

Topological Organic Chemistry. 5.¹ Graph Theory, Matrix Hafnians and Pfaffians, and Topological Indices of Alkanes

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Received March 13, 1992

Hafnians and pfaffians of the adjacency and distance matrices that describe structures of alkanes were calculated. Hafnians of the distance matrices, being single-sum, apparently unique, and having monotonic series of values, appeared to be useful as topological indices for alkanes.

INTRODUCTION

Graph theory offers the means to numerically characterize chemical structures. Rouvray² has summarized many techniques for calculating topological indices, techniques that continue to increase in number. This paper extends the study of the utility of structure-descriptive matrices of alkanes as sources of single-sum numbers descriptive of alkane structures.

The adjacency and distance matrices that describe the structures of molecular graphs are square, symmetrical matrices. Earlier papers of this series have evaluated the utility of matrix determinants and permanents (positive determinants), among other matrix functions, as topological indices. Allied with matrix determinants and permanents are pfaffians, old and well-known functions, and hafnians, the newest of such related matrix functions to be described. Minc³ has observed that hafnians are related to pfaffians in the same way that permanents are related to determinants. The hafnians are all positive values and, hence, are more easily manipulated; for this reason the account of experiments with the matrix hafnians precedes that of the matrix pfaffians.

HAFNIANS

Caianiello^{4,5} devised and represented with his own unique symbolism a new matrix function which he named the hafnian, wherein Σ' was defined as the summation over all permutations i_1, i_2, \dots, i_{2n} of $1, 2, \dots, 2n$ which satisfy the limitations $i_1 < i_2, i_3 < i_4, \dots, i_{2n-1} < i_{2n}; i_1 < i_3 < i_5 \dots < i_{2n-1}$.

$[1 \ 2 \ \dots \ 2n] =$

$$\begin{bmatrix} [12] & [13] & \dots & [1, & 2n] \\ & [23] & \dots & [2, & 2n] \\ & & \ddots & & \\ & & & [2n-1, & 2n] \end{bmatrix} = \Sigma' [i_1 i_2] [i_3 i_4] \dots [i_{2n-1} i_{2n}]$$

The hafnian is analogous to the permanent in that it can be expanded by the elements of one of its lines in the triangular array, omitting those lines and columns possessing either of the numerical subscripts of the chosen index, regardless of which is first or second. What remains is a new hafnian, the minor of the chosen index; like the permanent of a matrix, the hafnian always has a positive value. A hafnian is equal to the sum of the products of each element of a prefixed line by its minor, each term being positive.

Minc³ peripherally touched on the mathematics of hafnians, observing that hafnians are related to pfaffians in the same way that permanents are related to determinants. Minc also observed that "unfortunately, there is no known efficient method for computing hafnians". The limited illustrative material of Caianiello and Minc involved only even-numbered square matrices, as well as symmetrical matrices such as are encountered in the instances of adjacency and distance matrices of alkanes.

It is the purpose of this paper to explore the utility of the matrix hafnians and pfaffians as potential molecular topological indices. The operations utilized to attain this end were, as Minc advised, inefficient and were so lengthy as to limit this paper to square matrices of no more than eight units.

Attention was first focused on the even-numbered adjacency and distance matrices. The general solution of the hafnian of the square matrix $n = 6$ was derived with the matrix represented in traditional fashion.

$$D_6^6(G) = \begin{bmatrix} a_{11} & a_{12} & a_{13} & a_{14} & a_{15} & a_{16} \\ a_{21} & a_{22} & a_{23} & a_{24} & a_{25} & a_{26} \\ a_{31} & a_{32} & a_{33} & a_{34} & a_{35} & a_{36} \\ a_{41} & a_{42} & a_{43} & a_{44} & a_{45} & a_{46} \\ a_{51} & a_{52} & a_{53} & a_{54} & a_{55} & a_{56} \\ a_{61} & a_{62} & a_{63} & a_{64} & a_{65} & a_{66} \end{bmatrix}$$

The traces of the adjacency and distance matrices were omitted, for each element of the trace equals zero.

$$\text{trace elements} = a_{11} = a_{22} = a_{33} = a_{44} = a_{55} = a_{66} = 0$$

