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MODELING MOLAR REFRACTION AND CHROMATOGRAPHIC RETENTION BY SZEGED INDICES

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ABSTRACT. Modeling the molar refraction and the chromatographic retention by using Szeged topological indices as molecular descriptors, is presented.

INTRODUCTION

Physico-chemical properties, such as the boiling point, molar refraction, critical pressure, viscosity, chromatographic retention, etc. are rather simple experimental available properties of chemical compounds. They are tabulated and may be used e.g., in projecting industrial instalations. Sometimes, it happends that a given compound is toxic, or dangereus or simply not available. In such conditions, it is of interest to have a theoretical tool, say an equation, that can help one in obtaining a desired parameter by structure-related calculations. In this respect, the topological indices (i.e., single numbers encoding the topology of chemical structures) were widely used in the last decade.

In the present paper, we used the Szeged indices as molecular descriptors in modeling the molar refraction and the chromatographic retention of some organo-phosphoruc compounds.

SZEGED TOPOLOGICAL INDICES

Gutman has introduced the *Szeged index*,[12] *SZ*, as

$$I_{e/p} = \sum_e N_{i,(i,j)} N_{j,(i,j)} \quad (1)$$

where the quantities $N_{i,(i,j)}$ and $N_{j,(i,j)}$ represent the cardinality of the vertex sets lying closer to i and to j, respectively and are defined by

$$N_{i,(i,j)} = \left| \{ v \mid v \in V(G);\ D_{iv} < D_{jv} \} \right| \quad (2)$$

$$N_{j,(i,j)} = \left| \{ v \mid v \in V(G);\ D_{jv} < D_{iv} \} \right| \quad (3)$$

In the above relations, V(G) denotes the set of vertices in a connected graph and D_{iv} , D_{jv} are the topological distances (i.e., the number of edges on the shortest path) joining the vertices i and j , respectively, with a vertex v. Vertices equidistant to i and j are not counted.

When defined on edge, (i.e., (i,j) is an edge, e), I_e is just the classical *Szeged index*,[12] in the following symbolizsd by SZ_e . When defined on path, ((i,j) is a path, p), I_p is the *hyper-Szeged* index,[14] SZ_p.

The Szeged unsymmetric matrix, $\mathbf{SZ}_u$, was defined by Diudea et al.[14,18] by analogy to the Cluj matrix,[15-17] $\mathbf{CJ}_u$,

$$[\mathbf{SZ}_u]_{ij} = N_{i,(i,j)} \quad (4)$$

where $N_{i,(i,j)}$ has the meaning given by eq. 2. The diagonal entries are zero. $\mathbf{SZ}_u$ is a square array of dimensions **N**x**N**, in general unsymmetric. It allows the calculation of two Szeged indices, by

$$SZ_{e/p} = \sum_{e/p} [\mathbf{SZ}_u]_{ij} [\mathbf{SZ}_u]_{ji} \quad (5)$$

As an extension to $SZ_{\mathbf{u}}$, *Szeged property matrices*[19-21] have been defined

$$[\mathbf{SZ}_u\mathbf{P}]_{ij} = P_{i,(i,j)} \quad (6)$$

$$P_{i,(i,j)} = f(P_v) \mid v \in V(G);\ D_{iv} < D_{jv} \mid \quad (7)$$

$$f(P_v) = m \sum_v P_v ; \quad (8)$$

case : (a) $P_v = 1$; $m = 1$ (classical SZ_u matrix)

(b) $P_v = \sum_v A_v$; $m = 1/12$ (SZ_uA matrix)

$f(P_v) = (\prod_v P_v)^{1/v}$; $P_v = X_v$ (group electronegativity) (SZ_uX matrix) (9)

Entries in a Szeged property matrix are defined by a function $\mathbf{f(P_v)}$, evaluated on the vertices v which obey the Szeged index condition (see eq 12). The set of such vertices can be viewed as a fragment (i.e., a subgraph) since a molecular graph is alwais a connected one. Two types of $\mathbf{f(P_v)}$ are here proposed: an additive and a multiplicative one. Only two cases of the additive function are here considered:

(a) $\mathbf{P_v = 1}$ (i.e., the cardinality) and the factor **m = 1**; it is just the case of classical $SZ_{\mathbf{u}}$ matrix.

