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Topological Organic Chemistry. 4.[1] Graph Theory, Matrix Permanents, and Topological Indices of Alkanes

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The permanents of the distance matrices that describe the structures of alkanes were calculated and demonstrated to be useful as molecular topological indices. Additionally, the easily derived products of the row sums of the distance matrices were observed also to be useful as molecular topological indices.

INTRODUCTION

Weiner,[2] Hosoya,[3] and Randić[4] are among many who have devised various ways of utilizing graph theory to numerically characterize chemical structures. Rouvray[5] has summarized numerous techniques for calculating topological indices. An earlier paper[6] of this series reported on the use of matrix determinants as potential topological indices. It was a project, also studied by Knop et al.,[7] that met with only partial success. This paper further extends the use of structure-descriptive matrices of alkanes as sources of single-sum numbers that serve as descriptors or codes of alkane structures; it reports the results of experiments involving permanents, matrix functions related to the determinants.

The adjacency and distance matrices that describe the structures of molecular graphs are square ($n \times n$) matrices. If $M = (a_{ij})$ is any $n \times n$ matrix, the permanent of M is defined by

$$\text{per }(M) = \sum_{\sigma} a_{1\sigma(1)} a_{2\sigma(2)} \cdots a_{n\sigma(n)}$$

where the summation extends over all one-to-one functions from $\{1, ..., n\}$ to $\{1, ..., n\}$. The sequence $a_{1\sigma(1)}, ..., a_{n\sigma(n)}$ is called a diagonal of M, and the product $a_{1\sigma(1)} \cdots a_{n\sigma(n)}$ is a diagonal

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product of M. Thus, the permanent of M is the sum of all the diagonal products of M.[8]

The definition of the permanent of M contrasts interestingly with the definition of the determinant of M:

$$\det(M) = \sum_{\sigma} \text{sgn}(\sigma)\, a_{1\sigma(1)} a_{2\sigma(2)} \cdots a_{n\sigma(n)}$$

The two expressions differ only in the omission of the ± sign of the permutation in the expression for the permanent. Indeed, the permanent is frequently referred to as the plus, or positive, determinant. Therefore, the same Laplace expansion, which serves for the calculation of a determinant, is even more easily applied to the computation of a permanent, since no sign changes need be injected into the Laplace expansion. Experimentation demonstrated that the permanent of a square matrix was an invariant value, independent of the number sequence of the graph vertices. Trinajstić[9] discussed the permanent of the adjacency matrix and outlined several of its properties.

COMPUTATIONS

Molecular graphs, hydrogen-suppressed and with the interatomic carbon-carbon edge counts set at unity, were derived from the alkanes listed in Table I. The matrix permanents were computed on a Data General MV/7800XP minicomputer

Table I. Topological Indices Derived from the Permanents and Related Functions of the Adjacency and Distance Matrices of Representative C_1-C_{15} Alkanes