The hafnian of the upper triangle was then represented according to Caianiello's style of presentation, but with the use of more traditional notation.

$$\text{haf}(D_6^6(G)) = \begin{bmatrix} a_{12}a_{13}a_{14}a_{15}a_{16} \\ a_{23}a_{24}a_{25}a_{26} \\ a_{34}a_{35}a_{36} \\ a_{45}a_{46} \\ a_{56} \end{bmatrix}$$

The minor was developed along the first row, eliminating those rows and columns possessing any of the subscript numbers

of the chosen element in the upper triangle.

$$\begin{bmatrix} a_{12}a_{34}a_{35}a_{36} \\ a_{45}a_{46} \\ a_{56} \end{bmatrix}$$

Expansion continued, omitting those columns and rows having any subscript numbers of the utilized index. Each new minor formation eliminated two rows of the preceding hafnian.

$$a_{12}a_{34}[a_{56}] + a_{12}a_{35}[a_{46}] + a_{12}a_{36}[a_{45}] = a_{12}a_{34}a_{56} + a_{12}a_{35}a_{46} + a_{12}a_{36}a_{45}$$

In the same fashion, expansion was continued by using separately and then in turn each of the other elements of the first row (a_{13} , a_{14} , a_{15} , and a_{16}).

Caianiello⁴ referred to the "hafnian formed by the elements lying above the leading diagonal"—the matrix trace, all of whose elements equal zero. This hafnian of a six-unit, square, symmetrical matrix is represented as shown below, and in this paper is referred to as the short hafnian (shaf).

$$\begin{aligned} \text{shaf}(D_6^6(G)) = & a_{12}a_{34}a_{56} + a_{12}a_{35}a_{46} + a_{12}a_{36}a_{45} \\ & + a_{13}a_{24}a_{56} + a_{13}a_{25}a_{46} + a_{13}a_{26}a_{45} \\ & + a_{14}a_{23}a_{56} + a_{14}a_{25}a_{36} + a_{14}a_{26}a_{35} \\ & + a_{15}a_{23}a_{46} + a_{15}a_{24}a_{36} + a_{15}a_{26}a_{34} \\ & + a_{16}a_{23}a_{45} + a_{16}a_{24}a_{35} + a_{16}a_{25}a_{34} \end{aligned}$$

Minc³ pictured the hafnian as being formed by the elements in the matrix triangles lying both above and below the trace, each individual upper element being allied with its "reflected" lower element. The Minc presentation of the structure of the hafnian is referred to in this paper as the long hafnian (lhaf).

$$\begin{aligned} \text{lhaf}(D_6^6(G)) = & a_{12}a_{21}a_{34}a_{43}a_{56}a_{65} + a_{12}a_{21}a_{35}a_{46}a_{54}a_{63} + a_{12}a_{21}a_{36}a_{45}a_{53}a_{64} \\ & + a_{13}a_{31}a_{24}a_{42}a_{56}a_{65} + a_{13}a_{31}a_{25}a_{46}a_{54}a_{63} + a_{13}a_{31}a_{26}a_{45}a_{53}a_{64} \\ & + a_{14}a_{41}a_{23}a_{32}a_{56}a_{65} + a_{14}a_{41}a_{25}a_{36}a_{54}a_{63} + a_{14}a_{41}a_{26}a_{35}a_{53}a_{64} \\ & + a_{15}a_{51}a_{23}a_{32}a_{46}a_{64} + a_{15}a_{51}a_{24}a_{36}a_{42}a_{63} + a_{15}a_{51}a_{26}a_{34}a_{43}a_{62} \\ & + a_{16}a_{61}a_{23}a_{32}a_{45}a_{54} + a_{16}a_{61}a_{24}a_{35}a_{42}a_{53} + a_{16}a_{61}a_{25}a_{34}a_{43}a_{52} \end{aligned}$$

