The Story of Zagreb Indices

Sonja Nikolić

CSD 5 - Computers and Scientific Discovery 5

University of Sheffield, UK, July 20--23, 2010

Sonja Nikolic
sonja@irb.hr
Rugjer Boskovic Institute
Bijenicka cesta 54, P.O.Box 180
10002 ZAGREB
CROATIA

Zagreb

Zagreb

Collaborators

- Nenad Trinajstić
  - The Rugjer Bošković Institute Zagreb, Croatia
- Ante Miličević
  - *The Institute of Medical Research and Occupational Health, Zagreb, Croatia*

- Measuring complexity in chemical systems, biological organisms or even poetry requires the counting of things.
  - S.H. Bertz and W.F. Wright
    - *Graph Theory Notes of New York,* ***35*** *(1998) 32-48*

The structure of the lecture

- Introduction
- Original formulation of the Zagreb indices
- Modified Zagreb indices
- Variable Zagreb indices
- Reformulated original Zagreb indices
- Reformulated modified Zagreb indices
- Zagreb complexity indices
- General Zagreb indices
- Zagreb indices for heterocyclic systems
- A variant of the Zagreb complexity indices
- Modified Zagreb complexity indices and their variants
- Zagreb coindices and outlined
- Properies of Zagreb indices
- Zagreb indices of line graphs
- Zagreb co-indices
- Analytical formulas for computing Zagreb indices
- Application
- Conclusion

Introduction

- We applied a family of Zagreb indices to study molecules and complexity of selected classes of molecules

Motivation

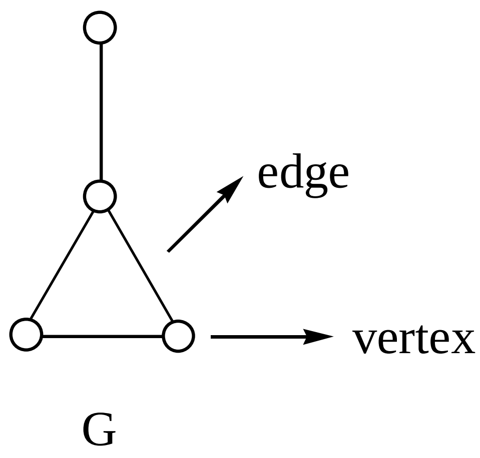
- Zagreb indices, have been introduced 38 years ago (I. Gutman and N. Trinajstić, *Chem. Phys. Lett.* **17** (1972) 535-538) by Zagreb Group

- Current interest in Zagreb indices which found use in the QSPR/QSAR modeling (R. Todeschini and V. Consonni, *Handbook of Molecular Descriptors*, Wiley-VCH, Weinheim, 2009)

- Zagreb indices are included in a number of programs used for the routine computation of topological indices
  - POLLY
  - DRAGON
  - CERIUS
  - TAM
  - DISSIM

