On structural ordering and branching of acyclic saturated hydrocarbons *

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We consider the problem of ordering acyclic graphs corresponding to saturated hydrocarbons and the problem of defining molecular branching. In particular, we consider the recently introduced graph theoretical invariant $\lambda\lambda_1$, as the basis for the ordering of graphs and the definition of molecular branching. $\lambda\lambda_1$ is defined as the leading eigenvalue of the path matrix in which the element (i, j) represents the leading eigenvalue for the path connecting vertex i and vertex j. Among 35 nonane isomers and 75 decane isomers no two structures have the same $\lambda\lambda_1$. Normalized leading eigenvalue $\lambda\lambda_1/n$ is suggested as the index of molecular branching. For smaller alkanes the new index parallels previously suggested indices of molecular branching yet it shows no degeneracy that limited the use of earlier descriptors of molecular branching.

1. Introduction

Is there an alternative to the use of the serial register number as molecular ID, as has been practiced by Chemical Abstract Service? Limitations of serial numbers are apparent, the number assigned to a structure bears no relationship to the structure and its properties. However, the number is unique. This, however, does not necessarily prevent duplication of records, because the same structure could be registered under different names [9].

Alternative (to the official IUPAC) chemical names, if based on mathematical considerations [14,15,48,49], may reflect inherent structural elements and facilitate the search for structurally similar compounds. But, if one can come up with a single molecular ID number that is based on *properties* of the structure (in contrast to names that are based on a *convention*, even if based on structural considerations), one could expedite searching for similar structures. Moreover, if the ID numbers reflect various structural components it is possible that the ordering of structures will parallel relative magnitudes of selected molecular properties and even allow one to interpolate for unknown data. Some success has been obtained with partial ordering of structures [3,12,20–22,32,34,37,39,42,44–47,51,52]. However, here we are interested in absolute

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* Dedicated to Professor Norman March, an old friend of Mathematical Chemistry.

order. We will restrict out attention to acyclic graphs representing saturated hydrocarbons. We will see that even for this special class of structures the problem of finding unique ID labels is difficult, even though it may be in sight. If this special case can be solved one can then consider extension to more general cases.

2. Orderly algorithms

One of the earliest algorithms for assigning a single integer to acyclic graphs representing saturated hydrocarbons was proposed by Gordon and Kennedy [16]. The number implies an algorithm for the generation of trees (with maximal valence four). The order in which trees are arranged is based on increases of vertices from the central vertex. While the assigned integer is unique, because of the way it is derived, the obtained ID numbers do not reflect structural similarities among alkanes. An alternative is to use the smallest binary label as the criterion for the ordering of structures [31]. The resulting order (based on the smallest label derived by reading the rows of the adjacency matrix from left to right and from top to bottom) is absolute, but except for smaller graphs and selection of a family of graphs (e.g., cubic graphs) the approach is not practical for the construction and ordering of general graphs.

Orderly algorithms have been outlined and discussed by Read [7,8]. In fact, any computer construction of graphs implies an absolute order, as the resulting structures are delivered serially. For example, in figure 1 we illustrate the computer output for the 35 C_9H_{20} nonane isomers as reported by Knop et al. [23]. This particular algorithm, which used n-tuple code for trees [24], first produces trees with the maximal valence (four), then those with lesser valence (three and two). In table 1 we have ordered the 18 isomers of octane according to lexicographic order (based on the longest chain),
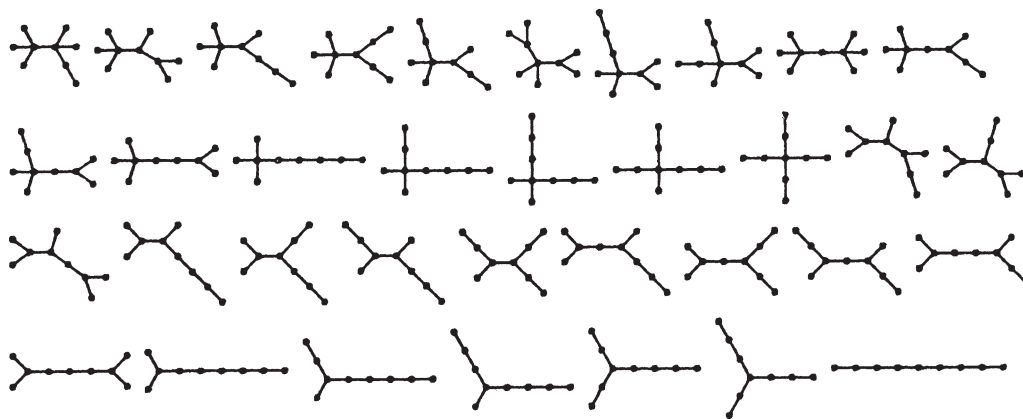
N=9

