

Appendix 5.

Structural interpretation of contribution of matrix elements to the best combined topological index for the van der Waals constant a_0 represented here by Tc^2/Pc .

The best observed topological index for Tc^2/Pc derived from six elements of the Universal matrix is presented in Table A5 and Figure A5.

Table A5. Best observed correlation to Tc^2/Pc of combination of six matrix elements and the contributions of individual matrix elements.

$u_{ij} \times k_{ij}$	R	IC (%)
$u_{64}(-3.2, -1.19, 1.10) \times -0.04619$	0.747	37.9
$u_{75}(0.35, -0.65, -2.8) \times 0.74585$	0.661	28.2
$u_{54}(-0.48, 0.27, -0.014) \times -0.109594$	0.591	21.8
$u_{72}(-1.19, -0.92, 0.28) \times -0.090734$	-0.326	6.2
$u_{52}(5.1, 2.2, -2.5) \times 6.2E-05$	0.133	1.0
$u_{32}(-3.2, 2.4, 1^c) \times -0.00757$	0.085	0.4
$\sum u_{ij} \times k_{ij}$	0.999	95.5

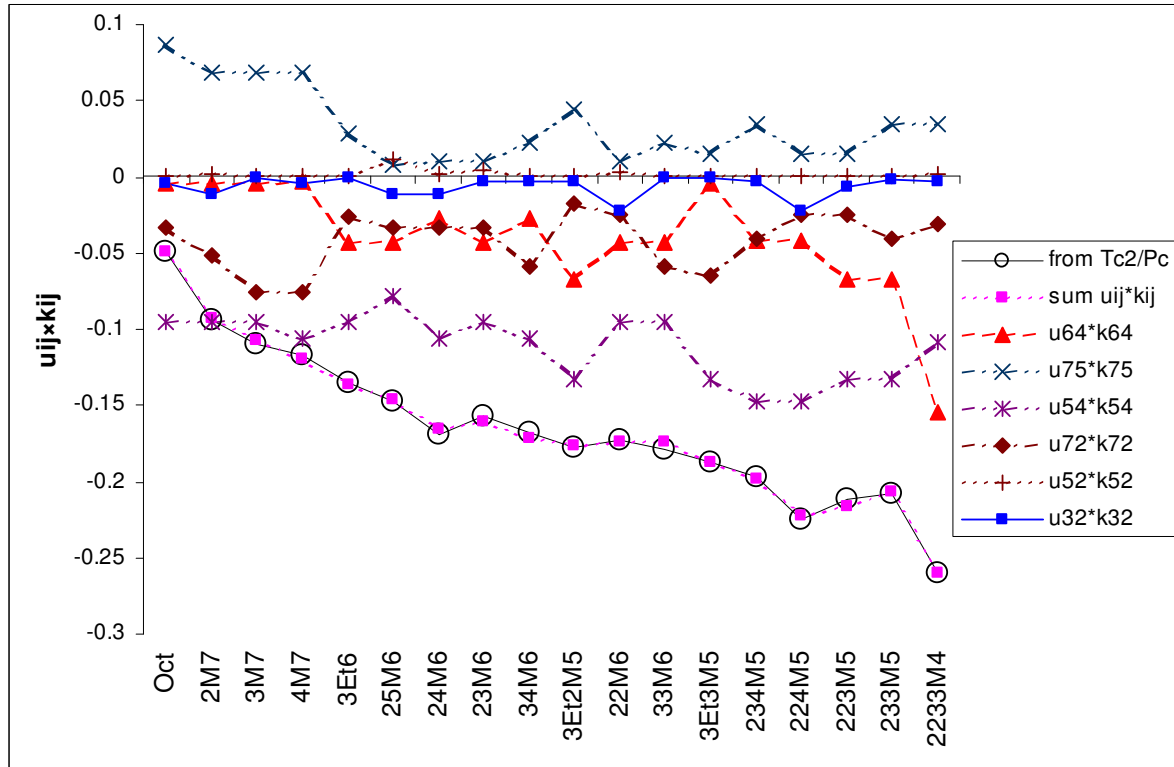


Figure A5. Contribution of particular matrix elements (u_{64} , u_{75} , u_{54} , u_{72} , u_{52} , and u_{32}) to the optimized combined topological index derived from them in the case of Tc^2/Pc .