no.	compound	PRS (A) index	per (D) index	PRS (D) index	SDDP (D) index	PDDSΔ (D) index	boiling points, °C		
							obsd	per (D) index calcd[a]	PRS (D) index calcd[b]
1	methane						-164		
2	ethane	1	1	1	2	1	-88.6	-103.7	-119.5
3	propane	2	4	18	6	3	-42	-41.3	-36.5
4	butane	4	64	576	18	24	-0.5	4.3	3.6
5	2-methylpropane	3	36	375	14	15	-11.7	-3.4	-0.6
6	pentane	8	1152	29400	66	300	36.1	36.9	37.1
7	2-methylbutane	6	656	17280	42	192	27.9	31.2	33.0
8	2,2-dimethylpropane	4	352	9604	30	105	9.5	24.6	28.4
9	hexane	16	34372	2205225	304	6480	68.7	67.5	67.1
10	3-methylpentane	12	15236	1054053	150	3240	63.2	60.7	62.4
11	2-methylpentane	12	19856	1290240	158	4356	60.3	62.9	63.7
12	2,2-dimethylbutane	8	8272	576000	90	1920	49.7	55.4	58.4
13	2,3-dimethylbutane	9	11028	717409	146	2016	54.3	57.9	59.8
14	heptane	32	1335008	228953088	1728	185220	98.4	95.2	94.8
15	2-methylhexane	24	809280	137332800	618	161280	90	91.7	91.9
16	3-methylhexane	24	573408	102702600	650	117504	92	89.2	90.2
17	2,2-dimethylpentane	16	322644	57788640	350	60840	79.2	85.0	87.0
18	3-ethylpentane	24	413904	76406976	582	66560	93.5	86.8	88.6
19	2,2,3-trimethylbutane	12	179040	31004064	218	35640	80.9	80.5	83.3
20	2,3-dimethylpentane	18	328512	57834000	374	58240	89.8	85.1	87.0
21	3,3-dimethylpentane	16	226528	41879552	318	41580	86	82.3	85.1
22	2,4-dimethylpentane	18	479936	79928560	620	65280	80.5	87.9	88.8
23	octane	64	69599744	31473598464	11700	7741440	125.7	121.4	120.6
24	4-methylheptane	48	26095936	12539109375	3798	4238325	117.7	115.2	116.0
25	3-methylheptane	48	30414912	14089420800	5078	4847040	119	116.2	116.6
26	2,2-dimethylhexane	32	17862288	8259093375	1350	4082400	106.9	112.8	113.9
27	2,2,3,3-tetramethylbutane	16	37758880	1677721600	1262	393120	106.3	117.6	105.6
28	3-ethyl-2-methylpentane	36	10799632	5122292175	1472	1468800	115.7	109.5	111.4
29	3,3-dimethylhexane	32	10411920	5090039955	1246	2240784	112	109.2	111.4
30	3,4-dimethylhexane	36	12337408	5780865024	2680	1632960	117.7	110.4	112.0
31	2,4-dimethylhexane	36	18658912	8305139115	2522	2138400	109.5	113.0	113.9
32	2,5-dimethylhexane	36	27714064	11754029056	5366	2154240	109.1	115.6	115.7
33	3-ethyl-3-methylpentane	32	7137744	3512320000	1218	1036800	119	106.7	109.5
34	nonane	128	4577345152	5537223659520	91608	396809280	150.8	146.1	145.0
35	decane	256	3.74491×10^{11}	1.21384×10^{15}	812014	2.72160×10^{10}	174.1	169.8	168.3
36	undecane	512	3.71540×10^{13}	3.24469×10^{17}	8026302	2.19158×10^{12}	196.8	192.4	190.6
37	dodecane	1024	4.40247×10^{15}	1.03900×10^{20}	87470486	2.23483×10^{14}	216.3	214.2	212.0
38	tridecane	2048	6.13681×10^{17}	3.92678×10^{22}	1041597714	2.60105×10^{16}	235.4	235.3	232.7
39	tetradecane	4096	9.94440×10^{19}	1.72963×10^{25}	13453226812	4.17183×10^{18}	253.7	255.8	252.8
40	pentadecane	8192	1.85347×10^{22}	8.78327×10^{27}	187303322688	6.64698×10^{20}	270.6	275.6	272.2
41	2,3-dimethyl-6-ethyl-5-isopropyloctane	1944	5.22431×10^{19}	2.32583×10^{25}	61661810	2.84291×10^{18}		253.2	253.7
42	2,6-dimethyl-5-ethyl-3-isopropyloctane	1944	5.96958×10^{19}	2.55378×10^{25}	28357362	4.13599×10^{18}		253.8	254.0

[a] Calculated by using bp, °C $= -103.706 + 80.384 \{\log (\text{per}[D])\}^{1/2}$. [b] Calculated by using bp, °C $= -119.521 + 74.109 \{\log (\text{PRS}[D])\}^{1/2}$.

using the published PERMAN program.[10] Permanents of the adjacency and distance matrices of alkanes 1–8 of Table I were also calculated by application of the Laplace expansion, a cumbersome computation.

