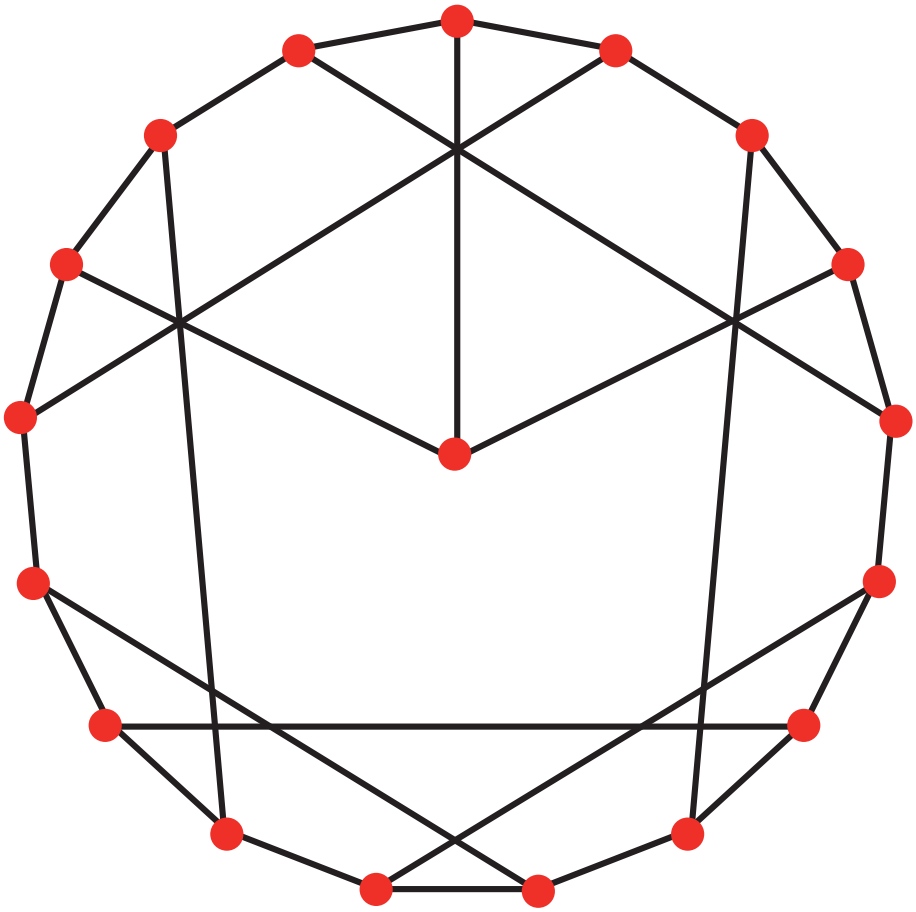
Graph-Theoretical Matrices in Chemistry



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Mathematics and chemistry make excellent partners.

Dennis H. Rouvray
Editorial Foreword
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Graph-Theoretical Matrices in Chemistry

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Contents

Preface to the Second Edition

The first edition of this monograph, entitled *Graph-Theoretical Matrices in Chemistry*, was published, under the editorship of Professor Ivan Gutman, by the University of Kragujevac, Kragujevac, Serbia (Janežić et al., 2007). That monograph appeared in the series Mathematical Chemistry Monographs as the third volume and sold out. Therefore, we decided to improve and enlarge the second edition of the monograph in order to include novel graph-theoretical matrices that appeared after the first edition was published. We also received quite a few comments on the first edition; the most detailed were by Professor Milan Randić, the foremost mathematical chemist of our times. In the second edition, we include most of his comments as well as his suggestions to include a few more graph-theoretical matrices from the early days of chemical graph theory. The term *chemical graph theory* was introduced in the early 1970s by the Theoretical Chemistry Group at the Rugjer Bošković Institute in Zagreb. Nenad Trinajstić first used this term that is now generally accepted for chemical applications of graph theory (Gutman, 2003).

Several new monographs have appeared since 2007 reporting in part on graph-theoretical matrices and related molecular descriptors, e.g., *Molecular Descriptors for Chemoinformatics* (Todeschini and Consonni, 2009), *Statistical Modelling of Molecular Descriptors in QSAR/QSPR* (Dehmer et al., 2012) and *Mathematical Chemistry and Chemoinformatics* (Kerber et al., 2014). Several new graph-theoretical matrices have also been proposed, such as the sum-connectivity matrix (Zhou and Trinajstić, 2010) and the distance-weighted adjacent matrix (Randić et al., 2010) and the matrix of dominant distances in a graph (Randić, 2013). The total number of graph-theoretical matrices considered here is 170.

