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Palindromic Perimeter Codes and Chirality Properties of Polyhexes†

Milan Randić

Department of Mathematics, Drake University, Des Moines, Iowa 50311

Paul G. Mezey*

Mathematical Chemistry Research Unit, Department of Chemistry and Department of Mathematics and Statistics, 110 Science Place, University of Saskatchewan, Saskatoon, Canada, S7N 5C9

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Two theorems are proven concerning the relations between two-chirality properties and palindromic perimeter codes of polyhexes. Two-dimensional chirality of polyhexes is an important shape descriptor of polycyclic aromatic hydrocarbons (PAHs) adsorbed on solid surfaces, for example, on graphite. The mutual arrangements of reflection lines of achiral polyhexes and the typical sites of lattice points of the underlying hexagonal grid of the plane provide an additional shape classification of achiral polyhexes.

1. INTRODUCTION

Extensive literature is available on the chemical aspects of polyhexes; for a selection the reader may consult refs 1−20. Polycyclic aromatic hydrocarbons (PAHs), many of which are important carcinogens and toxicants, are often modelled by polyhexes. All such planar structures are achiral in the ordinary, three-dimensional sense, however, if their motions are confined to a plane, for example, if planar displacements of PAH molecules adsorbed on a solid surface are considered, then their two-dimensional chirality becomes relevant. The role of chirality with respect to conformational invariants as well as its generalizations to dimensions other than 3 have many chemical applications, some of which are discussed in refs 21−28. A structure is chiral in two dimensions, *i.e.,* it is two-chiral, if no motion confined to the given two-dimensional plane can bring the structure into superposition with its mirror image generated by a mirror line within the plane. A polyhex that is not two-chiral is two-achiral. Simple shape codes of polyhexes which preserve as much as possible from the actual, chemical shape features of these molecules, are of importance in the toxicological characterization of polycyclic aromatic hydrocarbons.[29]

Two-dimensional motions of polycyclic aromatic hydrocarbons adsorbed on solid surfaces, such as displacements along a plane of a sheet of the graphite lattice, are energetically well-distinguished from the general, three-dimensional motions of these molecules. In such cases, two-dimensional shape properties, especially, two-dimensional chirality, are of importance. Similar, two-dimensional motions of essentially planar molecules are also significant in liquid crystals as well as in packing problems within more general crystal lattices. In all such instances, two-dimensional chirality affects the mutual arrangements, local and global shape-compatibility of molecules.[26]

A finite, connected subset of the infinite hexagonal lattice of the two-plane that contains only complete hexagons is often referred to as a *polyhex.* Each polyhex has a unique *perimeter*, defined as the unique set of all those edges where each edge borders only one hexagon of the polyhex. Here we shall be concerned only with simply connected polyhexes, that is, with polyhexes which, if interpreted as the unions of the corresponding hexagons and their interiors, are simply connected subsets of the plane. For any simply connected polyhex the perimeter is a Jordan curve, also called a Jordan cycle. Polyhexes have interesting mathematical properties as parts of hexagonal lattices, important in planar tiling and covering studies.

Some of the methods used in this study are based on some general relations between geometrical reflection and the inversion properties of molecular shape codes. These relations have not been applied yet for polyhexes; however, the same principles have been used in studies on knot theoretical chirality codes based on knot polynomials,[21] shape codes of lattice animals, also called square-cell configurations,[22−25] and chirality changes along reaction paths.[26,27] In particular, the symmetry and chirality analysis of a perimeter code of square-cell configurations represented on the complex plane have provided motivation for the present study.[25]

2. PERIMETER CODES AND SOME CHIRALITY PROPERTIES

A polyhex A uniquely determines its perimeter, and the perimeter of a polyhex A uniquely determines the polyhex. Consequently, any numerical code that determines the perimeter, usually called a *perimeter code,* uniquely determines the polyhex. For simply connected polyhexes, a pair of perimeter codes, the *Randić-Razinger code*[20] and the *Reverse Randić-Razinger code* are defined as binary sequences.