(b) $\mathbf{P_v = \sum_v A_v}$; $\mathbf{m = 1/12}$; $\mathbf{A_v}$ is the atomic mass and the matrix is $SZ_{\mathbf{u}}A$. The factor **m** indicates that $\mathbf{f(P_v)}$ is a a fragmental mass, relative to the carbon atomic mass.

The multiplicative function was used in calculating group electronegativities, $\mathbf{X_v}$, like **EC** (Sanderson-type group electronegativities[22]) for heteroatoms and fragments.

Indices are calculated on these matrices by the general relation

$$I_{e/p} = \sum_{e/p} [\mathbf{SZ}_u\mathbf{P}]_{ij} [\mathbf{SZ}_u\mathbf{P}]_{ji} \ ;\ I = SZ;\ SZA;\ SZX \quad (10)$$

MODELING THE MOLECULAR REFRACTION

In correlating tests, a multivariable regression equation is used [34]:

$$Y = a + \sum_i b_i X_i \quad (11)$$

where a and b_i are regression coefficients, Y is the modeled property and X_i independent variable (in paricular, topological indices). A satisfactory single variable regression is however a happy case. The quality of such an equation is

expressed by the following statistics: r
(correlation coefficient), s (standard error), v(%) (the percent of variance) and F (Fischer ratio).

Molar refraction, MR, is defined as

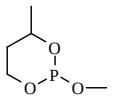
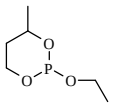
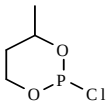
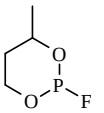
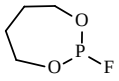
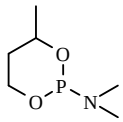
$$MR = \frac{n-1}{n+2}\frac{M}{d} \qquad (12)$$

where n is the refraction index, M is the molecular mass and d is the density. It is obvious that Mr is parallel to the molar volume. An electronic dependence is included in the refraction index.

A set of 10 pesticides, cyclic organo-phosphorus compounds (Table 1), was taken in this study. Statistics are presented in Table 2.

Table 1.

Szeged Indices and Molar Refractions for cyclic organo-phosphorus compounds.

NO	Graph	SZ_p	SZ_e	SZ_pA	SZ_eA	SZ_pX	SZ_eX	MR
1		481	146	880.403	265.743	50.541	12.615	35.808
2		751	193	1305.576	338.139	58.590	13.165	40.524
3		182	78	473.205	201.288	34.305	11.525	30.030
4		296	108	732.976	2653743	43.281	12.331	34.911
5		296	108	593.069	214.181	64.456	18.480	29.222
6		306	88	606.007	172.535	63.671	18.480	31.636
7		739	186	1278.347	323.139	56.675	12.737	43.005

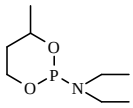
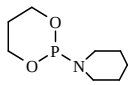
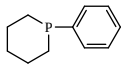
8		1518	290	2488.993	481.722	77.717	14.303	52.029
9		1684	360	2732.333	581.472	79.674	15.691	49.971
10		1684	360	2428.389	517.882	72.630	14.344	58.323

Table 2

Statistics of correlation equations: $Y = a + \sum b_i X_i$, for the set of Table 1

No	**X_i**	**b_i**	**a**	**r**	**s**	**v(%)**	**F**
1	SZ_p	0.016	27.851	0.9634	2.868	7.074	103.242
2	SZ_e	0.089	23.479	0.9587	3.041	7.500	90.961
3	SZ_pA	0.011	25.855	0.9487	3.381	8.338	72.079
4	SZ_eA	0.066	18.349	0.9370	3.736	9.214	57.575
5	SZ_pX	0.481	11.606	0.6997	7.641	18.846	7.673
6	SZ_eX	-0.467	47.248	0.1135	10.626	26.208	0.104
7	SZ_p SZ_pX	0.019 -0.157	34.882	0.9727	2.651	6.539	61.604
8	SZp SZ_eX	0.016 -0.631	36.821	0.9755	2.516	6.206	68.762

From Table 2 one can see that the molar refraction of these compounds is well modeled by two descriptors: one is topological (SZ_p) and anothe one is electronic (SZeX- the index waighted by electronegativity – entry 8, Table 2), the variance of estimation being about 6%. This result is in agreement with the meaning of formula 12.