The second edition is organized similarly as the first edition; that is, after the introduction the considered graph-theoretical matrices are presented in five chapters: "The Adjacency Matrix and Related Matrices," "Incidence Matrices," "The Distance Matrix and Related Matrices," "Special Matrices," and "Graphical Matrices." Each chapter is followed by a list of references. The monograph ends with concluding remarks and a subject index.

We thank Dr. Sc. Bono Lučić for his help with this manuscript by providing reprints of a number of papers we needed to consult. We also thank the master of engineering in landscape architecture Zdenko Blažeković for his help with figures. Comments by reviewers were most helpful. We thank them for their valuable suggestions.

REFERENCES

M. Dehmer, K. Varmuza, and D. Bonchev, Eds., *Statistical modelling of molecular descriptors in QSAR/QSPR*, Wiley-Blackwell, Weinheim, 2012.

I. Gutman, Preface to a special issue entitled *Graph-based molecular structure-descriptors—theory and applications*, *Ind. J. Chem.* 42A (2003) 1197–1198.

D. Janežić, A. Miličević, S. Nikolić, and N. Trinajstić, *Graph-theoretical matrices in chemistry*, Mathematical Chemistry Monographs, MCM-Vol. 3, I. Gutman, Ed., University of Kragujevac, Kragujevac, 2007.

A. Kerber, R. Laue, M. Meringer, Ch. Rücker, and E. Schymanski, *Mathematical chemistry and chemoinformatics*, De Gruyter, Berlin/Boston, 2014.

M. Randić, $\mathbf{D}_{MAX}$—Matrix of dominant distances in a graph, *MATCH Commun. Math. Comput. Chem.* 70 (2013) 221–238.

M. Randić, T. Pisanski, M. Novič, and D. Plavšić, Novel graph distance matrix, *J. Comput. Chem.* 31 (2010) 1832–1841.

R. Todeschini and V. Consonni, *Molecular descriptors for chemoinformatics*, Vols. I and II, Wiley-VCH, Weinheim, 2009.

B. Zhou and N. Trinajstić, On the sum-connectivity matrix and sum-connectivity energy of a (molecular) graph, *Acta Chim. Slov.* 57 (2010) 518–523.

Preface to the First Edition

Mathematical chemistry has a long history extending back to the times of Russian polymath Mikhail Vasilyevich Lomonosov (Oranienbaum, from 1948; Lomonosov, 1711–Sankt Peterburg, 1765), when he attempted in the mid-18th century to mathematize chemistry (Trinajstić and Gutman, 2002). A part of mathematical chemistry that we call chemical graph theory (Trinajstić, 1983, 1992) also has a distinguished past that extends to the second half of the 19th century when Arthur Cayley (Richmond, Surrey, 1821–Cambridge, 1895) was enumerating alkane isomers (Cayley, 1875) and James Joseph Sylvester (London, 1814–London, 1897) introduced the terms *algebraic chemistry* and *graph* (Sylvester, 1877/1878, 1878). Alexander Crum Brown (Edinburgh, 1838–Edinburgh, 1922), who was trained in both chemistry and mathematics, was probably the first chemist who did research in mathematical chemistry (Crum Brown, 1864, 1866/1867).

The term *algebraic chemistry* has in due course been replaced by the more general term *mathematical chemistry*, but a better term than *graph* has never been found. The seminal role of Cayley and Sylvester in the early development of mathematical chemistry in general and chemical graph theory in particular has been expertly reviewed by Dennis H. Rouvray (1989). It is important to point out why mathematical chemistry is relevant to chemistry. We could not do better than Jerome Karle, Nobel Prize Laureate 1985, who wrote: "Mathematical chemistry provides the framework and broad foundation on which chemical science proceeds" (Karle, 1986).

Mathematical chemistry and chemical graph theory were developing sluggishly with only a few leaps, such as Pólya's work on combinatorial enumeration (Polya, 1937), until the 1970s. Then there suddenly appeared several research groups, located worldwide, that started to speedily develop chemical graph theory. One of the directions in which this vigorous revival was moving was the introduction of a number of novel graph-theoretical matrices.