Individual matrix elements in this combination contribute different contributions to the combined effect. Positive in value are the contributions of the matrix elements $u_{75}(0.35, -0.65, -2.8) \times k_{75}$ and $u_{52}(5.1, 2.2, -2.5) \times k_{52}$, whereas negative in value are the contributions of $u_{64}(-3.2, -1.19, 1.10) \times k_{64}$, $u_{54}(-0.48, 0.27, -0.014) \times k_{54}$, $u_{72}(-1.19, -0.92, 0.28) \times k_{72}$, and $u_{32}(-3.2, 2.4, 1^c) \times k_{32}$. The sign of the contribution depends on the sign of factor k_{ij} .

$u_{64}(-3.2, -1.19, 1.10)$,

The matrix element $u_{64}(-3.2, -1.19, 1.10)$, which presents the most overall information to the combined index, presents the least to 4M7, little to Oct, 2M7, 3M7, and 3Et3M5, more to 24M7 and 34M6, additionally more to 224M5 and 234M5, followed by 3Et6, 25M6, 23M6, 33M6, 22M6, then by 233M5, 223M5, 3Et2M5 and the most to 2233M4. If we group the octane isomers by the substitution patterns, we observe that the contribution of the matrix element u_{64} to the best combined index for Tc^2/Pc is:

2233M4 ($CH_3-\gamma-CH_3$) > 233M5, 223M5, 3Et2M5 ($CH_3-\gamma-CH_2$) > 33M6, 22M6, 23M6, 25M6, 3Et6 ($CH_3-\beta-CH_2$) > 224M5, 234M5 ($CH_3-\gamma-CH$) > 34M6, 24M6 ($CH_3-\beta-CH$) > 3Et3M5, 3M7, 2M7, Oct ($CH_2-\beta-CH_2$) > 4M7 ($CH_2-\beta-CH$)

The exponent of -3.2 on the degree of vertex No. 6 indicates that the importance of its degree is high. However, the degree of vertex No. 6 is equal to 2 only at Oct, 2M7, 3M7, 4M7, and 3Et3M5, to which u_{64} contributes the least. In all other cases it is equal to one, so this exponent draws a distinction between the mentioned octane isomers and the other ones.

The exponent of -1.19 on the degree of vertex No. 4 indicates the importance of its degree. So, it causes $4M7 < Oct$, $2M7$, $3M7$, $3Et6$; and also $24M7$, $34M6 < 25M6$, $23M6$, $33M6$, $22M6$; as well as $224M5$, $234M5 < 233M5$, $223M5$.

The exponent of 1.10 on the distance values indicates that the importance of the distance between the vertex No. 6 and No. 4 is little higher than its original values. It draws a distinction between 2233M4, 233M, 223M5, 3Et2M5, 224M5, 234M5 and other octane isomers.

$u_{75}(0.35, -0.65, -2.8)$

The matrix element $u_{75}(0.35, -0.65, -2.8)$ contributes as in the case of MON the most to isomers Oct, 2M7, 3M7, and 4M7. At Tc^2/Pc they are followed by 3Et2M5 and some highly branched octane isomers, and it contributes little to other octanes having two branches:

Oct ($CH_2-\beta-CH_2$) > 2M7, 3M7, 4M7 ($CH_3-\beta-CH_2$) > 3Et2M5 ($CH_2-\gamma-CH_3$) > 2233M4, 233M5, 234M5 ($CH_3-\gamma-CH_3$) > 3Et6 ($CH_2-\gamma-CH_2$) > 34M6, 33M6 ($CH_3-\gamma-CH_2$) > 223M5, 224M5, 3Et3M5 ($CH_3-\delta-CH_3$) > 22M6, 23M6, 24M6 ($CH_3-\delta-CH_2$) > 25M6 ($CH_3-\delta-CH$).

The exponent on the vertex No. 7 causes some contribution to Oct, 3Et6, 3Et2M6 and nothing to other isomers.