The distance matrices of the alkanes are symmetrical matrices, hence $a_{12} = a_{21}$, $a_{34} = a_{43}$, etc; therefore, Minc pictured the above expression as follows:

$$\begin{aligned} \text{lhaf}(D_6^6(G)) = & a_{12}^2a_{34}^2a_{56}^2 + a_{12}^2a_{35}^2a_{46}^2 + a_{12}^2a_{36}^2a_{45}^2 \\ & + a_{13}^2a_{24}^2a_{56}^2 + a_{13}^2a_{25}^2a_{46}^2 + a_{13}^2a_{26}^2a_{45}^2 \\ & + a_{14}^2a_{23}^2a_{56}^2 + a_{14}^2a_{25}^2a_{36}^2 + a_{14}^2a_{26}^2a_{35}^2 \\ & + a_{15}^2a_{23}^2a_{46}^2 + a_{15}^2a_{24}^2a_{36}^2 + a_{15}^2a_{26}^2a_{34}^2 \\ & + a_{16}^2a_{23}^2a_{45}^2 + a_{16}^2a_{24}^2a_{35}^2 + a_{16}^2a_{25}^2a_{34}^2 \end{aligned}$$

The adjacency matrix of an alkane is not only square and symmetrical but is also composed exclusively of elements which have values of zero or one. Because $1^2 = 1$, the adjacency matrix is unusual in that the short hafnian value equals that of the long hafnian. Experimentation demonstrated that all hafnians of the alkane distance matrices were invariant, apparently unique, and constituted monotonic series of values.

When working with square, symmetrical distance matrices of odd number, the above technique for hafnian computation was also used; the last steps of the expansion were especially compact and swiftly executed. A more rapid solution to the problem of creating hafnian algorithms for odd-numbered matrices was to merely eliminate all the elements in the highest numbered column and row from the next highest even-numbered matrix hafnian algorithm. When this technique was used, all replicate element products, when encountered,

were cancelled. With care this methodology was used to work backward to any desired lower-level hafnian from any higher-level hafnian. The Caianiello short hafnian for the square, symmetrical, $n = 6$ matrix became transformed into the following short hafnian for the square $n = 5$ matrix.

$$\begin{aligned} \text{shaf}(D_5^5(G)) = & a_{12}a_{34} + a_{12}a_{35} + a_{12}a_{45} \\ & + a_{13}a_{24} + a_{13}a_{25} + a_{13}a_{45} \\ & + a_{14}a_{23} + a_{14}a_{25} + a_{14}a_{35} \\ & + a_{15}a_{23} + a_{15}a_{24} + a_{15}a_{34} \\ & + a_{23}a_{45} + a_{24}a_{35} + a_{25}a_{34} \end{aligned}$$

After the general solution for a matrix of given n number had been derived, the specific element values of the matrix of the alkane isomer were substituted into the algorithm and the hafnian was calculated, a most cumbersome process. The distance matrix for hexane numbered according to the IUPAC system of nomenclature (all these reported hafnian values were, however, invariant) is pictured.

$$D_6^6(G) = \begin{bmatrix} 0 & 1 & 2 & 3 & 4 & 5 \\ 1 & 0 & 1 & 2 & 3 & 4 \\ 2 & 1 & 0 & 1 & 2 & 3 \\ 3 & 2 & 1 & 0 & 1 & 2 \\ 4 & 3 & 2 & 1 & 0 & 1 \\ 5 & 4 & 3 & 2 & 1 & 0 \end{bmatrix}$$

The short hafnian of the matrix was then calculated.

$$\begin{aligned} \text{shaf} = & 1 \cdot 1 \cdot 1 + 1 \cdot 2 \cdot 2 + 1 \cdot 3 \cdot 1 \\ & + 2 \cdot 2 \cdot 1 + 2 \cdot 3 \cdot 2 + 2 \cdot 4 \cdot 1 \\ & + 3 \cdot 1 \cdot 1 + 3 \cdot 3 \cdot 3 + 3 \cdot 4 \cdot 2 \\ & + 4 \cdot 1 \cdot 2 + 4 \cdot 2 \cdot 3 + 4 \cdot 4 \cdot 1 \\ & + 5 \cdot 1 \cdot 1 + 5 \cdot 2 \cdot 2 + 5 \cdot 3 \cdot 1 \\ = & 174 \end{aligned}$$

The long hafnian was the sum of the squares of all the above multiplicands.