Matrices are the backbone of chemical graph theory. Classical graph-theoretical matrices are the (vertex-) *adjacency matrix*, the (vertex-edge) *incidence matrix*, and the (vertex-) *distance matrix* (Harary, 1971; Behzad and Chartrand, 1971; Johnson and Johnson, 1972; Wilson, 1972; Bondy and Murty, 1976; Rouvray, 1976; Chartrand, 1977; Cvetković et al., 1988, 1995; Buckley and Harary, 1990). Historically, incidence matrices appear to have been the first to be used (Poincaré, 1900). However, the most important graph-theoretical matrix is the vertex-adjacency matrix, as is well illustrated by Cvetković, Doob, and Sachs in their monograph *Spectra of Graphs—Theory and Applications* (Cvetković et al., 1995), the first edition of which appeared in 1982. An important source for the distance matrix is the monograph *Distance in Graphs* by Buckley and Harary (1990).

In the last 25 years perhaps more than 100 novel graph-theoretical matrices have been introduced. Among the literature sources reporting some of these matrices

and their uses are the monographs *Topological Indices and Related Descriptors in QSAR and QSPR*, edited by Devillers and Balaban (1999), *Handbook of Molecular Descriptors* by Todeschini and Consonni (2000), and *Molecular Topology* by Diudea et al. (2001), and the review articles "Molecular Graph Matrices and Derived Structural Descriptors" by Ivanciuc et al. (1997) and "Eigenvalues as Molecular Descriptors" by Randić et al. (2001).

We present 130 graph-theoretical matrices in the encyclopedic manner, classified into five groups: adjacency matrices and related matrices, incidence matrices, distance matrices and related matrices, special matrices, and graphical matrices. The motivation for preparing this monograph comes from the fact that among the matrices presented, several are novel, several are known only to a few, and the properties and potential usefulness of many graph-theoretical matrices in chemistry are yet to be investigated.

Most of the graph-theoretical matrices that we present here have been used as sources of molecular descriptors, usually referred to as topological indices—the term *topological index* was introduced 35 years ago by Hosoya (1971)—which have found considerable application in structure-property-activity modeling (Trinajstić, 1983, 1992; Gutman and Polansky, 1986; Devillers and Balaban, 1999; Karelson, 2000; Diudea, 2001; Diudea et al., 2001), usually abbreviated QSPR (quantitative structure-property relationship) (Sabljić and Trinajstić, 1981) and QSAR (quantitative structure-activity relationship) (Tichy, 1976). Graph-theoretical and related matrices, however, have also been used for many other purposes in chemistry (e.g., Randić, 1974; Hendrickson and Toczko, 1983; Lukovits, 2000, 2002, 2004; Lukovits and Gutman, 2002; Klein et al., 2002; Babić et al., 2004; Miličević and Trinajstić, 2006; Diudea et al., 2006) and in other sciences (e.g., Avondo-Bodino, 1962; Johnson and Johnson, 1972; Chartrand, 1977; Hage and Harary, 1986; Roberts, 1989).

Hopefully, this monograph will stimulate some readers to undertake research in this fruitful and rewarding area of chemical graph theory and introduce new kinds of graph-theoretical matrices that may find use in chemistry.

Finally, we wish to point out that this book is an outcome of the long-standing Croatian-Slovenian joint research collaboration in computational and mathematical chemistry.

The authors thank G.W.A. Milne, former editor-in-chief of the *Journal of Chemical Information and Computer Sciences*, for his editorial assistance with this book.

REFERENCES

G. Avondo-Bodino, *Economic applications of the theory of graphs*, Gordon & Breach, New York, 1962.

D. Babić, D.J. Klein, J. von Knop, and N. Trinajstić, Combinatorial enumeration in chemistry, in *Chemical modelling: Applications and theory*, ed. A. Hinchliffe, Vol. 3, Royal Society of Chemistry, Cambridge, 2004, pp. 126–170.

M. Behzad and G. Chartrand, *Introduction to the theory of graphs*, Allyn & Bacon, Boston, 1971.

J.A. Bondy and U.S.R. Murty, *Graph theory with applications*, North Holland/Elsevier, Amsterdam, 1976.