Graph

- Graph
  - vertices
  - edges



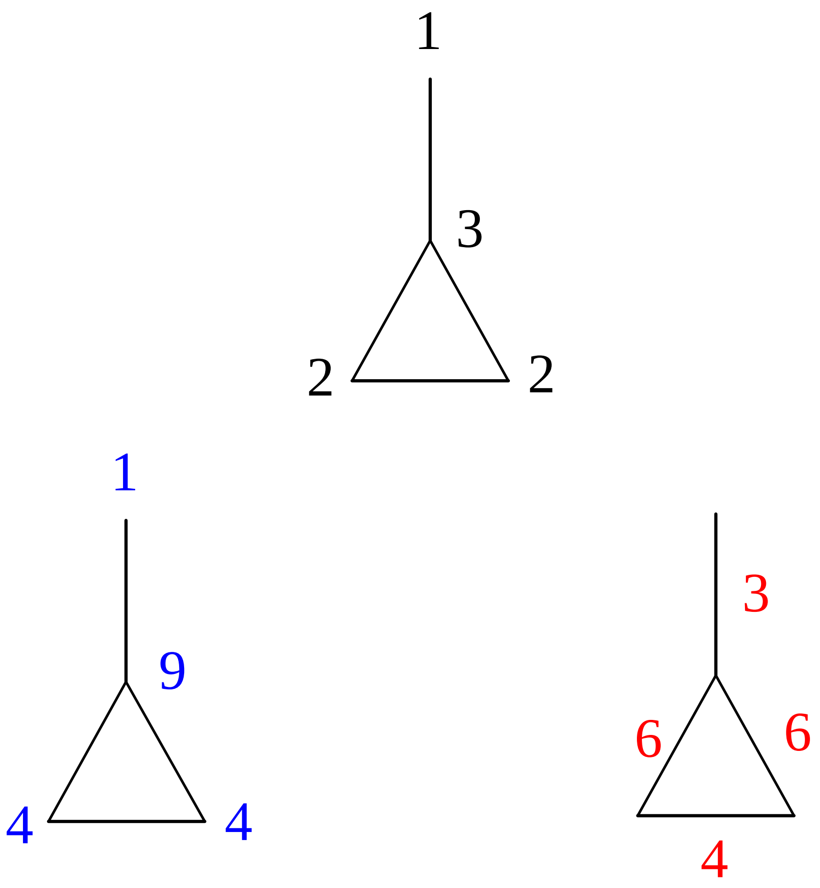
Original Zagreb indices

- $M_1 = \sum_{\text{vertices}} d_i^2$ *first Zagreb index*
  - d_i = the degree of a vertex *i*

- $M_2 = \sum_{\text{edges}} d_i \cdot d_j$ *second Zagreb index*
  - $d_i\, d_j$ = the degree of a edge *ij*

I. Gutman and N. Trinajstić, *Chem. Phys. Lett.* **17** (1972) 535-538.

I. Gutman, B. Ruščić, N. Trinajstić and C.F. Wilkox, Jr., *J. Chem. Phys.* 62 (1975) 3399-3405.



$M_1=18$ $M_2=19$

Zagreb indices via squared adjacency vertex matrices

- $$M_1 = \sum_{\text{vertices}} (\mathbf{A}^2)_{ii}\,(\mathbf{A}^2)_{ii}$$

$$(\mathbf{A}^2)_{ii} = d(i)$$

- $$M_2 = \sum_{\text{edges}} (\mathbf{A}^2)_{ii}\,(\mathbf{A}^2)_{ii}$$

M. Barysz, D. Plavšić and N. Trinajstić, *MATCH Comm.Math. Chem.* **19** (1986) 89-116.

Modified Zagreb indices

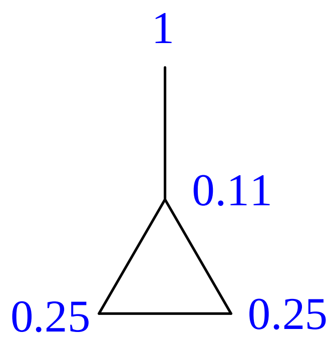
S. Nikolić, G. Kovačević, A. Miličević, N. Trinajstić,
Croat. Chem. Acta **76** (2003) 113.

- $$ {}^{m}M_1 = \sum_{\text{vertices}} d_i^{-1} $$

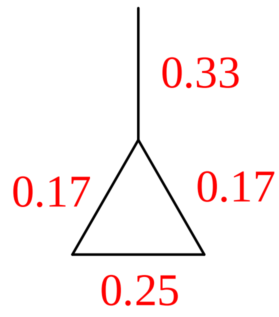
- $$ {}^{m}M_2 = \sum_{\text{edges}} (d_i \cdot d_j)^{-1} $$

- $$ {}^{m}M_2 = {}^{1}ON $$

D. Bonchev, J. Mol. Graphics Modell. **20** (2001) 65.



${}^{m}M_1 = 1.61$



${}^{m}M_2 = 0.92$

Variable Zagreb indices

A. Miličević, S. Nikolić, Croat. Chem. Acta **77** (2004) 97.

- $^{\lambda}M_1 = \sum d_i^{\ \lambda}$

  vertices

- $^{\lambda}M_2 = \sum (d_i \cdot d_j)^{\lambda}$

  edges

λ= variable parameter

$\lambda = 1$	M_1, M_2
$\lambda = -1$	$^{m}M_1, {}^{m}M_2$
$\lambda = -1/2$	χ

$^{\lambda}M_1/V \leq {}^{\lambda}M_2/E$

Reformulated Zagreb indices

$$EM_1 = \sum_{\text{edges}} [d(\mathrm{e}_i)\, d(\mathrm{e}_i)]$$

$$EM_2 = \sum_{\text{edges}} [d(\mathrm{e}_i)\, d(\mathrm{e}_j)]$$

e_i = *degree of edge i*

A. Miličević, S. Nikolić, N. Trinajstić, Mol. Diversity **8** (2004) 393.

Modified reformulated Zagreb indices

$$^{m}EM_1 = \sum_{\text{edges}} [d(e_i)\, d(e_i)]^{-1}$$

$$^{m}EM_2 = \sum_{\text{edges}} [d(e_i)\, d(e_j)]^{-1}$$

Zagreb complexity indices (2003)