$$\begin{aligned} \text{lhaf} = & 1^2 \cdot 1^2 \cdot 1^2 + 1^2 \cdot 2^2 \cdot 2^2 + 1^2 \cdot 3^2 \cdot 1^2 \\ & + 2^2 \cdot 2^2 \cdot 1^2 + 2^2 \cdot 3^2 \cdot 2^2 + 2^2 \cdot 4^2 \cdot 1^2 \\ & + 3^2 \cdot 1^2 \cdot 1^2 + 3^2 \cdot 3^2 \cdot 3^2 + 3^2 \cdot 4^2 \cdot 2^2 \\ & + 4^2 \cdot 1^2 \cdot 2^2 + 4^2 \cdot 2^2 \cdot 3^2 + 4^2 \cdot 4^2 \cdot 1^2 \\ & + 5^2 \cdot 1^2 \cdot 1^2 + 5^2 \cdot 2^2 \cdot 2^2 + 5^2 \cdot 3^2 \cdot 1^2 \\ = & 3110 \end{aligned}$$

The same invariant results were obtained when the hexane distance matrix was constructed using the CIP canonical system of numbering. When used as topological indices, therefore, the hafnians may properly be referred to as descriptors.

Experiments with the hafnians of the adjacency matrices of the hexane isomers disclosed that only the two very symmetrical molecules, hexane and 3-methylpentane, had hafnian values of 1; the other three hexane isomers had hafnian values of 0. As a consequence of these disappointing results, all further studies of hafnian values of adjacency matrices were terminated.

PFAFFIANS

Caianiello^{4,5} has recently, and most lucidly and succinctly, defined the pfaffian as a symbol, or triangular array, which is expanded according to the rule:

[1 2 ... 2n] =

$$\begin{bmatrix} [12] & [13] & \dots & [1, & 2n] \\ & [23] & \dots & [2, & 2n] \\ & & \ddots & \vdots \\ & & & [2n-1, & 2n] \end{bmatrix} = \Sigma'(-1)^r [i_1 i_2] [i_3 i_4] \dots [i_{2n-1} i_{2n}]$$

Σ' is the summation over all permutations i_1, i_2, \dots, i_{2n} of 1, 2, ..., 2n which satisfies the limitations $i_1 < i_2, i_3 < i_4, \dots, i_{2n-1} < i_{2n}$; $i_1 < i_3 < i_5 \dots < i_{2n-1}$. Cullis⁶ used the older and more traditional notation inherited from Sir Thomas Muir which regards $P_{1 \dots m}$ as a rational integral function of those elements which lie above the leading diagonal of the matrix.

$$P_{1 \dots m} = \begin{bmatrix} a_{12} a_{13} a_{14} \dots a_{1m} \\ a_{23} a_{24} \dots a_{2m} \\ a_{34} \dots a_{3m} \\ \dots \\ a_{m-1, m} \end{bmatrix}$$

The pfaffian is analogous to the determinant. It too can be expanded by the elements of one of its lines in the triangular array, omitting those lines and columns possessing either of the numerical subscripts of the chosen element, regardless of which is the first or second number. It is interesting to note that the triangular expressions for the hafnian and the pfaffian differ only in the sign $((-1)^r)$ inserted into the definition of the pfaffian.

Quoting Caianiello but utilizing the more traditional representation of Muir, the above observation concerning the expansion of the pfaffian is continued. "The element (a_{ij}) belongs to the lines i and j ; crossing these lines out, what is left is a new pfaffian, the minor of (a_{ij}) A pfaffian is equal to the sum of the products of each element (a_{ij}) of a prefixed line by its minor, each term in the sum being given the sign $(-1)^{i+j+1}$."

Referring to the derivation of the algorithm of the hafnian of the square matrix, $n = 6$, the expansion is replicated with further attention given to the insertion of the \pm signs derived from the term $(-1)^{i+j+1}$ into the various stages of the expansion so as to arrive at the algorithm for the pfaffian. In essence, if the term is even ($i + j$ is odd), the element sign is plus; if the term is odd ($i + j$ is even), the element sign is minus.

$$\text{pfa}(\mathbf{D}_6^6(\mathbf{G})) = \begin{bmatrix} +a_{12}a_{13}a_{14}a_{15}a_{16} \\ +a_{23}a_{24}a_{25}a_{26} \\ +a_{34}a_{35}a_{36} \\ +a_{45}a_{46} \\ +a_{56} \end{bmatrix}$$

The minor was developed along the first row, as was done in developing the hafnians, eliminating those rows and columns possessing any of the element subscript numbers of the chosen index in the upper triangle. The "new" pfaffian was renumbered in order to ascertain the correct sign for each element.