Definition 1. For each vertex i ($i = 0,1,...,m-1$) of the perimeter of a simply connected polyhex A, the *Randić-Razinger code* $RRC_i(A)$ is a binary sequence, obtained by assigning a binary number to each vertex according to the following rule:

Starting at vertex i, and following a clockwise motion along the perimeter, assign 1 to each inward turn and 0 to each outward turn.

Definition 2. For each vertex i ($i = 0,1,...,m-1$) of the perimeter of a simply connected polyhex A, the *Reverse Randić-Razinger code* $RRRC_i(A)$ is a binary sequence,

* Author for correspondence.

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obtained by assigning a binary number to each vertex according to the following rule:

Starting at vertex i, and following a counter-clockwise motion along the perimeter, assign 1 to each inward turn and 0 to each outward turn.

We shall use the following convention: the m vertices on the perimeter of a simply connected polyhex A are labeled by integers $i = 0,1,...,m-1$, assigned in a clockwise order. The labels belong to the vertices, and a reflection of A implies that in the reflected image the index numbers follow a counterclockwise order. In various index manipulations, the indices are taken mod m; for example, if $m = 14$, both $i = 20$ and $i = -8$ are interpreted as $i = 6$.

In some special cases, these codes show special symmetries. In particular, a simply connected polyhex A has interesting properties if reading the code forward and backward, the same, palindromic binary number is obtained.

Definition 3. A polyhex A is *true palindromic,* or simply *palindromic* , if for some i

$$\mathrm{RRC}_i(\mathrm{A}) = \mathrm{RRRC}_{i-1}(\mathrm{A}) \tag{1}$$

A somewhat weaker condition, described below, is more often fulfilled by polyhexes.

Definition 4. Polyhex A is *cyclic-permutation-palindromic,* or simply *cp-palindromic,* if there exist vertices i and j such that

$$\mathrm{RRC}_i(\mathrm{A}) = \mathrm{RRRC}_j(\mathrm{A}) \tag{2}$$

If A is true palindromic then A is, evidently, cp-palindromic: if one chooses

$$j = i-1 \tag{3}$$

then the definition of the cp-palindromic property is fulfilled.

Chirality in two dimensions, that is, two-chirality, is a property of some simply connected polyhexes that can be easily deduced from the Randić-Razinger code. In particular, we prove the following theorem.

Theorem 1. A polyhex A is two-achiral if and only if A is cp-palindromic.

Proof. (a) If A is cp-palindromic then A is two-achiral. If A is cp-palindromic, then, by definition, $\mathrm{RRC}_i(\mathrm{A}) = \mathrm{RRRC}_j(\mathrm{A})$ for some i and j. Take vertex j and the reverse Randić-Razinger code $\mathrm{RRRC}_j(\mathrm{A})$ for which $\mathrm{RRC}_i(\mathrm{A}) = \mathrm{RRRC}_j(\mathrm{A})$. A reflection of A by a planar reflection line converts A into its mirror image $\mathrm{A}^{\diamond}$ and converts the counterclockwise list of vertex turns into a clockwise list of vertex turns. Consequently, $\mathrm{RRRC}_j(\mathrm{A}) = \mathrm{RRC}_j(\mathrm{A}^{\diamond})$. However, since $\mathrm{RRC}_i(\mathrm{A}) = \mathrm{RRRC}_j(\mathrm{A})$, the equality $\mathrm{RRC}_i(\mathrm{A}) = \mathrm{RRC}_j(\mathrm{A}^{\diamond})$ follows. Two pairs of adjacent vertices of any two polyhexes can always be superimposed, consequently, the vertices i of A and j of $\mathrm{A}^{\diamond}$ as well as vertices $i+1$ of A and $j+1$ of $\mathrm{A}^{\diamond}$ can always be superimposed. Since the same Randić-Razinger code is obtained for A and $\mathrm{A}^{\diamond}$, the entire polyhexes A and $\mathrm{A}^{\diamond}$ must be superimposed, hence A is two-achiral.