Figure 1.

Table 1
Ordering of isomers of octane with respect to different generating algorithms.
In columns indicated by asterisk, the smallest index is listed first.

	Lexico-graphic	n-tuple*	Smallest binary	Budding*	$\lambda\lambda$
n	1	1	1	1	1
2-M	2	5	7	2	2
3-M	3	4	3	4	3
4-M	4	3	6	5	4
3-E	5	2	2	6	6
2,2-MM	6	14	15	12	9
2,3-MM	7	10	9	8	8
2,4-MM	8	7	10	6	7
2,5-MM	9	6	13	3	5
3,3-MM	10	13	11	14	12
3,4-MM	11	8	4	9	10
2-M, 3-E	12	9	8	10	11
3-M, 3-E	13	12	5	15	15
2,2,3-MMM	14	17	16	16	16
2,2,4-MMM	15	15	17	13	13
2,3,3-MMM	16	16	14	17	17
2,3,4-MMM	17	11	12	11	14
2,2,3,3-MMMM	18	18	18	18	18

according to Knop et al. n-tuple ordering [24], the smallest binary label [31], and Balaban et al. "budding" order [2].

3.   Ordering of isomers

In table 2 we continue to show ordering of the 18 octane isomers based on selected molecular invariants. Because several invariants show degeneracy already among octane isomers (e.g., Wiener index [54], Hosoya index [18], the connectivity index [30], molecular topological index [53]), these were excluded. The topological indices included are: the leading eigenvalue of the distance spectrum [26], Harary index [26], Balaban's J index [1], hyper-Wiener index [35], and the leading eigenvalue of Wiener matrix [36].

As we see most orderings agree for n-octane and 2,2,3,3-tetramethylbutane, the two extreme structures that represent the least and the most branched structure. But that is where most cases agree, while for the remaining structures different procedures generate different order. We are interested in an ordering that will satisfy the following conditions:

(1) The ordering is based on an invariant.

(2) The underlying invariant has transparent structural interpretation.

(3) Ordering is complete, i.e., no two isomers may have an identical index.

Table 2

Ordering of isomers of octane with respect to different structural invariant (topological index).

	Lexico-graphic	Distance leading eigenvalue*	Harary H index*	Balaba nJ index*	Hyper-Wiener WW	Wiener leading eigenvalue
n	1	1	1	1	1	1
2-M	2	2	2	2	2	2
3-M	3	3	3	3	3	3
4-M	4	4	4	4	4	5
3-E	5	8	5	6	6	8
2,2-MM	6	6	9	8	7	6
2,3-MM	7	7	8	9	9	9
2,4-MM	8	9	7	7	8	7
2,5-MM	9	5	6	5	5	4
3,3-MM	10	11	12	12	11	12
3,4-MM	11	9	10	10	10	10
2-M, 3-E	12	12	11	11	12	13
3-M, 3-E	13	16	15	15	15	16
2,2,3-MMM	14	15	16	16	16	15
2,2,4-MMM	15	13	14	13	13	11
2,3,3-MMM	16	17	17	17	17	17
2,3,4-MMM	17	12	13	14	14	14
2,2,3,3-MMMM	18	18	18	18	18	18