F. Buckley and F. Harary, *Distance in graphs*, Addison-Wesley, Reading, MA, 1990.
A. Cayley, Über die analytischen Figuren, welche in der Mathematik Bäume gennant werden und ihre Anwendung auf die Theorie chemischer Verbindungen, *Ber. Dtsch. Chem. Ges.* 8 (1875) 1056–1059.
G. Chartrand, *Graphs as mathematical models*, Prindle, Weber and Schmidt, Boston, 1977.
A. Crum Brown, On the theory of isomeric compounds, *Trans. R. Soc.* (*Edinburgh*) 23 (1864) 707–719.
A. Crum Brown, On an application of mathematics to chemistry, *Proc. R. Soc.* (*Edinburgh*) VI(73) (1866–1867) 89–90.
D. Cvetković, M. Doob, I. Gutman, and A. Torgašev, *Recent results in the theory of graph spectra*, North-Holland, Amsterdam, 1988.
D. Cvetković, M. Doob, and H. Sachs, *Spectra of graphs—Theory and applications*, 3rd ed., Johann Ambrosius Barth Verlag, Heidelberg, 1995.
J. Devillers and A.T. Balaban, eds., *Topological indices and related descriptors in QSAR and QSPR*, Gordon & Breach, Amsterdam, 1999.
M.V. Diudea, ed., *QSPR/QSAR studies by molecular descriptors*, Nova, Huntington, NY, 2001.
M.V. Diudea, M.S. Florescu, and P.V. Khadikar, *Molecular topology and its applications*, EfiCon Press, Bucharest, 2006.
M.V. Diudea, I. Gutman, and J. Lorentz, *Molecular topology*, Nova, Huntington, NY, 2001.
I. Gutman and O.E. Polansky, *Mathematical concepts in organic chemistry*, Springer, Berlin, 1986.
P. Hage and F. Harary, *Structural models in anthropology*, Cambridge University Press, Cambridge, 1986.
F. Harary, *Graph theory*, 2nd printing, Addison-Wesley, Reading, MA, 1971.
J.B. Hendrickson and A.G. Toczko, Unique numbering and cataloging of molecular structures, *J. Chem. Inf. Comput. Sci.* 23 (1983) 171–177.
H. Hosoya, Topological index. A newly proposed quantity characterizing the topological nature of structural isomers of saturated hydrocarbons, *Bull. Chem. Soc. Jpn.* 44 (1971) 2332–2339.
O. Ivanciuc, T. Ivanciuc, and M.V. Diudea, Molecular graph matrices and derived structural descriptors, *SAR QSAR Environ. Res.* 7 (1997) 63–87.
D.E. Johnson and J.R. Johnson, *Graph theory with engineering applications*, Ronald, New York, 1972.
M. Karelson, *Molecular descriptors in QSAR/QSPR*, Wiley-Interscience, New York, 2000.
J. Karle, Letter of welcome (dated October 10, 1986) to D.H. Rouvray on the occasion of the first issue of the *Journal of Mathematical Chemistry*. Physical chemist Jerome Karl (born as Jerome Karfunkle; New York, 1918–Annandale, Virginia, 2013) and mathematician Herbert Aaron Hauptman (New York, 1917–Buffalo, NY, 2011) were awarded the Nobel Prize for Chemistry in 1985 for their work in mathematical chemistry, more specifically for developing the mathematical approach by which they solved the phase problem in x-ray chrystallography.
D.J. Klein, D. Babić, and N. Trinajstić, Enumeration in chemistry, in *Chemical modelling: Applications and theory*, ed. A. Hinchliffe, Vol. 2, Royal Society of Chemistry, Cambridge, 2002, pp. 56–95.
I. Lukovits, A compact form of the adjacency matrix, *J. Chem. Inf. Comput. Sci.* 40 (2000) 1147–1150.
I. Lukovits, The generation of formulas for isomers, in *Topology in chemistry: Discrete mathematics of molecules*, ed. D.H. Rouvray and R.B. King, Horwood, Chichester, 2002, pp. 327–337.
I. Lukovits, Constructive enumeration of chiral isomers of alkanes, *Croat. Chem. Acta* 77 (2004) 295–300.
I. Lukovits and I. Gutman, On Morgan trees, *Croat. Chem. Acta* 75 (2002) 563–576.