Using the early work of Binet[11] and Cauchy,[12] Minc[8] described formulas that afford precise values, or approximations, or bounds of the permanent values of matrices. These methods utilized the products of the matrix row sums, adequately and extensively corrected to afford a precise value or an approximate value of a matrix permanent, depending upon the correction itself. The above observations and the relative simplicity of the calculations provided motivation for determining the products of the row sums (PRS) of the adjacency and distance matrices for those alkanes in Table I. Experimentation demonstrated that these appeared to be invariant. Continued experimentation showed that the products of the column sums (PCS), in view of the diagonal symmetry of the two types of matrices, were of course the same as the PRS values and that the sums of the row (column) products were, obviously, all equal to zero.

In the process of calculating data for the PRS function of the distance matrices, the observation was made that the sums of the horizontal vectors of the matrices reflected priority orders for the vertices of the graphs represented by the matrices; the lower the row sum, the higher that vertex priority. In almost all instances the priorities thus deduced were the same as those CIP values referred to below and in the preceding paper of this series. However, in four instances (**15**, **22**, **25**, and **32**) these priorities (referred to as RS priorities) differed in one element from the CIP priority values. The row sums of these four distance matrices, listed according to the CIP priority calculations and with the single disparate priority for the one vector sum of each compound underlined, are as follow: **15**, 12 <u>11</u> 12 15 17 17 20; **22**, 11 11 <u>10</u> 16 16 16 16; **25**, 14 14 18 <u>16</u> 20 20 24 26; and **32**, 16 16 <u>14</u> <u>14</u> 22 22 22 22. Additionally, compounds **41** and **42** reflected several minor changes in priority, but none was amenable to intuitive priority analysis: **41**, 33 38 <u>36</u> 42 37 50 <u>49</u> <u>49</u> 55 55 <u>54</u> 63 63 <u>62</u> <u>62</u> and **42**, 36 36 <u>35</u> 45 45 <u>43</u> 47 54 56 58 58 58 58 60 67. Because the calculations of the row sums of matrices were simpler operations to execute than the n-iteration calculations that led to CIP priorities, the RS priorities in some instances may be of utility.

With anticipation, but little mathematical justification, a sequence of experiments was executed that evolved out of the

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earlier cited definition of the matrix permanent, "...the permanent of M is the sum of all the diagonal products of M".[8] Scant experimentation with the above concept showed early on that such values were variant. Therefore, all the graph vertices used in such computations were canonically numbered by the Herndon[13] method to attain priority designations for all vertices, described as CIP priorities and expanded upon in the previous paper[1] of this series by a technique which utilized *n*-iterations (where *n* is the number of vertices in the molecular graph) of the adjacency matrix. For the sake of operational uniformity, all graph vertices were always numbered according to the above-referenced CIP canonical priority numbers, regardless of the variant or invariant character of the derived molecular index.

Four variant, diagonal, distance matrix operations were investigated. As a preludium to this portion of the study, the dexter and sinister diagonals were defined as is done in heraldry. That is, the trace (all zeroes) of the distance matrix was designated a dexter diagonal, as were all related parallel diagonals of the matrix. Three operations experimented with were the products of the sinister diagonal sums (PSDS), the sums of the sinister diagonal products (SSDP), and the sums of the dexter diagonal products (SDDP). In this last instance the single values in the upper right and lower left corners of the matrix (a_{1j} and a_{i1}) were included in the SDDP calculations.

A fourth possibility exists. The products of the dexter diagonal sums (PDDS) by definition had values of zeroes in all instances because the sum of each matrix trace (one of the multipliers) was always zero; hence, so also were its products. However, the products of the dexter diagonal sums of the upper or lower identical triangular portions of the symmetrical distance matrix (PDDS Δ) could be evaluated, for the operation then excluded all the zero values that comprise the dexter trace of the matrix. Again, the single value a_{1j} (or a_{i1}) was included in the computations.

RESULTS

Studies with the adjacency matrices of the substances listed in Table I resulted in permanent values of only 0 or 1; 10 compounds (**2, 4, 9, 10, 23, 25, 30, 33, 37,** and **39**) had values of 1. All the normal alkanes of even-carbon atom content, plus a very few symmetrical branched-chain alkanes of even-carbon atom content, were in the above listing. Although it was interesting to observe that the PRS adjacency matrix descriptors of the normal alkanes were in each instance twice the value of the preceding normal alkane, as displayed in column 3 of Table I, as well as seemingly constituting a monotonic series of numbers, the PRS adjacency matrix values were not unique for even this limited sample of alkanes. Studies involving the adjacency matrix were therefore quickly terminated.