"new" pfaffian; old numbers "new" pfaffian; new numbers

$$\begin{bmatrix} +a_{12} [+a_{34}a_{35}a_{36}] \\ +a_{45}a_{46} \\ +a_{56} \end{bmatrix} \quad a_{ij} [+a_{12}a_{13}a_{14}] \begin{bmatrix} +a_{23}a_{24} \\ +a_{34} \end{bmatrix}$$

Although no sign changes were observed in this first step, sometimes sign changes were encountered in succeeding steps

of the expansion. Expansion continued, omitting again those rows and columns having any element subscripts of the utilized index. Each "new" minor formation eliminated two rows of the prior pfaffian.

$$\begin{aligned} & +a_{12}a_{34}a_{56} + a_{12}a_{35}a_{46} + a_{12}a_{36}a_{45} \\ & = +a_{12}a_{34}a_{56} + a_{12}a_{35}a_{46} + a_{12}a_{36}a_{45} \\ & = +a_{12}a_{34}a_{56} - a_{12}a_{35}a_{46} + a_{12}a_{36}a_{45} \end{aligned}$$

In a parallel fashion, expansion was continued using separately and in turn each of the other elements of the first row (a_{13} , a_{14} , a_{15} , and a_{16}) and remembering that each "new" pfaffian required new numbering and hence new signs; that is, each of the new triangular systems and the last one-unit systems were renumbered and resigned as shown

$$\begin{bmatrix} -a_{13} [+a_{24}a_{25}a_{26}] \\ +a_{45}a_{46} \\ +a_{56} \end{bmatrix}; \begin{bmatrix} +a_{14} [+a_{23}a_{25}a_{26}] \\ +a_{35}a_{36} \\ +a_{56} \end{bmatrix}; \begin{bmatrix} -a_{15} [+a_{23}a_{24}a_{26}] \\ +a_{34}a_{36} \\ +a_{46} \end{bmatrix}; \begin{bmatrix} +a_{16} [+a_{23}a_{24}a_{25}] \\ +a_{34}a_{35} \\ +a_{45} \end{bmatrix}$$

which gave

$$\begin{aligned} & +a_{13}a_{24}a_{56} + a_{13}a_{25}a_{46} + a_{13}a_{26}a_{45} \\ & +a_{14}a_{23}a_{56} + a_{14}a_{25}a_{36} + a_{14}a_{26}a_{35} \\ & +a_{15}a_{23}a_{46} + a_{15}a_{24}a_{36} + a_{15}a_{26}a_{34} \\ & +a_{16}a_{23}a_{45} + a_{16}a_{24}a_{35} + a_{16}a_{25}a_{34} \end{aligned}$$

which reduced to the algorithm of the pfaffian.

$$\begin{aligned} \text{pfa}(\mathbf{D}_6^6(\mathbf{G})) &= a_{12}a_{34}a_{56} - a_{12}a_{35}a_{46} + a_{12}a_{36}a_{45} \\ &- a_{13}a_{24}a_{56} + a_{13}a_{25}a_{46} - a_{13}a_{26}a_{45} \\ &+ a_{14}a_{23}a_{56} - a_{14}a_{25}a_{36} + a_{14}a_{26}a_{35} \\ &- a_{15}a_{23}a_{46} + a_{15}a_{24}a_{36} - a_{15}a_{26}a_{34} \\ &+ a_{16}a_{23}a_{45} - a_{16}a_{24}a_{35} + a_{16}a_{25}a_{34} \end{aligned}$$

Referring to the distance matrix for hexane, numbered according to the IUPAC system of nomenclature, the pfaffian of the matrix was calculated as below.