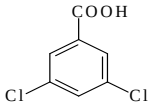
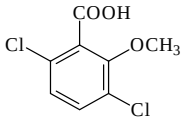
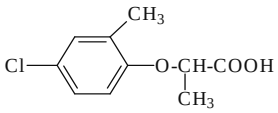
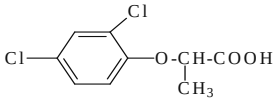
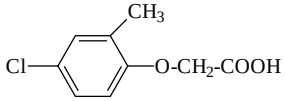
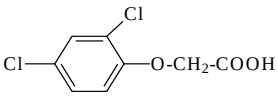
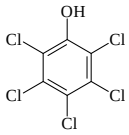
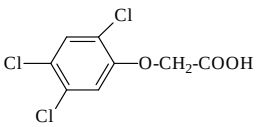
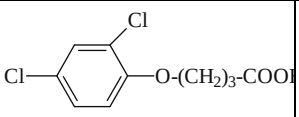
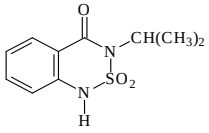
MODELING THE CHROMATOGRAPHIC RETENTION

The retention chromatographic index, I_{CHR}, is a measure of the interaction between a given compound and two phases: a mobile phase (i.e., the eluent) and a stationary one. This interaction is function of more than one factor, the polarity, lipophylicity and size included. These factors are joined in a "global" molecular property, that is the chromatographic index. It is easily seen that the values of I_{CHR} vary with varying the chromatographic systems, pressure and temperature. This is the reason that, in correlating studies, values I_{CHR} from a single experient are requested.

A set of 10 herbicides (Table 3) was modeled by the Szeged indices. The statistics are given in Table 4.

Table 3.

Retention chromatographic index, I_{chr} , and Szeged indices for some organo-phosphorus herbicides

No.	Compound	Structure	I_{CHR}+	SZe	SZeA	SZpE	SZeE
1	Acid 3,5-dichlorbenzoic		7.4	236	526.677	79.026	15.956
2	DICAMBA		9.8	340	725.736	110.788	18.614
3	MCPP (MECOPROP)		10.3	441	775.545	118.200	18.373
4	DICHLORPROP		11.0	441	923.316	124.570	19.535
5	MCPA		11.5	378	670.715	104.590	17.620
6	2,4-D		11.8	378	806.385	110.576	18.810
7	Pentachloro-phenol		12.4	282	1050.444	98.619	18.324
8	2,4,5-T		14.3	453	1121.528	133.206	20.991
9	2,4-DB		14.6	572	1161.483	141.009	20.745
10	BENTAZON		18.5	731	852.472	172.764	24.957

(+) 1995/1996 HP Environmental Solutions Catalog, p. 88.

Table 4

Statistics of correlation: $Y = a + \sum b_i X_i$, for the set in Table 3.

No	X_i	b_i	a	r	s	v(%)	F
1	SZ_pX	0.1068	-0.5862	0.8982	1.428	11.743	33.381
2	SZ_eX	1.1797	-10.7168	0.9388	1.118	9.198	57.460
3	SZeX SZeA	1.0678 0.0026	-10.7940	0.9506	1.0776	8.862	32.837

Table 4 shows that the retention chromatographic index depends both on the size (through the mass weighted index, SZeA) and electronic characteristics (by SZeX). The correlation is satisfactory (r= 0.951, v < 9% - entry 3, Table 4).

Szeged indices have proved here their ability in modeling physico-chemical properties of organo-phosphorus compounds.

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