The values for the permanents of the distance matrices of the alkanes listed in Table I, column 4, were observed to be apparently invariant, single-sum, unique, and members of a monotonic series of values. The calculated permanent values of those substances with 10 or more carbon atoms in the molecule were so large that the data were recorded as six significant figures to the appropriate power of 10. In a given family of alkane isomers, the straight-chain parent member of the series possessed the greatest permanent, the permanents of the distance matrices decreasing with the apparent increase of molecular intricacy of the branched-chain alkane isomers of the series. The heptane isomers, for example, presented the following order of complexity: **14, 15, 16, 22, 18, 20, 17, 21, 19,** with heptane the least and 2,2,3-trimethylbutane the most complex of the series, an intuitively acceptable sequence. Column 9 lists the predicted boiling points based upon the

distance matrix permanents of the alkanes of Table I; the values reflected a linear relationship described by

$$\text{bp, } ^\circ\text{C} = -103.706 + 80.384 \{\log (\text{per } [D])\}^{1/2}$$

with an r^2 of 0.993 and *F* test of 5514, methane excluded.

The PRS values of the distance matrices, like the permanent values, were apparently invariant, unique, and single-sum, and they constituted a monotonic series of values, and like the permanent values increased in size very rapidly as the carbon atom content of the alkanes increased. Indeed, so large were the PRS descriptors that, commencing with decane, the tabulated PRS values were also recorded as powers of 10 to six significant figures, sufficient for quantitative-structural comparisons, although not for bibliographic application. Column 5 displays the PRS values and column 10 lists the corresponding predicted boiling points derived from the distance matrix data of the alkanes in Table I. The boiling points based upon the PRS index values possessed a linear relationship described by

$$\text{bp, } ^\circ\text{C} = -119.521 + 74.109 \{\log (\text{PRS}[D])\}^{1/2}$$

with an r^2 of 0.989 and *F* test of 3436, methane excluded. The order of complexity of the heptane isomers was identical to that extracted from the permanent data derived from the distance matrices of the same alkanes.

The variant PSDS and SSDP index values were disappointing to observe, for neither series appeared to be monotonic, hence the data were not listed in Table I. However, the SDDP figures listed in column 6 appeared to be of a monotonic sequence, as well as apparently single-sum and unique. Based upon these latter SDDP data, the increasing intricacy of the various heptane isomers was of the order **14, 16, 22, 15, 18, 20, 17, 21, 19,** with heptane the least and 2,2,3-trimethylbutane the most intricate. The above sequence is intuitively reasonable, although in not exactly the same order as deduced from the permanent and PRS index values cited above. Calculated boiling points, not listed in Table I, based upon the SDDP indices displayed a linear relationship described by

$$\text{bp, } ^\circ\text{C} = -124.855 + 124.196 \{\log (\text{SDDP}[D])\}^{1/2}$$

with an r^2 of 0.968 and *F* test of 1119, methane excluded.

The variant PDDSΔ data of column 7 appeared to be single-sum and unique, and presented a monotonic sequence of values. Compounds **14** and **19** were recognized by the PDDSΔ values as being first and last in the heptane isomer complexity sequence; there were some intermediate differences, however, from the sequences described by the other indices discussed in this study. As with the PRS index values, the great size of the PDDSΔ indices dictated that the values from decane and higher be expressed simply as powers of 10 to six significant figures. Calculated boiling points based upon the PDDSΔ indices, not listed in Table I, were linear, described by

$$\text{bp, } ^\circ\text{C} = -93.487 + 81.7233 \{\log (\text{PDDS}\Delta[D])\}^{1/2}$$

with an r^2 of 0.995 and *F* test of 7049, methane excluded. Figure 1 displays the observed versus the calculated boiling points obtained by using this equation.

