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ON THE CLASSIFICATION OF POLYHEX HYDROCARBONS

Nenad TRINAJSTIĆ *
Department of Marine Sciences, Texas A&M University, Galveston, Texas 77553, USA

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Abstract

A novel classification scheme for polyhex hydrocarbons is proposed.

There has been considerable discussion about the classification of polyhex hydrocarbons at the Third International Mathematical Chemistry Conference held (March 5–9, 1989) in Galveston, Texas. Several classification schemes have been discussed, but not a single one was complete enough to embrace all possible cases. This prompted us to propose in the present note a novel classification of polyhex hydrocarbons. The present classification is based on the graph-theoretical and topological characteristics of polyhexes.

The carbon skeletons of polyhex hydrocarbons may graph-theoretically be depicted by polyhexes [1–6]. Polyhexes are graphs which can be obtained by any combination of regular hexagons such that two hexagons have exactly one common edge or are disjoint. Polyhexes may be planar or non-planar graphs. A polyhex is a planar graph if, and only if, it can be mapped onto the graphite lattice. Otherwise, a polyhex is a non-planar graph.

Here, we will consider only finite polyhexes. Infinite polymeric polyhexes [7,8] may be classified much as finite polyhexes. One class among these extended systems appears to be particularly intriguing: This is the class of fractal benzenoid hydrocarbons [8b]. These structures are representative of fractal aromatic systems [8c].

Planar and non-planar polyhexes may be partitioned into two classes: 1-factorable polyhexes and non-1-factorable polyhexes. A polyhex is a 1-factorable graph if, and only if, it possesses 1-factors [9]. A 1-factorable polyhex may serve as a model for a Kekuléan hydrocarbon, while a non-1-factorable polyhex depicts a non-Kekuléan hydrocarbon [10]. 1-factorization implies that the polyhex hydrocarbon in question possesses Kekulé structure(s) [11].

1-factorable polyhexes may conveniently be split into benzenoid graphs and coronoid graphs [12,13]. Benzenoid graphs or benzenoids are simply connected polyhexes [4,9] which correspond to benzenoid hydrocarbons [10]. Benzenoids may be cata-

*Permanent address: The Rugjer Bošković Institute, P.O.B. 1016, 41001 Zagreb, Croatia.

condensed (cata-benzenoids) or peri-condensed (peri-benzenoids) polyhexes [1,4,10,14,15]. The difference between cata-benzenoids and peri-benzenoids is related to the presence of the inner (internal) vertices [16]. A cata-benzenoid is a benzenoid graph which does not contain inner vertices, while a peri-benzenoid is a benzenoid graph with inner vertices of valency 3. The necessary but not sufficient condition for a peri-condensed polyhex to be a peri-benzenoid is that the number of inner vertices is even. If inner vertices of valency 2 appear, then the benzenoid contains a hole [17]. A hole is a finite region of size greater than a hexagon [18]. Polyhexes containing one or more holes are named corona-condensed polyhexes [19] or coronoids [12].

Cata-benzenoids may be branched or unbranched structures. Unbranched cata-benzenoids may be linear, e.g. acenes [20], or angular. The extreme case of angular planar cata-benzenoids is the class of zig-zag cata-benzenoids or polyphenanthrenes [21]. The class of peri-benzenoids consists of unbranched peri-benzenoids and branched peri-benzenoids. Branching of peri-benzenoids may occur in a "cata" or "peri" manner.

Coronoids consist of three groups of structures [12,13,22]: primitive coronoids, multiple coronoids and complex coronoids. Primitive coronoids are polyhexes containing a single hole, while multiple coronoids contain two or more holes. Complex coronoids contain one or more holes and cata- and/or peri-condensed fragments.

Planar non-Kekuléan polyhexes may by divided into three classes: peri-non-Kekuléans, multiple coronoid and complex coronoid non-Kekuléans. Note that cata-polyhexes and primitive coronoids cannot be non-Kekuléan because they do not contain inner vertices.

Non-planar polyhexes also differ among themselves with respect to 1-factorization. Thus, they may also be split, in a manner similar to planar polyhexes, into 1-factorable (or Kekuléan) non-planar polyhexes (benzenoids) and non-1-factorable (or non-Kekuléan) non-planar polyhexes.