(b) If A is two-achiral, then A is cp-palindromic. If A is two-achiral then A and $\mathrm{A}^{\diamond}$ are superimposable. For such a superimposed arrangement, a vertex i of A is superimposed on a vertex j of $\mathrm{A}^{\diamond}$. Consequently, the Randić-Razinger codes $\mathrm{RRC}_i(\mathrm{A})$ and $\mathrm{RRC}_j(\mathrm{A}^{\diamond})$ must agree, $\mathrm{RRC}_i(\mathrm{A}) = \mathrm{RRC}_j(\mathrm{A}^{\diamond})$. Carrying out a reflection of $\mathrm{A}^{\diamond}$, the clockwise list of vertex turns of the Randić-Razinger code $\mathrm{RRC}_j(\mathrm{A}^{\diamond})$ becomes the counterclockwise list of vertex turns of the reverse Randić-Razinger code $\mathrm{RRRC}_j(\mathrm{A}^{\diamond\diamond}) = \mathrm{RRRC}_j(\mathrm{A})$, where the fact that $\mathrm{A}^{\diamond\diamond} = \mathrm{A}$ is recognized. Hence, $\mathrm{RRC}_i(\mathrm{A}) = \mathrm{RRC}_j(\mathrm{A}^{\diamond}) = \mathrm{RRRC}_j(\mathrm{A})$, that is, $\mathrm{RRC}_i(\mathrm{A}) = \mathrm{RRRC}_j(\mathrm{A})$, a relation that implies that A is cp-palindromic.

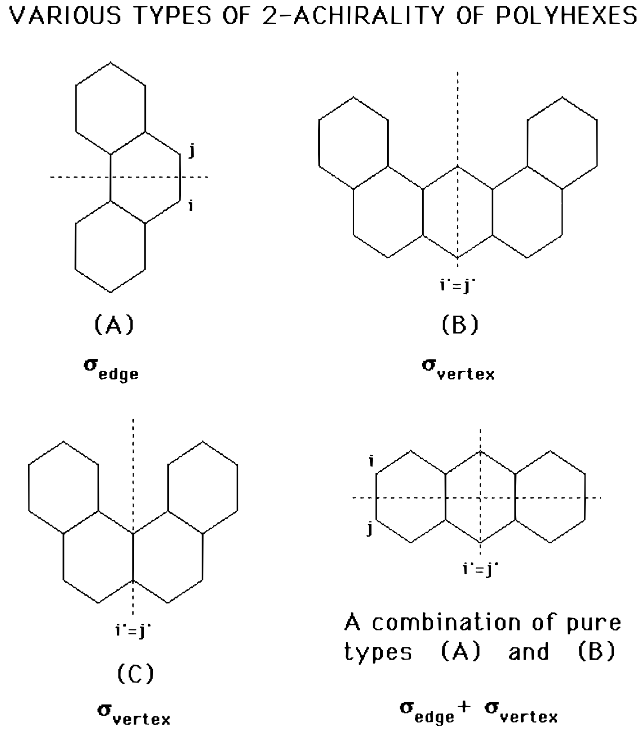

Figure 1. Examples for the three pure types, (A), (B), and (C), of two-achiral polyhexes, and a mixed-type two-achiral polyhex. In case (A), there exists a reflection line σ_{edge} that bisects an edge of the perimeter of the polyhex. In case (B), there exists a reflection line σ_{vertex} that passes through two vertices at opposite sites of a hexagon of the polyhex. In case (C), no hexagon is reflected onto itself, and a reflection line σ_{vertex} passes through two vertices at neighboring sites shared by two hexagons of the polyhex. The fourth, mixed-type two-achiral polyhex shown has two reflection lines, σ_{edge} (necessarily of type (A)), and σ_{vertex} of type (B).

Combining parts (a) and (b), the statement of the theorem follows. Q.E.D.

Since a true palindromic polyhex A is cp-palindromic, any true palindromic polyhex A is also two-achiral.

More distinctions can be made if one considers the various possible mutual arrangements of two-achiral simply connected polyhexes and their self-superimposing reflection lines in the two-plane. The three pure types, (A), (B), and (C), as well as a mixed case are illustrated in Figure 1.