A. Miličević and N. Trinajstić, Combinatorial enumeration in chemistry, in *Chemical modelling: Applications and theory*, ed. A. Hinchliffe, Vol. 4, Royal Society of Chemistry, Cambridge, 2006, pp. 408–472.

H. Poincaré, Second complément à l'Analysis Situs, *Proc. London Math. Soc.* 32 (1900) 277–308.

G. Pólya, Kombinatorische Anzahlbestimmungen für Gruppen, Graphen und chemische Verbindungen, *Acta Math.* 68 (1937) 145–254. Translation of this paper appeared in the book form: G. Pólya and R.C. Read, *Combinatorial enumeration of groups, graphs and chemical compounds*, Springer, New York, 1987.

M. Randić, On the recognition of identical graphs representing molecular topology, *J. Chem. Phys.* 60 (1974) 3920–3928.

M. Randić, M. Vračko, and M. Novič, Eigenvalues as molecular descriptors, in *QSPR/QSAR studies by molecular descriptors*, ed. M.V. Diudea, Nova, Huntington, NY, 2001, pp. 147–211.

F.S. Roberts, ed., *Applications of combinatorics and graph theory to the biological and social sciences*, Springer-Verlag, New York, 1989.

D.H. Rouvray, The topological matrix in quantum chemistry, in *Chemical applications of graph theory*, ed. A.T. Balaban, Academic, London, 1976, pp. 175–221.

D.H. Rouvray, The pioneering contributions of Cayley and Sylvester to the mathematical description of chemical structure, *J. Mol. Struct.* (*Theochem*) 185 (1989) 1–14.

A. Sabljić and N. Trinajstić, QSAR: The role of topological indices, *Acta Pharm. Jugosl.* 31 (1981) 189–214; to our knowledge, the abbreviation *QSPR* was used for the first time in print in this report.

J.J. Sylvester, Chemistry and algebra, *Nature* 17 (1877/1878) 284.

J.J. Sylvester, On an application of the new atomic theory to the graphical representation of the invariants and covariants of binary quantities, with three appendices, *Am. J. Math.* 1 (1878) 64–125.

M. Tichy, ed., *Quantitative structure-activity relationships*, Akademiai Kiado, Budapest, 1976. This book is a collection of papers based on the reports presented at the Conference on Chemical Structure-Biological Activity Relationships: Quantitative Approach, Prague, June 1973. To our knowledge, the abbreviation *QSAR* was used for the first time in print in this book.

R. Todeschini and V. Consonni, *Handbook of molecular descriptors*, Wiley-VCH, Weinheim, 2000.

N. Trinajstić, *Chemical graph theory*, Vols. I and II, CRC, Boca Raton, FL, 1983.

N. Trinajstić, *Chemical graph theory*, 2nd ed., CRC, Boca Raton, FL, 1992.

N. Trinajstić and I. Gutman, Mathematical chemistry, *Croat. Chem. Acta* 75 (2002) 329–356.

R.J. Wilson, *Introduction to graph theory*, Oliver and Boyd, Oxford, 1972.

1 Introduction

The aim of this monograph is to present a number of the graph-theoretical matrices and related matrices that are frequently encountered in chemical graph theory. Matrices are convenient devices for the algebraic representation of graphs—they allow numerical handling of graphs (e.g., Randić, 1974; Hendrickson and Toczko, 1983; Lukovits, 2000, 2002, 2004; Lukovits and Gutman, 2002; Klein et al., 2002; Babić et al., 2004; Miličević and Trinajstić, 2006; Diudea et al., 2006). A *graph* is a mathematical object, usually denoted by G, which consists of two nonempty sets; one set, usually denoted by V, is a set of elements called *vertices*, and the other, usually denoted by E, is a set of unordered pairs of distinct elements of V called *edges* (Wilson, 1972). Thus, $G = (V, E)$. Note in the parlance of Harary (1971), vertices are called *points* and edges *lines*. The degree of a given vertex in G is equal to the number of adjacent vertices, denoted by d.

We are here concerned with a special class of graphs called *chemical graphs*, that is, graphs representing chemical structures. If chemical structures under consideration are molecules, we call this type of chemical graph a *molecular graph*. They are generated by replacing atoms and bonds with vertices and edges, respectively (Trinajstić, 1983, 1992; Gutman and Polansky, 1986). Hydrogen atoms are ordinarily neglected. A picture of a simple molecular graph G_1 representing the hydrogen-depleted carbon skeleton of 1-ethyl-2-methylcyclobutane is given in Figure 1.1.