Kekuléan non-planar benzenoids consist of helicenes, composite helicenes and toroidal structures. Helicenes are angularly (ortho) annelated benzenoids which possess helical symmetry [24,25]. Composite helicenes are composed of helicenes and cata-benzenoids, peri-benzenoid and/or coronoid fragments [24,25]. Toroidal structures represent a class of very unusual Kekuléan non-planar polyhex hydrocarbons [23]: toroidal benzenoids are those structures that have a π-network equivalent to that of a graphitic fragment with cyclic boundary conditions. Toroidal benzenoids may be imagined as structures mapped onto the surface of a torus, and are expected to be an aromatic species [23b]. These benzenoids may cover the surface of the torus with hexagons, but there is also the possibility of having (coronoid) holes, which is also possible on closed surfaces with higher genus. The possibility of polyhex structures on surfaces not embeddable in three-dimensional Euclidean space evidently has not been explored.

Non-Kekuléan non-planar polyhexes may also be divided into two classes: peri-non-Kekuléan and non-Kekuléan complex coronoids containing helical fragments (so-called heli-coronoids [15]). As we have already stated, all these and other polyhex classes may serve as graph-theoretical models [26] of polyhex hydrocarbons. The proposed classification of polyhex hydrocarbons is diagrammatically summarized in fig. 1.

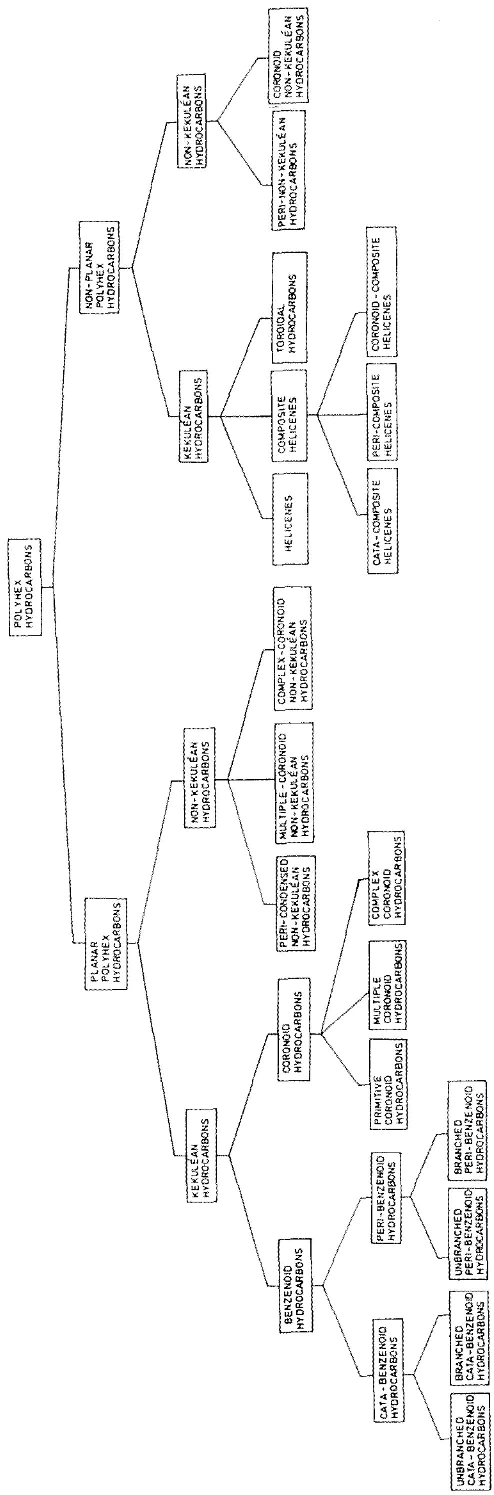

Fig. 1. The classification scheme for polyhex hydrocarbons.

Among the classes of polyhex hydrocarbons, the members of the following are known [20,25,27,28]: benzenoid hydrocarbons, coronoid hydrocarbons, helicenes and certain composite helicenic hydrocarbons. The most studied are benzenoid hydrocarbons [15,20,27,28]. Planar and non-planar non-Kekuléan polyhex hydrocarbons are practically unknown, in agreement with Clar's postulate [29], according to which polyhex hydrocarbons without Kekulé structures are expected to be unstable.