It is not easy to satisfy simultaneously all the three criteria. In order to minimize the possibility that two molecules will have identical invariant-based ID numbers, the property considered becomes more convoluted, and, hence, the interpretation of the invariant in terms of familiar structural concepts becomes cumbersome. Consider, for example, the recently proposed powerful topological index of Hu and Xu [19]. They describe a procedure that leads to a unique index for all trees having $n = 22$ vertices or less (and, hopefully, may show differentiation for even higher alkane skeletons on which no tests are available), but structural interpretation of their index is not so simple. Interpretation should not be confused with definition of an index. For example, the Wiener index [54] is well defined, and in a way one may say has a simple structural *definition* – yet *interpretation* of the index W is at best somewhat vague. According to Wiener, the index is a measure of "compactness" of a molecule, but compactness remains undefined. Platt was the first to try to offer structural interpretation of W, which he associates with molecular volume [28]. On the other hand, Bonchev and Trinajstić [4–6] use W to *define* molecular branching, or better to say, to guide them in arriving at the rules that define molecular branching.

Can we arrive at a structural invariant that will allow complete ordering of isomers and yet sustain simple structural interpretation? Or, alternatively, in the spirit of the approach of Bonchev and Trinajstić, can we arrive at some invariant that can be the basis for the definition of some more familiar molecular structural features? We

will expand upon the recent suggestion [33] that the leading eigenvalue of a specially designed matrix in which the element (i, j), the leading eigenvalue of the path subgraph between vertices i and j, appears to be a promising structural invariant that satisfies our requirements, at least for the smaller acyclic graphs for which it was tested. The matrix considered is a special case of a path matrix [41] which is constructed from subgraphs containing all paths between vertices i and j.

4. Molecular branching

Branching is a structural concept the rigorous definition of which is elusive. It is, however, an important intuitive concept even if not uniquely defined [13,17]. According to Rouvary [50], one should avoid sophistry in trying to derive a rigorous definition for branching. It seems to us, therefore, that the definition of the branching (1) ought to rest on some simple structural concepts, and (2) ought to discriminate among isomers. Branching, if it is numerically to be characterized, ought to be different for different isomers, just as, say, fingerprints are different for different fingers. Different molecules can have for a number of properties the same numerical values, such as molecular volume or molecular area, but branching, like connectivity and geometry, is expected to be unique to a structure. If we take such a position then attempts to derive branching and the problem of assigning a unique invariant to a structure considerably overlap. They differ only in the relaxed requirement that branching be distinctive for structures of the same size (isomers), while unique ID should apply to structures of any size. Of course, combining a branching index with a size index (such as n, the number of vertices) will convert one problem into the other.

We see now why the definition of molecular branching so elusive: it implies solving the problem of representation of graphs by a single invariant. That problem is itself elusive, as there is a belief that no simple invariant suffices to discriminate all graphs. But nobody clarified what is a simple invariant and what is not! If the problem of representing structures uniquely by a single invariant is solved, and such may appear to be the approach of Hu and Xu [19], this does not solve the problem of branching. An invariant that solves the uniqueness for graphs, if found and confirmed, need not have the desired interpretation as branching index, i.e., it need not parallel molecular branching for the structures not in dispute. We will approach the problem from the position outlined by Bonchev and Trinajstić: we will search for a molecular invariant that parallels molecular branching (for cases of no dispute) and then use that invariant as the definition of branching. Before we continue, let us briefly review one of the earlier attempts to define molecular branching.

Lovasz and Pelikan [25] suggested the leading eigenvalue of the adjacency matrix as an index of molecular branching. The leading or the largest eigenvalue of a matrix is associated with the first eigenvector which is everywhere positive (having no nodal lines). There is considerable mathematical literature on this subjects as surveyed by Cvetković and Rowlinson [11]. Polansky and Gutman [29] considered calculation of the largest eigenvalue for molecular graphs. Except for the early sug-

Table 3
The leading eigenvalues of the adjacency matrix (A), the distance matrix (D), the Wiener matrix (W) and the path matrix (P).