The exponent on the value of vertex No. 5 puts the octane isomers into three different groups: 3Et2M5, 3Et3M5, 223M5, 224M5, 233M5, 234M5, 2233M4 > Oct, 2M7, 3M7, 4M7, 3Et6, 23M6, 24M6, 34M6, 22M6, 33M6 > 25M6.

The exponent on the distance puts the octane isomers into three groups: Oct, 2M7, 3M7, 4M7 > 3Et2M5, 2233M4, 233M5, 234M5, 3Et6, 34M6, 33M6 > 223M5, 224M5, 3Et3M5, 22M6, 23M6, 24M6, 25M6.

$u_{54}(-0.48, 0.27, -0.014)$

The matrix element $u_{54}(-0.48, 0.27, -0.014)$ contributes the most to the "numerical volume" of the combined index, especially at higher branched isomers including 3Et2M5 and 3Et3M5:

234M5, 224M5 ($CH_3-\alpha-CH$) > 3Et2M5, 3Et3M5, 223M5, 233M5 ($CH_3-\alpha-CH_2$) > 2233M4 ($CH_3-\gamma-CH_3$) > 4M7, 24M6, 34M6 ($CH_2-\alpha-CH$) > Oct, 2M7, 3M7, 3Et6, 22M6, 33M6, 23M6 ($CH_2-\alpha-CH_2$) > 25M6 ($CH-\alpha-CH_2$)

Among the isomers having equal number of branches, it contributes the most at isomers having a branch in position No. 4.

The exponent of -0.48 on the value of vertex No. 5 puts the octane isomers into three different groups: 3Et2M5, 3Et3M5, 223M5, 224M5, 233M5, 234M5, 2233M4 > Oct, 2M7, 3M7, 4M7, 3Et6, 23M6, 24M6, 34M6, 22M6, 33M6 > 25M6.

The exponent of 0.27 on the degree of vertex No. 4 indicates that the importance of its degree is not high but in spite of that it separates the octane isomers into three groups: 4M7, 24M7, 34M6, 224M5, 234M5 > Oct, 2M7, 3M7, 3Et3M5, 3Et6, 25M6, 23M6, 33M6, 22M6, 2233M5, 223M5, 3Et2M5 > 2233M4.

The exponent of -0.014 , to which the distance between vertices No. 5 and No. 4 is raised, causes a slightly higher contribution of $(\text{CH}_3\text{-}\alpha\text{-CH})$ and $(\text{CH}_3\text{-}\alpha\text{-CH}_2)$ groups than of $(\text{CH}_3\text{-}\gamma\text{-CH}_3)$ groups in the structure of octanes.

$u_{72}(-1.19, -0.92, 0.28)$

The matrix element $u_{72}(-1.19, -0.92, 0.28)$ contributes some fine-tuning to the combination of matrix elements contributing to:

3M7, 4M7 ($\text{CH}_3\text{-}\varepsilon\text{-CH}_2$) > 3Et3M5 ($\text{CH}_3\text{-}\gamma\text{-CH}_2$) > 34M6, 33M6 ($\text{CH}_3\text{-}\beta\text{-CH}_2$) > 2M7 ($\text{CH}_3\text{-}\varepsilon\text{-CH}$) > 234M5, 233M5 ($\text{CH}_3\text{-}\beta\text{-CH}$) > 25M6, 24M6, 23M6 ($\text{CH}_3\text{-}\alpha\text{-CH}$) > Oct ($\text{CH}_2\text{-}\varepsilon\text{-CH}_2$) > 2233M4 ($\text{CH}_3\text{-}\beta\text{-Cq}$) > 3Et6 ($\text{CH}_2\text{-}\beta\text{-CH}_2$) > 22M6, 224M5, 223M5 ($\text{CH}_3\text{-}\alpha\text{-Cq}$) > 3Et2M5 ($\text{CH}_2\text{-}\beta\text{-CH}$)

Vertex No. 7 contributes to other octane isomers more than to Oct, 3Et6, and 3Et2M6. Vertex No. 2 contributes to Oct, 3M7, 4M7, 3Et6, 34M6, 33M6, 3Et3M6 > 2M7, 25M6, 24M6, 23M6, 3Et2M5, 234M5, 233M5 > 22M6, 224M6, 223M6, 2233M4.