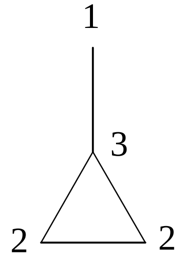
- $TM_1 = \sum_{(s)} \sum_{vertices} d_i^2(s) = \sum M_1(s)$

- $TM_2 = \sum_{(s)} \sum_{edges} d_i \cdot d_j(s) = \sum M_2(s)$

- Computation starts with the creation of the library containing all connected subgraphs of a molecular graph. Then each vertex in a subgraph is given the degree that the vertex possesses in the graph.
- Bonchev in 1997 originated this approach based on the subgraphs to construct topological indices

S. Nikolić, N. Trinajstić, I.M. Tolić, G. Rücker, C. Rücker, u: Complexity - Introduction and Fundamentals. D. Bonchev, D.H. Rouvray, editors, Taylor & Francis, London, 2003, str. 29-89.

Example of the subgraph library

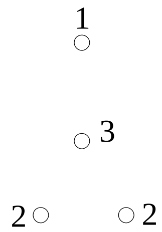


G

$TM_1=230$

$TM_2=145$

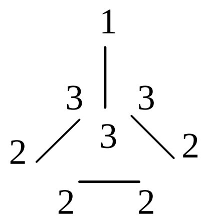
The methane subgraphs



$\sum_i d_i^2(s)=18$

$\sum_i d_i \cdot d_j \ (s)=0$

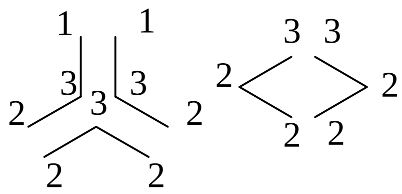
The ethane subgraphs



44

19

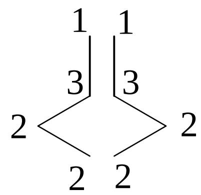
The propane subgraphs



79

50

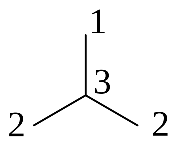
The butane subgraphs



36

26

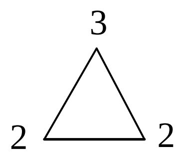
The isobutane subgraph



18

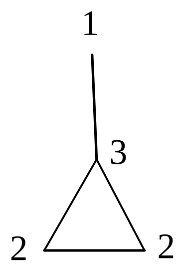
15

The cyclopropane subgraph



17
16

Graph G as its own subgraph



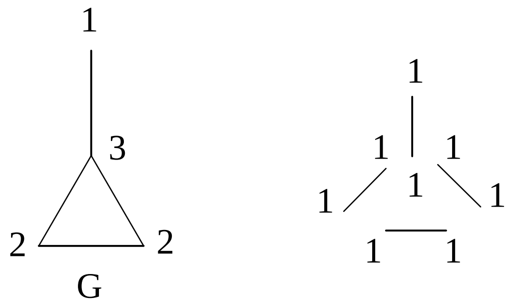
18
19

A variant of the Zagreb complexity indices* (2003)

- $$TM_1^* = \sum_{(s)} \sum_{vertices} d_i^{*2}(s)$$

  - d_i^* = the degree of a vertex *i* as in a subgraph *s*
  - s = the subgraph in G

- $$TM_2^* = \sum_{(s)} \sum_{edges} d_i^* \, d_j^* \, (s)$$



$$\sum d_i^{*2}(s) = 8$$

$$\sum d_i^{*} \cdot d_j^{*} (s) = 4$$

$TM_1^* = 100$ $TM_2^* = 80$

Modified Zagreb complexity indices

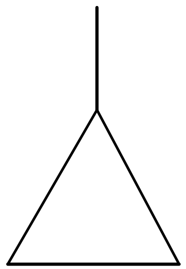
$$ {}^{m}TM_1 = \sum_{(s)} \sum_{\text{vertices}} d_i^{\,-2}(s) $$

$$ {}^{m}TM_2 = \sum_{(s)} \sum_{\text{edges}} (d_i \cdot d_j)^{-1}(s) $$

Variants of Modified Zagreb complexity indices

$$ {}^{m}TM_1^{*} = \sum_{(s)} \sum_{\text{vertices}} d_i^{*\,-2}(s) $$

$$ {}^{m}TM_2^{*} = \sum_{(s)} \sum_{\text{edges}} (d_i^{*} \cdot d_j^{*})^{-1}(s) $$