$$\begin{aligned} \text{pfa} &= 1 \cdot 1 \cdot 1 - 1 \cdot 2 \cdot 2 + 1 \cdot 3 \cdot 1 \\ &- 2 \cdot 2 \cdot 1 + 2 \cdot 3 \cdot 2 - 2 \cdot 4 \cdot 1 \\ &+ 3 \cdot 1 \cdot 1 - 3 \cdot 3 \cdot 3 + 3 \cdot 4 \cdot 2 \\ &- 4 \cdot 1 \cdot 2 + 4 \cdot 2 \cdot 3 - 4 \cdot 4 \cdot 1 \\ &+ 5 \cdot 1 \cdot 1 - 5 \cdot 2 \cdot 2 + 5 \cdot 3 \cdot 1 \\ &= 0 \end{aligned}$$

When the same computation was executed for the distance matrix of hexane numbered according to the CIP canonical system of nomenclature, the pfaffian had the value 60.

Unfortunately, experimentation with all five of the hexane isomers indicated that not only was the pfaffian of each isomer a variant value but also the pfaffian values for all the hexane isomers by any system of numbering were wildly chaotic, displaying no evidence of cohesion or monotonic series of values. These data are summarized, with the IUPAC and CIP pfaffian values for each hexane isomer: 9, 0, 60; 10, 0, -8; 11, 0, -12; 12, -4, 32; 13, 0, 12. In view of these disappointing results, no further attention was given the pfaffian function.

CALCULATIONS

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 upper limit of eight-

Table I. Topological Indices Derived from Hafnians of the Distance Matrices of Representative C₁–C₈ Alkanes

no.	compd	shaf(D) index	lhaf(D) index	boiling points, °C		
				obsd	shaf(D) index calcd ^a	lhaf(D) index calcd ^b
1	methane			-161		
2	ethane	1	1	-88.6	-114.8	-110.6
3	propane	4	6	-42	-22.1	-24.9
4	butane	8	26	-0.5	-1.3	5.0
5	2-methylpropane	6	12	-11.7	-9.4	-9.7
6	pentane	58	310	36.1	43.8	42.7
7	2-methylbutane	48	174	27.9	40.1	34.8
8	2,2-dimethylpropane	36	96	9.5	34.2	26.2
9	hexane	174	3 110	68.7	64.0	71.0
10	2-methylpentane	132	1 664	60.3	59.2	63.8
11	3-methylpentane	114	1 062	63.2	56.5	58.4
12	2,3-dimethylbutane	98	854	58	53.8	55.7
13	2,2-dimethylbutane	84	528	49.7	50.9	49.7
14	heptane	1 840	56 280	98.4	101.1	101.1
15	2-methylhexane	1 480	34 840	90	97.9	96.4
16	3-methylhexane	1 276	23 160	92	95.7	92.4
17	2,4-dimethylpentane	1 176	20 976	80.5	94.5	91.4
18	3-ethylpentane	1 108	15 808	93.5	93.7	88.5
19	2,3-dimethylpentane	1 000	13 336	89.8	92.1	86.7
20	2,2-dimethylpentane	996	13 320	79.2	92.1	86.7
21	3,3-dimethylpentane	856	8 904	86	89.8	82.5
22	2,2,3-trimethylbutane	768	7 368	80.9	88.1	80.4
23	octane	7 360	1 018 584	125.7	120.1	127.5
24	2-methylheptane	5 868	637 064	117.6	117.1	123.4
25	3-methylheptane	4 840	389 224	119	114.5	119.1
26	2,5-dimethylhexane	4 652	395 720	109.1	114.0	119.2
27	4-methylheptane	4 440	293 712	117.7	113.4	116.6
28	2,4-dimethylhexane	3 792	235 536	109.4	111.2	114.6
29	3-ethylhexane	3 724	189 576	118.9	111.0	112.6
30	2,2-dimethylhexane	3 708	219 144	106.9	110.9	113.9
31	2,3-dimethylhexane	3 428	167 944	115.3	109.8	111.5
32	3,4-dimethylhexane	3 054	136 360	117.7	108.2	109.5
33	2,2,4-trimethylpentane	2 880	130 656	99.3	107.4	109.1
34	3-ethyl-2-methylpentane	2 844	105 688	115.7	107.2	107.1
35	3,3-dimethylhexane	2 796	101 768	112	107.0	106.8
36	2,3,4-trimethylpentane	2 624	94 672	113.4	106.1	106.1
37	3-ethyl-3-methylpentane	2 308	63 112	119	104.3	102.2
38	2,2,3-trimethylpentane	2 292	73 032	110.5	104.2	103.6
39	2,3,3-trimethylpentane	2 108	55 112	114.6	103.0	100.9
40	2,2,3,3-tetramethylbutane	1 692	38 088	106.3	99.9	97.3