Reference isomer	eig A	eig D	eig W	eig P	W	WW
n-octane	21.8364	28.3908	57.1698	10.3981	84	210
2-M	20.4792	25.8407	52.6122	10.2866	79	185
3-M	19.7628	24.9881	48.4059	10.2359	76	170
4-M	19.5420	24.7474	46.6606	10.2211	75	165
2,5-MM	19.1115	23.3045	47.7238	10.1712	74	161
3-E	18.7788	22.3642	42.2041	10.1696	72	150
2,2-MM	18.4133	22.7522	44.4713	10.0816	71	149
2,4-MM	18.3964	21.7890	43.4185	10.1151	71	147
2,3-MM	18.1815	22.4563	42.0589	10.0900	70	143
3,4-MM	17.6759	21.9365	39.2901	10.0484	68	134
3,3-MM	17.4426	20.6735	38.5332	9.9994	67	131
2-M, 3-E	17.4187	20.5212	37.4277	10.0329	67	129
2,2,4-MMM	17.0338	20.3752	39.1411	9.9543	66	127
2,3,4-MMM	16.8079	20.1793	37.0246	9.9526	65	122
3-M, 3-E	16.6705	19.6954	34.1415	9.9314	64	118
2,2,3-MMM	16.3152	19.9044	34.9935	9.8771	63	115
2,3,3-MMM	16.0683	19.6049	33.4679	9.8512	62	111
2,2,3,3-MMMM	14.9373	18.1965	30.3305	9.6938	58	97

gestion of Lovasz and Pelikan to view the largest eigenvalue as the branching index, until recently there were no other applications of leading eigenvalues. For example, the leading eigenvalue of the distance matrix apparently has not received similar attention. However, recently the leading eigenvalue of the so called D/D matrix was interpreted as the folding index [38] and applied to the characterization of folding of mathematical curves and long chains, as models for characterization of protein folding [40,43]. The leading eigenvalue of matrices appears to have been undeservedly overlooked in the past. We will see here how the leading eigenvalue of the path matrix can be used as the basis for a revised definition of the branching index for molecular graphs.

In table 3 in the first numerical column we listed the leading eigenvalues (λ_1) of the adjacency matrix for 18 isomers of octane. The isomers have been ordered in decreasing value of the eigenvalue, the order that fully coincides with the ranking based on Wiener number (W), except that two pairs of isomers have the identical W. If, however, we use the hyper-Wiener number WW [35], the coincidences in W are removed and ordering of λ_1 parallels that of WW. Because of the parallelism between λ_1 and W, it is not surprising that Bonchev and Trinajstić based their discussion of the molecular branching on the Wiener index. All they had to be concerned with are the cases of W degeneracy, of which λ_1 is not free when considerations are extended to larger alkanes.

An alternative would be to use WW as an index on which to base a definition of molecular branching, since WW shows fewer degeneracies, but WW was not available at the time of earlier discussions of molecular branching. However, one can also explore the leading eigenvalue of other graph matrices and see if they may offer a useful definition of molecular branching. In table 3 we show the first eigenvalue of the distance matrix δ_1 [27], Wiener matrix ω_1 [35], and path matrix $\lambda\lambda_1$ (this work). The leading eigenvalue of the distance matrix and Wiener matrix show the occasional minor discrepancy in the parallelism with W. For example, the relative order of 2,5-MM and 3-E for D matrix and 4-M and 2,5-MM for the W matrix. The leading eigenvalue of the path matrix fully parallels W, though it reverses the relative values for the isomers associated with degenerate W (cases $W = 71$ and $W = 67$) in comparison with the ordering induced by λ_1. However, the question, which is more branched 2,2-dimethylhexane or 2,4-dimethylhexane ($W = 71$), and 3,3-dimethylhexane or 2-methyl-3-ethylpentane ($W = 67$), is open to debate, because we are comparing structures of different branching patterns. Hence, we should first focus attention to cases for which there is no dispute and then reconsider questions like the above in order to select the approach on which to base the definition of the branching. All the approaches listed in table 3, i.e., λ_1, δ_1, ω_1, $\lambda\lambda_1$, W, WW, are the candidates, and one with the least degeneracy may be given the preference. We already know that λ_1, δ_1, W, WW show the degeneracy, leaving as candidates ω_1 and $\lambda\lambda_1$ to be further explored. But, before we opt for one of the two alternatives, we should explore how the candidate procedures characterize molecular branching for cases of no dispute.