A *simple graph* is defined as a graph that contains no multiple edges or loops. Two or more edges that join a pair of vertices are called *multiple* edges. A graph containing multiple edges is called the *multiple graph* or *multigraph* (Harary, 1971). A *loop*

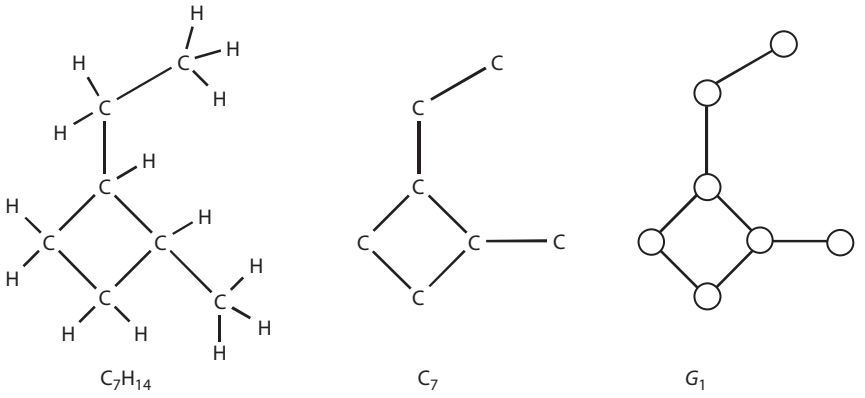

FIGURE 1.1 1-Ethyl-2-methylcyclobutane C_7H_{14}, its hydrogen-depleted carbon skeleton C_7, and the corresponding molecular graph G_1.

is an edge joining a vertex to itself. Graphs containing multiple edges and loops are called *general graphs* (Wilson, 1972).

Labeling vertices and edges of a graph is important, because the structure of any graph-theoretical matrix depends on the labeling (Trinajstić, 1983, 1992). In other words, two graphs may be identical, but because they are differently labeled, the corresponding matrices will appear to be different in their manifested arrangements.

REFERENCES

D. Babić, D.J. Klein, J. von Knop, and N. Trinajstić, Combinatorial enumeration in chemistry, in *Chemical modelling: Applications and theory*, ed. A. Hinchliffe, Vol. 3, Royal Society of Chemistry, Cambridge, 2004, pp. 126–170.

M.V. Diudea, M.S. Florescu, and P.V. Khadikar, *Molecular topology and its applications*, EfiCon Press, Bucharest, 2006.

I. Gutman and O.E. Polansky, *Mathematical concepts in organic chemistry*, Springer, Berlin, 1986.

F. Harary, *Graph theory*, 2nd printing, Addison-Wesley, Reading, MA, 1971.

J.B. Hendrickson and A.G. Toczko, Unique numbering and cataloging of molecular structures, *J. Chem. Inf. Comput. Sci.* 23 (1983) 171–177.

D.J. Klein, D. Babić, and N. Trinajstić, Enumeration in chemistry, in *Chemical modelling: Applications and theory*, ed. A. Hinchliffe, Vol. 2, Royal Society of Chemistry, Cambridge, 2002, pp. 56–95.

I. Lukovits, A compact form of the adjacency matrix, *J. Chem. Inf. Comput. Sci.* 40 (2000) 1147–1150.

I. Lukovits, The generation of formulas for isomers, in *Topology in chemistry: Discrete mathematics of molecules*, ed. D.H. Rouvray and R.B. King, Horwood, Chichester, 2002, pp. 327–337.

I. Lukovits, Constructive enumeration of chiral isomers of alkanes, *Croat. Chem. Acta* 77 (2004) 295–300.

I. Lukovits and I. Gutman, On Morgan trees, *Croat. Chem. Acta* 75 (2002) 563–576.

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M. Randić, On the recognition of identical graphs representing molecular topology, *J. Chem. Phys.* 60 (1974) 3920–3928.

N. Trinajstić, *Chemical graph theory*, Vols. I and II, CRC, Boca Raton, FL, 1983.

N. Trinajstić, *Chemical graph theory*, 2nd ed., CRC, Boca Raton, FL, 1992.

R.J. Wilson, *Introduction to graph theory*, Oliver and Boyd, Oxford, 1972.