^a Calculated by using bp, °C = -114.824 + 119.477 (log shaf(D))^{1/2}. ^b Calculated by using bp, °C = -110.608 + 97.147 (log lhaf(D))^{1/2}.

carbon atom alkanes was dictated by the cumbersome character of the calculations. The algorithm for determining the hafnians of the matrices of the octane isomers, for example, involved arithmetic manipulations upon 105 sets of four multiplicands each, all tedious and error-fraught operations. Experimentation demonstrated that the hafnian values were invariant; in practice, each value was computed twice, using the IUPAC and the CIP numbering systems separately.

RESULTS

Table I displays the short and long hafnians of the distance matrices and boiling points of the 40 alkanes included in this study. The nonbranched alkanes of each family of isomers possessed the highest short and long hafnian values, with the values decreasing in magnitude as the complexity of the related isomers increased. If the derived hafnian topological index is viewed as a description of molecular intricacy, then 3-ethylhexane can be regarded as slightly more complex than, for example, 3-methylheptane. Certainly octane as the least complex, and 2,2,3,3-tetramethylbutane as the most complex, of the octane isomers listed in Table I is an intuitively acceptable order of octane isomer complexity, but slight variations in the order of complexity of the various octane isomers were displayed when the short was contrasted with the long hafnian series. The order of octane isomer complexity is interestingly similar to Bertz's⁷ and several others, as so well summarized by Mihalić et al.⁸

Inspection of the data in Table I confirmed the orderly, monotonic character of the series of short and long hafnians, also single-sum, and apparently unique within this limited list of compounds. However, in compound pairs 25/26, 29/30, and 37/38, slight and surprising inversions were noted in the hafnian values. Also, overlap of the hafnians of alkanes 14 and 40 was evident.

It was observed that the plot of the square roots of the logs of short hafnians of the distance matrices versus the boiling points of the alkanes of Table I gave a straight line expressed by the equation

$$\text{bp, } ^\circ\text{C} = -114.824 + 119.477 (\log \text{shaf(D)})^{1/2}$$

with an *r*² value of 0.962 and an *F* value of 947.6. In a similar exercise using long hafnians, the boiling points possessed a linear relationship described by the expression

$$\text{bp, } ^\circ\text{C} = -110.608 + 97.147 (\log \text{lhaf(D)})^{1/2}$$

with a slightly better *r*² value of 0.971 and *F* test of 1233.

Of all the matrix functions thus far studied in this series of papers, it appears that the hafnians were the most efficacious, utilizing in calculations only the one or two triangles of the square, symmetric matrix, as well as avoiding use of the all-zero trace. This was an advantage which was somewhat cancelled, as Minc observed, because "there is no known efficient method for computing hafnians". Future applications

of the hafnians to bibliographic and structure-relationship ends await the programmed computation of their values.

One circumstance regarding the hafnians remains obscure. Caianiello⁴ stated "without proof.... A symmetric permanent of even order with vanishing elements in the leading diagonal ... is the exact square of the hafnian formed by the elements lying above the leading diagonal". This statement appears to be true only of the even-order distance matrices of ethane (shaf, 1; per, 1), butane (shaf, 8; per, 64), and 2-methylpropane (shaf, 6; per, 36). None of the squares of the short hafnians of the hexanes or of the octanes fulfilled the Caianiello statement, when compared with recently published¹ values of permanents.

CONCLUSIONS

The hafnians of the structure-descriptive distance matrices of alkanes appear to be unique and to have monotonic series of values, as well as being invariant and of efficient formulation. The hafnians can also serve as single-sum molecular topological indices. Extensive hafnian calculations, however, require formulation of the appropriate computer program. Pfaffians appear to be useless as molecular topological indices.

ACKNOWLEDGMENT

We are grateful to Professor A. T. Balaban (Technical University, Romania) for his constructive comments.

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