5. Cases of no dispute

The cases of no dispute involve short sequences of isomers that have a regular branching pattern, such as the sequence 2-M, 3-M, 4-M, and 2,2-MM, 3,3-MM. In each sequence the center of branching is moving toward the center of the molecule and this is fully reflected in all the branching descriptors of table 3. Observations like this lead Bonchev and Trinajstić [4–6] to their rules that define relative degree of branching. The above is their Rule 7: The branching increases when, for a constant number of vertices, a branch displaces from the terminal to a more central vertex in the largest graph chain. The sequel 2,5-MM, 2,4-MM, 2,3-MM suggests more branched isomers, one at which the branching vertices are at shorter distance. By combining this rule with the already stated Rule 7 we conclude that 3,4-MM should be viewed as more branched than 2,3-MM, and all the six descriptors of table 3 satisfy such an expectation. Comparison of the relative magnitude for the six descriptors of table 3 for 2-M and 3-E leads to the observation that, other things being equal, a more branched structure has longer branches. This observation is the basis for Rule 5 of Bonchev and Trinajstić [19]: In acyclic graphs branching increases when, for a constant number of vertices, the length of branches increases at the expense of shortening the largest graph chain.

The ambiguities and differences in opinions may arise when we want to establish the relative branching for isomers that have distinct branching patterns. For example, should 4-methylheptane be viewed as more branched than 2,5-dimethylhexane?
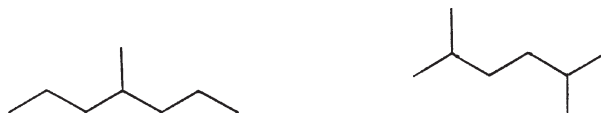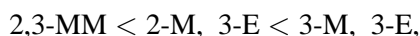

This is the case of overlap of distinct structural traits, which have been summarized in two distinct rules. But how do the two rules interlace? Here we had to rely on a selected descriptor and, as we see from table 3, different descriptors may give different answers. Even some cases of different branching patterns can be rationalized. Consider, for example, 2,2-dimethylhexane, 2,3-dimethylhexane and 3,3-dimethylhexane:

We can view the branching of 2,3-MM as between 2,2-MM and 3,3-MM, which is consistent with the already mentioned rules. Take one methyl group of 2,2-MM as moved toward the *center* of the molecule, the process that increases the branching according to stated rules. When the second methyl group of 2,2-MM is moved, we further increase the branching (and obtain 3,3-MM), hence

$$2,2\text{-MM} < 2,3\text{-MM} < 3,3\text{-MM}.$$

All six descriptors of table 3 support the above inequality. The same argument applies to establish the following branching inequalities:

$$2,2,4\text{-MMM} < 2,3,4\text{-MMM} < 2,3,3\text{-MMM},$$

$$2,2,4\text{-MM} < 2,2,3\text{-MMM} < 2,3,3\text{-MMM},$$

$$2,3\text{-MM} < 2\text{-M},\ 3\text{-E} < 3\text{-M},\ 3\text{-E},$$

all of which are satisfied by the six descriptors of table 3. However, the relative ordering of some pairs remain unresolved, such as the already mentioned 4-M and 2,5-MM, or 2,5-MM and 3-E, or 3-E and 2,2-MM, or 3,3-MM and 2-M, 3-E. The sample of 18 octanes is perhaps limited to resolve all such cases. We will proceed by considering nonane and decane isomers.