The distance between vertices No. 7 and No. 2 contributes to Oct, 2M7, 3M7, 4M7 > 3Et3M5 > 3Et6, 3Et2M5, 34M6, 33M6, 234M5, 233M5, 2233M4 > 22M6, 25M6, 24M6, 23M6, 224M5, 223M5.

$u_{52}(5.1, 2.2, -2.5)$

The matrix element $u_{52}(5.1, 2.2, -2.5)$ contributes some fine-tuning to the combination of matrix elements contributing to 25M6 ($\text{CH-}\gamma\text{-CH}$) > 23M6 ($\text{CH}_2\text{-}\gamma\text{-CH}$) > 22M6 ($\text{CH}_2\text{-}\gamma\text{-Cq}$) > 24M6, 2M7 ($\text{CH}_2\text{-}\gamma\text{-CH}$) > 2233M4 ($\text{CH}_3\text{-}\alpha\text{-Cq}$) > 33M6, 34M6, 3Et6, 4M7, 3M7, Oct ($\text{CH}_2\text{-}\gamma\text{-CH}_2$) > 223M5, 224M5 ($\text{CH}_2\text{-}\gamma\text{-Cq}$) > 3Et2M5, 233M5, 234M5 ($\text{CH}_3\text{-}\gamma\text{-CH}$) > 3Et3M5 ($\text{CH}_3\text{-}\gamma\text{-CH}_2$), which results in 25M6 > 23M6 > 22M6 > 24M6, 2M7 > 2233M4 and very little to other octane isomers.

The exponent on the degree of vertex No. 5 puts the octane isomers in three different groups: Oct, 2M7, 3M7, 4M7, 3Et6, 23M6, 24M6, 34M6, 22M6, 33M6 >> 25M6 >> 3Et2M5, 3Et3M5, 223M5, 224M5, 233M5, 234M5, 2233M4.

The exponent on the degree of vertex No. 2 puts the octane isomers into three different groups: 22M6, 224M6, 223M6, 2233M4 > 2M7, 25M6, 24M6, 23M6, 3Et2M5, 234M5, 233M5 > Oct, 3M7, 4M7, 3Et6, 34M6, 33M6, 3Et3M6.

The exponent on the distance between vertices No. 5 and No. 2 puts the octane isomers into four different groups: 22M6, 25M6, 24M6, 23M6, 224M5, 223M5 > 3Et6, 3Et2M5, 34M6, 33M6, 234M5, 233M5, 2233M4 > 3Et3M5 > 3M7, 4M7, 2M7, Oct

$u_{32}(-3.2, 2.4, 1^\circ)$

The matrix element $u_{32}(-3.2, 2.4, 1^\circ)$ adds some additional fine-tuning to the combination of matrix elements, contributing to 22M6, 224M5 ($\text{CH}_2\text{-}\alpha\text{-Cq}$) > 2M7, 25M6, 24M6 ($\text{CH}_2\text{-}\alpha\text{-CH}$) > 223M5 ($\text{CH-}\alpha\text{-Cq}$) > Oct, 4M7 ($\text{CH}_2\text{-}\alpha\text{-CH}_2$) > 23M6, 3Et2M, 234M5 ($\text{CH-}\alpha\text{-CH}$) = 34M6 ($\text{CH-}\alpha\text{-CH}_2$) > 2233M4 ($\text{Cq-}\alpha\text{-Cq}$) > 233M5 ($\text{Cq-}\alpha\text{-CH}$) > 3M7, 3Et6 ($\text{CH-}\alpha\text{-CH}_2$) > 33M6, 3Et3M5 ($\text{Cq-}\alpha\text{-CH}_2$) resulting in 22M6, 224M5 > 2M7, 25M6, 24M6 > 223M5, and much less to the index values for other isomers. Overall, it contributes the most at isomers having a branch in position No. 2 as a consequence of the fact that the vertex degree in

position No. 2 is raised to the exponent 2.4, whereas the vertex degree in position No. 3 is raised to the exponent -3.2 . The distance between vertices No. 3 and No. 2 is in all cases equal to one, so it doesn't contribute anything.