$^{m}TM_1 = 15.57$

$^{m}TM_2 = 6.75$

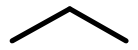
$^{m}TM_1^* = 29.72$

$^{m}TM_2^* = 14.17$

Application

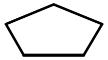
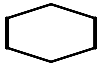
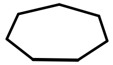
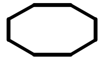
- Note some criteria for complexity indices
- CI indices should increase (or decrease) with
  - Molecular size
  - Branching
  - Cyclicity
  - And should be sensitive to symmetry (optional)

Chains

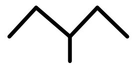
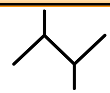
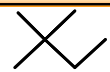
IK #									
	A	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**
M_1	2	6	10	14	18	22	26	30	34
M_2	1	4	8	12	16	20	24	28	32
${}^mM_1$	2	2.25	2.5	2.75	3	3.25	3.5	3.75	4
${}^mM_2$	1	1	1.25	1.5	1.75	2	2.25	2.5	2.75
TM_1	4	22	56	110	188	294	432	606	820
$TM_1{}^*$	2	10	28	60	110	182	280	408	570
TM_2	1	8	28	64	120	200	308	448	624
$TM_2{}^*$	1	6	19	44	85	146	231	344	489
${}^mTM_1$	4	7	11	16.25	23	31.50	42	54.75	70
${}^mTM_1{}^*$	2	6.25	13	22.50	35	50.75	70	93	120
${}^mTM_2$	1	2	4	7	11.25	17	24.50	34	45.75
${}^mTM_2{}^*$	1	3	6.25	11	17.50	26	36.75	50	66
twc	2	10	32	88	222	536	1254	2878	6500
N_T	3	6	10	15	21	28	36	45	55

Tests: total walk count twc (Rücker, Rücker, 2000)
Total number of all connected subgraphs N_T (Bonchev, 1997)

Cycles

I K #	 J	 K	 L	 M	 N	 O
$M_1 = M_2$	12	16	20	24	28	32
${}^mM_1$	0.75	1	1.25	1.5	1.75	2
${}^mM_2$	0.75	1	1.25	1.5	1.75	2
TM_1	84	176	320	528	812	118
$TM_1{}^*$	36	88	180	324	532	816
TM_2	48	112	220	384	616	928
$TM_2{}^*$	27	68	145	270	455	712
${}^mTM_1$	5.25	11	20	33	50.75	74
${}^mTM_1{}^*$	13.5	28	48.75	76.5	112	156
${}^mTM_2$	3	7	13.75	24	38.5	58
${}^mTM_2{}^*$	6.75	14	25	40.5	61.25	88
N_T	10	17	26	37	50	65
t w c	18	56	150	372	882	2032

Hexane trees

IK #	 I	 II	 III	 IV	 V
M_1	18	20	20	22	24
M_2	16	18	19	21	22
$^mM_1$	3	3.61	3.61	4.22	4.31
$^mM_2$	1.75	1.58	1.67	1.44	1.37
TM_1	188	277	300	404	505
TM_1^*	110	146	158	196	222
TM_2	120	172	199	264	290
TM_2^*	85	114	125	156	173
$^mTM_1$	23	33.53	35	48.44	55
$^mTM_1^*$	35	44.33	47.44	57.39	64.15
$^mTM_2$	11.25	12.83	14	15.11	15.50
$^mTM_2^*$	17.50	20.67	21.83	24.78	26.12
twc	222	268	284	330	370
N_T	21	24	25	28	30

Overall Zagreb indices

$${}^{s}OM_1 = \sum_{s} \sum_{i \in V} d(i)d(i)\ (s) = TM_1$$

$${}^{s}OM_2 = \sum_{s} \prod_{ij \in E} d(i)d(j)\ (s) \neq TM_2$$

D. Bonchev, N. Trinajstic, SAR QSAR Environ. Res. **12** (2001) 213.

Zagreb Matrices

$$M_1 = \sum_{\text{vertices}} [\, \mathbf{ZM} \,]_{ii}$$

$$M_2 = \sum_{\text{edges}} [\, \mathbf{ZM} \,]_{ij}$$

Zagreb matrices

$$[\mathbf{ZM}]_{ij} = \begin{cases} d(i)\, d(i) & \text{if} \quad i = j \\ d(i)\, d(j) & \text{if vertices } i \text{ and } j \text{ are adjacent} \\ 0 & \text{otherwise} \end{cases}$$