6. Isomers of nonane and decane

In table 4 we listed λ_1 [10], $\lambda\lambda_1$ (this work), W, WW [35] values for 35 isomers of nonane. As we see in the columns λ_1 and W, the leading eigenvalue of the adjacency matrix and the Wiener index are now of little use because of excessive degeneracy. Even, the WW index shows some degeneracy (2,2,5-MMM and 3,3-MM

Table 4
The leading eigenvalues of the adjacency matrix (A) and the path matrix (P) for
nonane isomers together with Wiener number and hyper-Wiener number WW.

Isomer	λ_1	$\lambda\lambda_1$	W	WW
n-octane	1.902	1.353080	120	330
2-M	1.962	1.341400	114	297
3-M	2	1.335624	110	275
4-M	2.015	1.333180	108	264
2,6-MM	2	1.329448	108	265
3-E	2.042	1.327308	104	242
4-E	2.053	1.324825	102	231
2,5-MM	2.036	1.323350	104	244
2,4-MM	2.061	1.320387	102	234
2,2-MM	2.117	1.319517	104	247
2,3-MM	2.084	1.319371	102	235
3,5-MM	2.074	1.316715	100	224
2-M, 4-E	2.084	1.314182	98	213
3,4-MM	2.112	1.312700	98	215
2-M, 3-E	2.119	1.310149	96	204
3,3-MM	2.165	1.309333	98	217
2,2,5-MMM	2.136	1.306821	98	217
4,4-MM	2.175	1.306327	96	207
2,3,5-MMM	2.117	1.306172	96	206
3-M, 4-E	2.136	1.305940	94	195
2,2,4-MMM	2.168	1.299633	94	198
3-M, 3-E	2.206	1.298488	92	188
2,3,4-MMM	2.165	1.297922	92	188
2,4-MM, 3-E	2.175	1.294829	90	178
2,2,3-MMM	2.216	1.294615	92	190
2,4,4-MMM	2.194	1.292480	92	189
2,3,3-MMM	2.236	1.290512	90	181
3,3-EE	2.236	1.290067	88	170
2,2-MM, 3-E	2.236	1.287282	88	171
3,3,4-MMM	2.247	1.286261	88	172
2,3-MM, 3-E	2.264	1.282085	86	163
2,2,4,4-MMMM	2.236	1.281855	88	173
2,3,3,4-MMMM	2.288	1.274028	84	156
2,2,3,4-MMMM	2.255	1.279160	86	164
2,2,3,3-MMMM	2.334	1.266410	82	149

have $WW = 217$, while 3-M, 3-E and 2,3,4-MMM have $WW = 188$). One may
even speculate that if λ_1 and W were initially examined for nonane and higher alkanes,
perhaps they would not have been suggested as the branching index or used as a guide
in defining molecular branching. The index WW shows limited degeneracy, but as
the size of the graph increases so also will the number of structures with identical
WW. Only $\lambda\lambda_1$ shows no degeneracy (and this is also true for the 75 decane isomers).

A number of larger trees that may result in producing the same leading eigenvalue $\lambda\lambda_1$ have been tested and so far all graphs have unique $\lambda\lambda_1$. Although larger alkanes have not yet been tested systematically, 35 nonanes and 75 decanes offer a sufficiency large pool of structures that may offer enough insight and allow their molecular branching to be quantified. So a derived definition of branching can then be extended to even larger structures.

The first thing to notice is that there is no longer a strict parallelism between W, WW and the leading eigenvalue $\lambda\lambda_1$. Again, if we consider well-defined sequences of structurally related isomers, we see that there is no dispute on the relative branching among such. Thus we arrive at inequalities

$$2\text{-M} < 3\text{-M} < 4\text{-M} < 5\text{-M},$$

$$2,5\text{-MM} < 2,4\text{-MM} < 2,3\text{-M} < 2,2\text{-MM},$$

$$2,2,5\text{-MMM} < 2,2,4\text{-MMM} < 2,2,3\text{-MMM},$$

$$2,2,4,4\text{-MMMM} < 2,2,3,4\text{-MMMM} < 2,3,3,4\text{-MMMM},$$

$$2,2,4,4\text{-MMMM} < 2,2,3,4\text{-MMMM} < 2,2,3,3\text{-MMMM},$$

etc.