First we consider cases where there is at least one hexagon that is reflected onto itself. Since a polyhex cannot have higher symmetry than the symmetry of a hexagon, and there are precisely two types of reflection lines for a hexagon, there are also two possibilities for the mutual arrangements of reflection lines and polyhexes.

A reflection line that reflects a two-achiral polyhex A onto itself as well as a hexagon of the polyhex onto itself, (A) either bisects a positive even number of edges of the polyhex where each pair of edges must belong to the same hexagon, or (B) it passes through at least two vertices at opposite sites of a hexagon of the polyhex.

In case (A), no vertex is reflected upon itself, and the vertices of each of the bisected edges are reflected to each other. In case (B), each vertex contained in the reflection line is reflected onto itself.

If one considers the cases where no hexagon is reflected onto itself, then an additional alternative is recognized: (C) A reflection line that reflects a two-achiral polyhex A onto itself but reflects no hexagon of the polyhex onto itself must pass through at least two vertices of the polyhex at neighboring sites shared by two hexagons of A.

According to the following theorem, a sufficient and necessary condition for a two-achiral polyhex A to be true palindromic is the existence of a reflection line of type (A).

Theorem 2. A polyhex A is true palindromic if and only if there exists a reflection line of A that superimposes A onto $A^\diamond$ and bisects an edge of A.

Proof. (a) If polyhex A is true palindromic, then there exists a reflection line of A that superimposes A onto $A^\diamond$ and bisects an edge of A.

The polyhex A is *true palindromic,* hence by definition, there exists some vertex i fulfilling the condition

$$\mathrm{RRC}_i(\mathrm{A}) = \mathrm{RRRC}_{i-1}(\mathrm{A}) \tag{4}$$

Take the unique line that bisects the edge between vertices i and $i-1$ of A. Use this line to reflect A to generate a mirror image $A^\diamond$. Vertex i of A is reflected onto vertex i of $A^\diamond$, and the reflection converts the clockwise list of vertex turns of $\mathrm{RRC}_i(\mathrm{A})$ of A into a counterclockwise list of vertex turns of $\mathrm{RRRC}_i(\mathrm{A}^\diamond)$ of $A^\diamond$

$$\mathrm{RRC}_i(\mathrm{A}) = \mathrm{RRRC}_i(\mathrm{A}^\diamond) \tag{5}$$

However, the true palindromic property

$$\mathrm{RRC}_i(\mathrm{A}) = \mathrm{RRRC}_{i-1}(\mathrm{A}) \tag{6}$$

implies that the right hand sides must agree, that is,

$$\mathrm{RRRC}_i(\mathrm{A}^\diamond) = \mathrm{RRRC}_{i-1}(\mathrm{A}) \tag{7}$$

must also hold. Since vertex i of A is reflected onto vertex i of $A^\diamond$, and vertex $i-1$ of A is reflected onto vertex $i-1$ of $A^\diamond$, the edge $(i-1,i)$ of A is superimposed on the edge $(i-1,i)$ of $A^\diamond$. The superpositon of both vertices of an edge and the equality $\mathrm{RRRC}_i(\mathrm{A}^\diamond) = \mathrm{RRRC}_{i-1}(\mathrm{A})$ of the reverse Randić-Razinger codes imply that the entire reflected image $A^\diamond$ is superimposed on A.

(b) If there exists a reflection line of A that superimposes A onto $A^\diamond$ and bisects an edge of A, then A is true palindromic.

Choose index i as the index of the vertex of A that (i) is incident to one bisected edge and (ii) lies in the clockwise direction from the other vertex of the same edge.

Clearly, this second vertex has the serial index $i-1$ within A. The superposition of A and $A^\diamond$ by the reflection line that bisects the edge $(i-1,i)$ also implies that vertex $i-1$ of $A^\diamond$ is superimposed on vertex i of A, vertex i of $A^\diamond$ is superimposed on vertex $i-1$ of A, and, in general, the respective vertices in the sequence

$$i-1,\ i-2,\ i-3,\ ...,\ i \tag{8}$$

of $A^\diamond$, are superimposed on the

$$i,\ i+1,\ i+2,\ ...,\ i-1 \tag{9}$$

vertices in the vertex sequence of A.