Zagreb matrices of weighted graphs

$$
[\mathbf{ZM}]_{ij} = \begin{cases} d(i)\,d(i) & \text{if } i = j \\ d(i)\,d(i)\,w^2 & \text{if the vertex } i \text{ is weighted} \\ d(i)\,d(j) & \text{if vertices } i \text{ and } j \text{ are adjacent} \\ d(i)\,d(j)\,w & \text{if one vertex in the edge } i\text{-}j \text{ is weighted} \\ 0 & \text{otherwise} \end{cases}
$$

Example

$$\mathbf{ZM} = \begin{bmatrix} 1 & 3 & 0 & 0 & 0 & 0 \\ 3 & 9 & 6w & 0 & 0 & 3 \\ 0 & 6w & 4w^2 & 4w & 0 & 0 \\ 0 & 0 & 4w & 4 & 2 & 0 \\ 0 & 0 & 0 & 2 & 1 & 0 \\ 0 & 3 & 0 & 0 & 0 & 1 \end{bmatrix}$$

w = weighted parameter

Some properties of Zagreb indices

$$M_1/V \leq M_2/E$$

Pierre Hansen valid for monocyclic graphs - Caporossi *et al.* (2010)

$$M_1/V = M_2/E = 4$$

all monocyclic graphs, Vukičević, Graovac, Hansen (2007, 2008)

$${}^{v}M_1/V \leq {}^{v}M_2/E$$

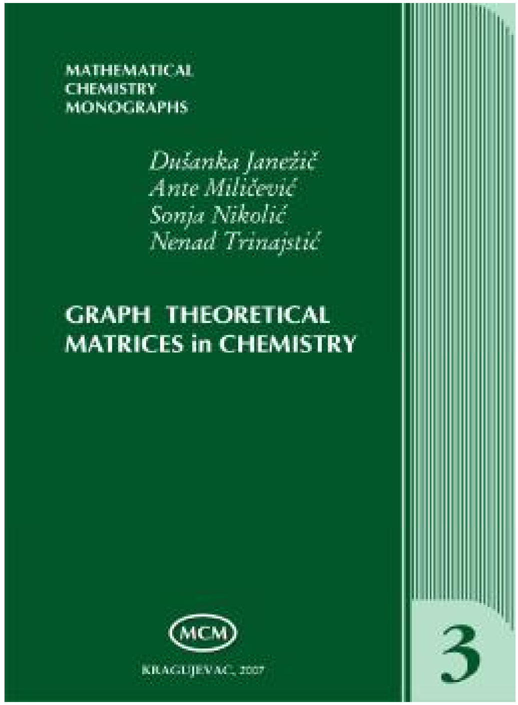
all graphs with $v \in [0,1/2]$, Vukičević (2007)
all chemical graphs with $v \in [0,1]$
all graphs $v \in [-\infty, 0]$, Huang *et al*. (2010)
all monocyclic graphs $v \in [1,+\infty]$, Zhang, Liu (2010)

Perspectives

Apparently, Zagreb indices as well as the family of all connectivity indices represent a mathematically-attractive invariants. Thus, we expect many more studies on these indices and look forward to further development of this area of matematical chemistry.

X. Li and I. Gutman, *Mathematical Aspects of Randić-type Molecular Structure Descriptors*, University of Kragujevac, Kragujevac, Serbia, 2006.

MATHEMATICAL CHEMISTRY MONOGRAPHS, No. 3



Publisher: University of Kragujevac and Faculty of Science Kragujevac
http://www.pmf.kg.ac.yu/match/mcm3.htm

D. Janezic, A. Milicevic, S. Nikolic, and N. Trinajstic

Graph-Theoretical Matrices in Chemistry

2007, VI + 205 pp., Hardcover, ISBN: 86-81829-72-6

Eighth International Conference of Computational Methods in Sciences and Engineering - ICCMSE 2010
Psalidi, Kos, Greece, 03-08 October 2010
http://www.iccmse.org/

Symposium 4

Title: **8th Symposium on Mathematical Chemistry**

Organizer: **Dr. Sonja Nikolic, The Rugjer Boskovic Institute, Zagreb, Croatia**

Enquiries and contributions to E-mail: sonja@irb.hr

Scope and Topics: **Graph theory development, studying complexity of molecules and reactions, development of molecular descriptors, development of mathematical invariants of chemical and biological systems, modelling structure-property-activity, advanced chemometrics and chemoinformatics algorithms as the tools required by chemical engineers and analytical chemists to explore their data and build predictive models.**