CONCLUSIONS

The permanents and products of the row sum (PRS) values of the distance matrices of the alkanes of Table I appear to be invariant, unique, single-sum, and members of monotonic sequences of values that can serve as molecular topological indices. An appropriate computer program is necessary for calculating the permanents. Experiments with the variant products of the sinister diagonal sums (PSDS) and sums of the sinister diagonal products (SSDP) values of the distance
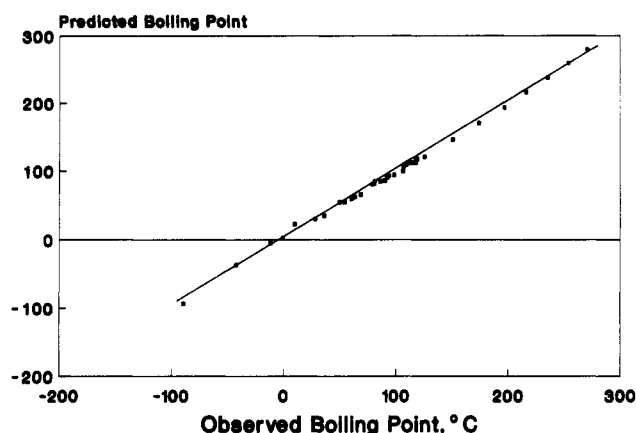
Figure 1. Boiling points, observed versus predicted, derived from the PDDSΔ(D) index values of the alkanes listed in Table I, methane excluded.

matrices justified the conclusion that the data did not constitute monotonic series and hence were useless as topological indices. However, the sums of the dexter diagonal products (SDDP) and the products of the dexter diagonal sums of the upper (lower) triangle (PDDSΔ) of the distance matrices, even though variant and representing canonically numbered graphs, were easily calculated index values and also appeared to be unique and single-sum, and constituted a monotonic series of values. The permanent, PRS, SDDP, and PDDSΔ indices can be utilized as topological indices for quantitative-structural property relationship comparisons. Additionally, the row sums of the distance matrices were demonstrated to have potential utility for establishing priority sequences of graph vertices.

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Notes on Fully Benzenoid Hydrocarbons and Their Constant-Isomer Series

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All-benzenoids (corresponding to fully benzenoid or total resonant sextet hydrocarbons) are treated. The possible values of n and s in an all-benzenoid formula C_nH_s are specified in general terms. Many other general formulations are reported, such as the general expressions of C_nH_s formulas for protrusive all-benzenoids, circular all-benzenoids, and extremal all-benzenoids. All these classes are precisely defined. The latter class (extremal all-benzenoids) contains exactly (if biphenyl is added) the members of constant-isomer series of all-benzenoids, the main subject of this work. Associated all-benzenoids give the link of these members to the members of the (ordinary) constant-isomer series of benzenoids. Supercircumscribing, a kind of an augmented circumscribing, is a crucial concept in these studies. Finally, the previously known numerical data for constant-isomer all-benzenoid series are supplemented.

INTRODUCTION

The fully benzenoid hydrocarbons are known to be of great importance in organic chemistry.[1-3] A necessary and sufficient condition, which defines a fully benzenoid hydrocarbon, is the existence of Kekulé structures where all the double bonds belong to aromatic sextets.[3] Here it is adhered to the term[4-6] "all-benzenoids" as an abbreviation for all-benzenoid *systems*,[7] which, considered as chemical graphs,[8] correspond to the fully benzenoid *hydrocarbons*, chemically known or unknown.

The present work was prompted by a recent paper of Dias[9] dealing with "total resonant sextet benzenoids", a concept which actually is synonymous with "all-benzenoids".[10] Among the interesting findings of Dias[9] is the existence of constant-isomer series of all-benzenoids in correspondence with the ordinary constant-isomer series of benzenoids.[11-18] In the present work these findings are extended by some general formulations. Also the numerical data are supplemented.

RESULTS AND DISCUSSION

Notation. Let the formula C_nH_s for a benzenoid hydrocarbon be denoted alternatively as

$$C_nH_s \equiv (n; s)$$

The class of benzenoids with this formula, viz., the C_nH_s benzenoid isomers, also has a fixed number of hexagons (h) and a fixed number of internal vertices (n_i). A benzenoid