Consequently, the *clockwise* list of turns in the Randić-Razinger code $\mathrm{RRC}_{i-1}(\mathrm{A}^\diamond)$ of $A^\diamond$ at vertices $i-1$, i-2, i-3, ..., i is equivalent to the also clockwise list of turns in the Randić-Razinger code $\mathrm{RRC}_i(\mathrm{A})$ of A at vertices i, $i+1$, $i+2$, ..., $i-1$

$$\mathrm{RRC}_{i-1}(\mathrm{A}^\diamond) = \mathrm{RRC}_i(\mathrm{A}) \tag{10}$$

Reflecting $A^\diamond$ by the same reflection line leads to another superimposed version $A^{\diamond\diamond} = A$ of polyhex A, where the clockwise list of turns in the Randić-Razinger code $\mathrm{RRC}_{i-1}(\mathrm{A}^\diamond)$ of $A^\diamond$ at vertices $i-1$, i-2, i-3, ..., i becomes the counterclockwise list of turns of the reverse Randić-Razinger code $\mathrm{RRRC}_{i-1}(\mathrm{A})$ of A at the same vertices $i-1$, $i-2$, $i-3$, ..., i of A. That is,

$$\mathrm{RRC}_{i-1}(\mathrm{A}^\diamond) = \mathrm{RRRC}_{i-1}(\mathrm{A}) \tag{11}$$

Comparison of eqs 10 and 11 gives

$$\mathrm{RRC}_i(\mathrm{A}) = \mathrm{RRRC}_{i-1}(\mathrm{A}) \tag{12}$$

that is, polyhex A is true palindromic.

Combining parts (a) and (b), the statement of the theorem follows. Q.E.D.

3. SUMMARY

Some of the relations between the two-chirality properties and the palindromic properties of perimeter codes of polyhexes are described. Two theorems are proven, establishing the equivalence of the cp-palindromic property and two-achirality of polyhexes and the special role of edge bisecting mirror lines on hexagonal lattices.

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REFERENCES AND NOTES

(1) Herndon, W. C. Resonance Energies of Aromatic Hydrocarbons. A Quantitative Test of Resonance Theory. *J. Am. Chem. Soc.* **1973**, *95*, 2404−2406.
(2) Randić, M. Conjugated Circuits and Resonance Energies of Benzenoid Hydrocarbons. *Chem. Phys. Lett.* **1976**, *38*, 68−70.
(3) Randić, M. Aromaticity and Conjugation. *J. Am. Chem. Soc.* **1977**, *99*, 444−450.
(4) Gutman, I.; Randić, M. A Correlation Between Kekule Valence Structures and Conjugated Circuits. *Chem. Phys.* **1979**, *41*, 265−270.
(5) Balaban, A. T. Challenging Problems Involving Benzenoid Polycyclic and Related Systems. *Pure Appl. Chem.* **1982**, *54*, 1075−1096.
(6) Brown, R. L. Counting of Resonance Structures for Large Polynuclear Hydrocarbons. *J. Comput. Chem.* **1983**, *4*, 556−562.
(7) Hosoya, H.; Ohkami, N. Operator Technique for Obtaining the Recursion Formulas of Characteristic Polynomials and Matching Polynomials as Applied to Polyhex Graphs. *J. Comput. Chem.* **1983**, *4*, 585−593.
(8) Randić, M.; Hosoya, H.; Polansky, O. E. On the Construction of the Matching Polynomial for Unbranched Cata-Condensed Benzenoids. *J. Comput. Chem.* **1983**, *10*, 683−697.
(9) John, P.; Sachs, H. Calculating the Number of Perfect Matching and Pauling's Bond Orders in Hexagonal Systems Whose Inner Dual is Tree. *Proceedings of the International Conference on Graph Theory;* Eyba: Teubner, Leipzig, 1984; p 80.