However, we cannot immediately apply the rules to resolve, for example, which of the isomers 2,3,3,4-MMMM or 2,2,3,3-MMMM is more branched:

But, if we ignore the common part, 3,3-MM, of the two isomers and compare 2,4-dimethylpentane to 2,2-dimethylpentane (and analogous octane and nonane isomers 2,5-MM and 2,6-MM to 2,2-MM isomers, respectively), we can conclude that 2,2,3,3-MMMM is the most branched isomer.

There are a number of disagreements between the branching as determined by W and as determined by $\lambda\lambda_1$. These are illustrated in figure 2. None of the cases in dispute can be reduced to a simple structural rule, since in all cases *different* structural components are present in each isomer. Perhaps the only case that can be *reduced* is the case of 2,4-MM, 3-E and 2,4,4-MMM, which, when we eliminate one of the terminal methyl group it reduces to 2-methyl-3-ethylpentane and 3,3-dimethylhexane, respectively. The two isomers of octane have the same W, but the letter has smaller $\lambda\lambda_1$, showing consistency with the branching found for corresponding nonane isomers.

In table 5 we listed the branching indices (defined as $\lambda\lambda_1/n$) for 75 isomers of decane. It seems that it is simpler to propose a single invariant as governing the
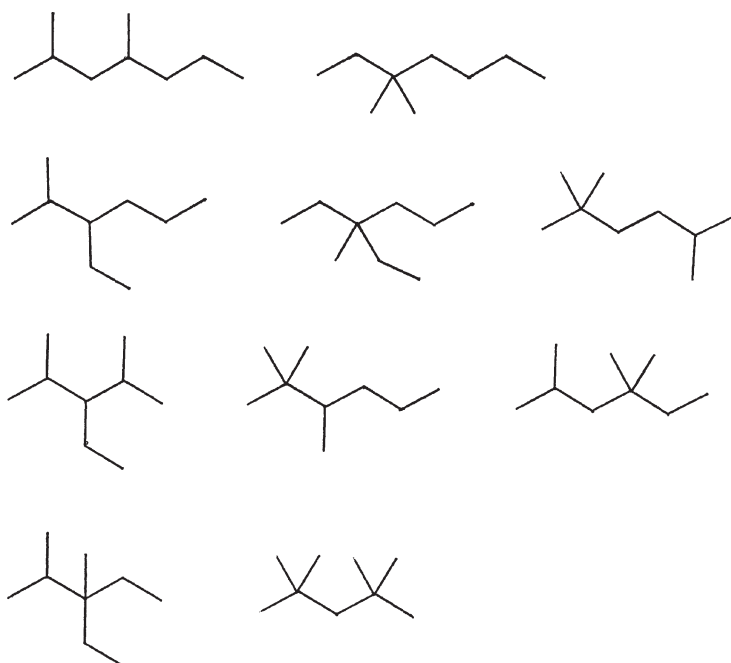
Figure 2.

definition of molecular branching than trying to extract a sequence of rules that only verbalizes the behavior of the chosen invariant. The selected invariant should parallel the regularities established for smaller alkanes (which can be formulated in a set of rules that hold for a family of closely related isomers). Ambiguities that originate when distinct structural families interlace are resolved by using the selected invariant as the criterion. Difficulty will arise when and if two non-isomorphic structures show the same invariant. So far this has not happened for either $\lambda\lambda_1$ and ω_1, but future work will show if these simple invariants will remain unique or not. We have selected here $\lambda\lambda_1$ as the chosen invariant for defining molecular branching for two reasons: (1) several larger acyclic graphs have been tested and did not produce duplicate $\lambda\lambda_1$, and (2) the path matrix has as entries real numbers while Wiener matrix has as entries integers. It is, thus, less likely that the leading eigenvalues of path matrix coincide.

