJK} is the triple product defining the sense of the path I → J → K as seen from the outside of the polyhedron constructed from the topological coordinates. The final column gives the topological signs of the enantiomers associated with the Schlegel diagrams illustrated in Figures 2–7. Unscaled topological coordinates are used throughout the table.

Molecule	G	A	B	R^{*}_{AB}	I	J	K	P_{IJK}	Sign
C_{10} (**1**)	C_2	5	6	-3.816×10^{-2}	7	8	9	-1.1×10^{-1}	$\tau(-)$
C_{12} (**2**)	C_1	6–7	8	-2.681×10^{-3}	7	8	9	-9.5×10^{-3}	$\tau(-)$
C_{16} (**3**)	C_3	7–9	10–11	-8.148×10^{-3}	11	14	16	$+2.1 \times 10^{-2}$	$\tau(+)$
C_{28} (**4**)	T	14–16	17–19	-1.005×10^{-2}	3	2	1	-2.4×10^{-3}	$\tau(-)$
C_{28} (**5**)	D_2	14	15	-3.212×10^{-3}	3	2	1	-1.1×10^{-2}	$\tau(-)$
C_{76} (**6**)	D_2	38	39	$+9.518 \times 10^{-5}$	1	2	3	$+7.8 \times 10^{-4}$	$\tau(-)$
C_{78} (**7**)	D_3	39	40	$+1.126 \times 10^{-4}$	1	2	3	-7.3×10^{-4}	$\tau(+)$
C_{80} (**8**)	D_2	40	41	-1.580×10^{-5}	1	2	3	-7.3×10^{-4}	$\tau(-)$
C_{84} (**9**)	D_2	42	44*	-3.674×10^{-4}	1	2	3	-7.4×10^{-4}	$\tau(-)$
C_{140} (**10**)	I	70–73	74–77	-6.834×10^{-5}	3	2	1	-2.0×10^{-4}	$\tau(-)$

logical coordinates produced by the diagonalisation, or with its opposite, a triple IJK with clockwise orientation was chosen in the central portion of each Schlegel diagram and the triple product P_{IJK} evaluated from the three-dimensional coordinates. Thus the topological sign follows as the sign of R^{*}_{AB} (if P_{IJK} is negative) or its opposite (if P_{IJK} is positive). The final column of Table 1 shows the computed topological signs.

Note that the results of this calculation differ in principle from those of the various conventions already in use. The topological signs attached to each Schlegel diagram (Table 1) would remain the same under any scrambling of the vertex labels. It is possible to label the fullerenes **6**, **7** and **9** in the ${}^{\mathrm{f}}A$/${}^{\mathrm{f}}C$ and A/C conventions, and the illustrated enantiomers are ${}^{\mathrm{f}}C$, ${}^{\mathrm{f}}C$, ${}^{\mathrm{f}}C$ and A, C, A, respectively, (compare our figures with Figures 1 and 4 of ref. [19] and with Figures 4, 5 and 12 of ref. [1a, b]). If a new chiral fullerene comes under discussion, it is necessary to go through a rather complicated procedure to find a canonical labelling before ${}^{\mathrm{f}}A$/${}^{\mathrm{f}}C$ and A/C descriptors can be assigned and, as Thilgen and Diederich remark on p. 141 of ref. [21] it is necessary to know *which* numbering convention has been used. In contrast, the present procedure delivers a $\tau(+/-)$ sign automatically for any chiral polyhedron once the set of bond connections is specified. For example, the topological sign of the enantiomer of D_2 isolated-pentagon C_{80} **8**, corresponding to the Schlegel diagram in Figure 5 is $\tau(-)$.

Chirality Content of a Polyhedral Graph

Assignment of a topological sign to a chiral polyhedral graph uses only one member of the set of pseudo-scalar quantities, R_{AB}. The set has the property that the sums $\sum_{\mathrm{B}} R_{\mathrm{AB}}$ are zero, but quantities such as the sum of the squares $\sum_{\mathrm{A}}\sum_{\mathrm{B}}(R_{\mathrm{AB}})^2$ are non-vanishing, provided that at least one topological rotational strength is non-zero. It is plausible to consider such quantities as measures of the "chirality content" of the graph. We take a natural root-mean-square definition:

$$ {}^{\tau}\chi = \sqrt{\frac{2}{P(P-1)}\sum_{\mathrm{A<B}}(R_{\mathrm{AB}})^2} \qquad (17) $$

where P is the number of degenerate sets of adjacency eigenvalues.

This purely topological quantity is presented for the graphs **1**–**10** in Table 2, where the raw topological coordinates have been normalised to an average unit sphere by the factor $\left(\sqrt{N/3}\right)^3$. All definitions of chirality content suffer from a degree of arbitrariness,[37] and it remains to be seen what ${}^{\tau}\chi$ predicts for example for the "most chiral" fullerene(s). A *physical* analogue of ${}^{\tau}\chi$, can be envisaged: it could for instance be obtained by measurement of rotational strengths of the set of all possible transitions within the valence space of a chiral system.

Table 2. Chirality content of graphs **1**–**10**. P is the number of distinct adjacency eigenvalues, and ${}^{\tau}\chi$ is the rms measure defined in Equation (16). Topological coordinates normalised to the unit sphere are used in the calculation of ${}^{\tau}\chi$.

Molecule	P	${}^{\tau}\chi$
C_{10} (**1**)	10	1.205×10^{-1}
C_{12} (**2**)	11	5.290×10^{-2}
C_{16} (**3**)	9	3.239×10^{-2}
C_{28} (**4**)	10	1.227×10^{-1}
C_{28} (**5**)	25	3.684×10^{-2}
C_{76} (**6**)	76	8.648×10^{-3}
C_{78} (**7**)	52	1.383×10^{-2}
C_{80} (**8**)	79	8.335×10^{-3}
C_{84} (**9**)	68	1.014×10^{-2}
C_{140} (**10**)	37	2.835×10^{-2}

Conclusion

Chirality descriptors can be assigned for spheroarenes and fullerenes without invoking any specific labelling scheme. The purely graph-theoretical approach gives a sign for both the three-dimensional polyhedron and its corresponding two-dimensional Schlegel diagram, and thus could "facilitate communication between chemists"[1b] of the identity of an enantiomer. The approach further suggests a definition of the chirality content for a polyhedron and its graph. The discussion in this paper has been restricted to purely graph-theoretical objects, using the properties of the adjacency matrix to define an implicit geometry. It is perhaps useful to note that the approach may be adapted to deal with "real" molecules, using coordinates derived from experiment or from calculation.

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