(10) Hosoya, H. How to Construct Non-Kekulé Polyhex Graphs. *Croat. Chem. Acta* **1986**, *59*, 583−590.
(11) Randić, M.; Klein, D. J. Innate Degrees of Freedom of Pi-electron Coupling. In Mathematical and Computational Concepts in Chemistry; Trinajstic, N. Ed.; Ellis Horwood Ltd.: Chichester, England, 1986; pp 274−282.
(12) Graovac, A.; Babic, D. Enumeration of Kekulé Structures in One-dimensional Polymers. *Croat. Chem. Acta* **1986**, *59*, 731−744.
(13) Randić, M. A Statistical Approach to Resonance Energies of Large Molecules. *Chem. Phys. Lett.* **1986**, *128*, 193−197.
(14) Randić, M.; Hosoya, H.; Ohkami, N.; Trinajstic, N. The Generalized Wheland Polynomial. *J. Math. Chem.* **1987**, *1*, 97−122.
(15) Klein, D. J.; Hite, G. E.; Schmalz, T. G. Transfer-matrix Method for Subgraph Enumeration: Applications to Polypyrene Fusenes. *J. Comput. Chem.* **1986**, *7*, 443−456.
(16) Randić, M.; Pisanski, T. On Maximal Valence Structures. *Rep. Mol. Theory* **1990**, *1*, 107−114.
(17) Randić, M.; Tsukano, Y.; Hosoya, H. On Enumeration of Kekule Structures for Benzenoid Tori. *Nat. Sci. Rep. Ochanomizu Univ.* **1994**, *45*, 101−119.
(18) Guo, X.; Randić, M. Recursive Method for Enumeration of Linearly Independent and Minimal Conjugated Circuits of Benzenoid Hydrocarbons. *J. Chem. Inf. Comput. Sci.* **1994**, *34*, 339−348.
(19) Zivkovic, T.; Randić, M.; Klein, D. J.; Zhu, H.; Trinajstić, N. Analytical Approach to Very Large Benzenoid Polymers. *J. Comput. Chem.* **1995**, *16*, 517−526.
(20) Randić, M.; Razinger, M. On Characterization of Molecular Shapes. *J. Chem. Inf. Comput. Sci.* **1995**, *35*, 594−606.
(21) Mezey, P. G. Tying Knots Around Chiral Centres: Chirality Polynomials and Conformational Invariants for Molecules. *J. Am. Chem. Soc.* **1986**, *108*, 3976−3984.
(22) Harary, F.; Mezey, P. G. Chiral and Achiral Square-Cell Configurations and the Degree of Chirality. In New Developments in Molecular Chirality; Mezey, P. G., Ed.; Kluwer Academic Publ.: Dordrecht, 1991; pp 241−256.
(23) Mezey, P. G. A Global Approach to Molecular Chirality. In New Developments in Molecular Chirality; Mezey, P. G., Ed.; Kluwer Academic Publ.: Dordrecht, 1991; pp 257−289.
(24) Harary, F.; Mezey, P. G. Similarity and Complexity of the Shapes of Square-Cell Configurations. *Theor. Chim. Acta* **1991**, *79*, 379−387.
(25) Walker, P. D.; Mezey, P. G. Representation of Square Cell Configurations in the Complex Plane. Tools for the Characterization of Molecular Monolayers and Cross Sections of Molecular Surfaces. *Int. J. Quantum Chem.* **1992**, *43*, 375−392.
(26) Mezey, P. G. Shape in Chemistry: An Introduction to Molecular Shape and Topology; VCH Publishers: New York, 1993.
(27) Mezey, P. G. Rules on Chiral and Achiral Molecular Transformations. *J. Math. Chem.* **1995**, *17*, 185−202.
(28) Mezey, P. G. Rules on Chiral and Achiral Molecular Transformations II. *J. Math. Chem.* **1995**, *18*, 133−139.
(29) Mezey, P. G.; Zimpel, Z.; Warburton, P.; Walker, P. D.; Irvine, D. G.; Dixon, D. G.; Greenberg, B. A High-Resolution Shape-Fragment Database for Toxicological Shape Analysis of PAHs. *J. Chem. Inf. Comput. Sci.* **1996**, *36*, 602−611.

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