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References

[1] A.T. Balaban and F. Harary, Tetrahedron 24(1968)2505.
[2] A.T. Balaban, Tetrahedron 25(1969)2949.
[3] A.T. Balaban, in: *Chemical Applications of Graph Theory*, ed. A.T. Balaban (Academic Press, London, 1976) p. 63.
[4] J.V. Knop, K. Szymanski, Ž. Jeričević and N. Trinajstić, J. Comput. Chem. 4(1983)23.
[5] J.V. Knop, K. Szymanski, L. Klasinc and N. Trinajstić, Comput. Chem. 8(1984)107.
[6] J.V. Knop, W.R. Müller, K. Szymanski and N. Trinajstić, J. Comput. Chem. 7(1986)547.
[7] (a) A. Graovac, I. Gutman, M. Randić and N. Trinajstić, Colloid Polymer. Sci. 255(1977)480;
(b) A. Graovac, M. Randić and N. Trinajstić, Croat. Chem. Acta 53(1980)571;
(c) D.J. Klein, T.P. Živković and N. Trinajstić, J. Math. Chem. 1(1987)309;
(d) W.A. Seitz and T.G. Schmalz, in: *Valence Bond Theory and Chemical Sructure*, ed. D.J. Klein and N. Trinajstić (Elsevier, Amsterdam, 1990), p. 525.
[8] (a) D.J. Klein, W.C. Herndon and M. Randić, New. J. Chem. 12(1988)71;
(b) D.J. Klein, private communication (March, 1989);
(c) D.J. Klein, M. Cravey, T.P. Živković and G.E. Hite, in preparation.
[9] F. Harary, *Graph Theory*, 2nd ed. (Addison-Wesley, Reading, MA, 1971).
[10] N. Trinajstić, *Chemical Graph Theory* (CRC, Boca Raton, FL, 1983), Vol. 1, Ch. 3.
[11] S.J. Cyvin and I. Gutman, *Kekulé Structures in Benzenoid Hydrocarbons* (Springer-Verlag, Berlin, 1986),
[12] J. Brunvoll, B.N. Cyvin and S.J. Cyvin, J. Chem. Inf. Comput. Sci. 27(1987)14.
[13] A.T. Balaban, J. Brunvoll, J. Cioslowski, B.N. Cyvin, S.J. Cyvin, I. Gutman, Wenchen He, Wenjie He, J.V. Knop, M. Kovačević, W.R. Müller, K. Szymanski, R. Tošić and N. Trinajstić, Z. Naturforsch. 42a(1987)863.
[14] A.T. Balaban, Pure Appl. Chem. 54(1982)1075.
[15] J.V. Knop, W.R. Müller, K. Szymanski and N. Trinajstić, *Computer Generation of Certain Classes of Molecules* (Association of Croatian Chemists and Technologists, Zagreb, 1985).
[16] B. Džonova-Jerman-Blažič and N. Trinajstić, Comput. Chem. 6(1982)121.
[17] S. Nikolić, N. Trinajstić, J.V. Knop, W.R. Müller and K. Szymanski, J. Math. Chem., in press.

[18] N. Trinajstić, M. Randić and D.J. Klein, Int. J. Quant. Chem.: Quant. Chem. Symp. 20(1986)699.
[19] O.E. Polansky and D.H. Rouvray, Math. Chem. (Mülheim/Ruhr) 2(1976)63.
[20] E. Clar, *Polycyclic Hydrocarbons* (Academic Press, London, 1964).
[21] D.J. Klein, T.G. Schmalz, G.E. Hite, A. Metropoulos and W.A. Seitz, Chem. Phys. Lett. 120(1985)367.
[22] Wenchen He, Wenjie He, Q. Wang, J. Brunvoll and S.J. Cyvin, Z. Naturforsch. 43a(1988)693.
[23] (a) T.G. Schmalz, W.A. Seitz, D.J. Klein and G.E. Hite, J. Amer. Chem. Soc. 110(1988)1113; (b) D.J. Klein, T.G. Schmalz and W.A. Seitz, in preparation.
[24] M. Randić, S. Nikolić and N. Trinajstić, Croat. Chem. Acta 61(1988)821.
[25] M. Randić, B.M. Gimarc, S. Nikolić and N. Trinajstić, Gazz. Chim. Ital. 119(1989)1.
[26] N. Trinajstić, in: *MATH/CHEM/COMP 87*, ed. R.C. Lacher (Elsevier, Amsterdam, 1988), p. 83.
[27] J.R. Dias, *Handbook of Polycyclic Hydrocarbons, Part A: Benzenoid Hydrocarbons* (Elsevier, Amsterdam, 1987).
[28] J.R. Dias, *Handbook of Polycyclic Hydrocarbons, Part B: Polycyclic Isomers and Heteroatom Analogs of Benzenoid Hydrocarbons* (Elsevier, Amsterdam, 1988).
[29] E. Clar, W. Kemp and D.G. Stewart, Tetrahedron 3(1958)325.