7. Concluding remarks

Molecular branching will either remain a qualitative descriptor and as such be of limited use or the concept has to be rigorously defined and quantified. If we opt for the latter, then there appears to be two routes to such quantification: Either we set up a hierarchy of rules to cover all possible situations, or we search for a structural property that will discriminate among isomers. We advocate the latter route and propose the leading eigenvalue of the path matrix as the invariant that defines molecular branching.

Table 5
The leading eigenvalue $\lambda\lambda_1$ for 75 decane isomers.

	Isomer	$\lambda\lambda_1$		Isomer	$\lambda\lambda_1$
1	n-decane	1.398484			
2	2-M	1.388607	39	2,3,4-MMM	1.347694
3	3-M	1.383456	40	2,2,3-MMM	1.347064
4	4-M	1.380908	41	4-M, 4-E	1.346094
5	5-M	1.380133	42	2,4,4-MMM	1.344555
6	2,7-M	1.378562	43	2,2-MM 4-E	1.343963
7	3-E	1.375674	44	2-M, 3-iP	1.343529
8	2,6-MM	1.373237	45	3,4,5-MMM	1.343403
9	4-E	1.372299	46	2,3,3-MMM	1.342911
10	2,5-MM	1.370446	47	3,3,5-MMM	1.342715
11	2,2-MM	1.369885	48	2,3-MM, 4-E	1.341286
12	4-P	1.369694	49	2,4-MM, 3-E	1.340038
13	2,4-MM	1.369252	50	2,2,5,5-MMMM	1.339099
14	2,3-MM	1.369198	51	3,3-EE	1.338354
15	3,6-MM	1.367662	52	2,2-MM, 3-E	1.337368
16	2-M, 5-E	1.365032	53	3,3,4-MMM	1.337358
17	3,5-MM	1.364434	54	2,2,4,5-MMMM	1.337341
18	3,4-MM	1.362384	55	2,4-MM, 4-E	1.337264
19	2-M, 4-E	1.360985	56	3,4,4-MMM	1.336123
20	3,3-MM	1.360433	57	2,2,3,5-MMMM	1.335315
21	4,5-MM	1.360346	58	2,3,4,5-MMMM	1.334694
22	2-M, 3-E	1.359730	59	2,3-MM, 3-E	1.331870
23	2,2,6-MMM	1.359419	60	2,3,3,5-MMMM	1.330722
24	3-M, 5-E	1.358761	61	3,3-MM, 4-E	1.330491
25	2,3,6-MMM	1.358502	62	2,4-MM, 3-iP	1.329653
26	2,4,6-MMM	1.358140	63	3,4-MM, 3-E	1.328370
27	4-iP	1.356872	64	2,2,4,4-MMMM	1.327348
28	4,4-MM	1.355896	65	2,2,3,4-MMMM	1.327253
29	2,2,5-MMM	1.353570	66	2,3,4,4-MMMM	1.323866
30	3-M, 4-E	1.353408	67	2-M, 3,3-EE	1.323641
31	2,3,5-MMM	1.352217	68	2,2,4-MMM, 3-E	1.323444
32	3-E, 4-M	1.352167	69	2,3,3,4-MMMM	1.321811
33	2,4,5-MMM	1.350993	70	2,2,3,3-MMMM	1.319127
34	2,2,4-MMM	1.349920	71	2,3-MM, 3-iP	1.317098
35	2,5,5-MMM	1.349444	72	3,3,4,4-MMMM	1.312183
36	3-M, 3-E	1.349397	73	2,2,3-MMM, 3-E	1.310881
37	2,5-M, 3-E	1.348083	74	2,2,3,4,4-MMMMM	1.310514
38	3,4-EE	1.347830	75	2,2,3,3,4-MMMMM	1.304239

One can view the path matrix as evolving from the adjacency matrix and the distance matrix, being closely related to the latter. The leading eigenvalue of the adjacency matrix was initially proposed (by Lovasz and Pelikan) as a branching index. Our suggestion that this privileged position be awarded to the leading eigenvalue of the path matrix can be viewed as a natural extension of the initial definition of molecular branching.

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