Symmetry-Aided Computation of the Detour Matrix and the Detour Index

Gerta Rücker and Christoph Rücker*

Institut für Organische Chemie und Biochemie, Universität Freiburg, Albertstrasse 21,
D-79104 Freiburg, Germany

A computer program for calculating the graph-theoretical detour matrix is introduced, which uses the topological symmetry of a graph to minimize path-tracing. The high performance of the program allows one to treat graphs of the complexity of fullerenes (e.g., C_{60}). A more logical definition of the detour matrix and the detour index ω than is presently in use is proposed. Index ω is probed as a descriptor for boiling points of acyclic and cyclic alkanes. The detour index in combination with the Wiener index W is more useful than Hosoya's Z index for regression of the boiling points of a large sample of compounds containing all acyclic and cyclic alkanes with known boiling points from methane up to polycyclic octanes.

The graph-theoretical detour matrix Δ has recently found some interest in chemistry.[1] For a graph of n vertices it is a symmetric integer $[n \times n]$ - matrix, the i,j-entry of which $[(\Delta)_{ij}]$ is the length of the *longest* path from vertex i to vertex j. It is thus a complement to the distance matrix, whose i,j-element is the length of the *shortest* path from i to j. Just like the distance matrix, the detour matrix promises to be of some value as a source of useful graph-theoretical invariants.[1-3] The detour matrix as presently in use has zeros as the diagonal elements $(\Delta)_{ii}$, without a convincing reason.[4] It is, however, more logical to define the diagonal elements as the length of the longest path from vertex i to itself (i.e. the size of the longest cycle containing vertex i). Accordingly, instead of the detour index ω, defined as the half-sum of the traditional detour matrix elements, we propose to use ω', the half-sum of the detour matrix elements including non-zero elements in the main diagonal.

Although the distance matrix of a given graph is easily calculated from its adjacency matrix,[6] an efficient, that is, polynomial time method for calculating the detour matrix is not available. In fact, the problem of finding longest paths in a graph is said to be NP-complete,[5] which means that the effort (computer time) required for a particular instance increases exponentially with increasing n.

Accordingly, both available methods for calculating the detour matrix are exponential in n: The first is the natural paper-and-pencil approach of path-tracing, which was computerized and nicely illustrated recently.[7,8] The second method is constructing all spanning trees of the graph and finding the i,j-element of the detour matrix as the maximum i,j-element in the distance matrices of all the spanning trees.[9] The number of spanning trees to be constructed and evaluated increases exponentially with increasing size and cyclicity. For example, the numbers of spanning trees of the 18-vertex cubic graph in Figure 1 (the Blanusa graph) and of the graph of (perhydro)buckminsterfullerene are given as 1 037 136 and 375 291 866 372 898 816 000, respectively.[10]

In such a situation, a method is in demand that in spite of the unavoidable exponential dependence on n gives reasonable computing times in the cases of practical interest. It is

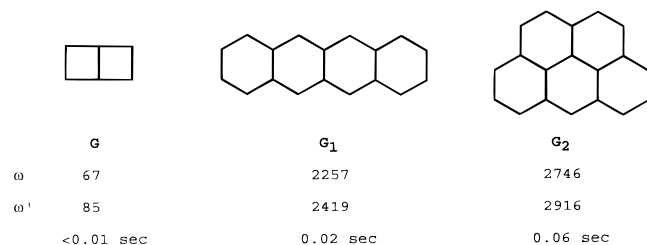

ω 2570
ω' 2723
0.23 sec
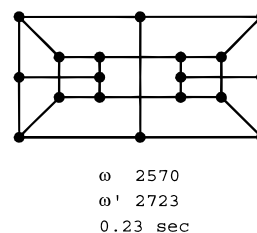
Figure 1. The Blanusa graph, its ω and ω' values, and the CPU time required to calculate them.

therefore essential to avoid path-tracing wherever possible, and this can be done above all by profiting from the symmetry that may be present in a given graph and by immediately using new information on the graph that may be uncovered in the process. In 1990, we published a computer program (POLCYC) that traces longest cycles and paths in a polycyclic graph for the purpose of IUPAC naming and numbering.[11] POLCYC uses the topological symmetry information as obtained in a prior run of TOPSYM, an efficient, mathematics-based[12] symmetry recognition program that depends on evaluation of the powers of the adjacency matrix and the class matrix.[13] TOPSYM partitions not only vertices and edges but also non-edges (pairs of vertices more than one edge apart) into equivalence classes. We now adjusted these procedures to the present problem, and here report on the resulting computer program DETOUR.

A DETOUR run is made of two parts. The first part is a TOPSYM run, the second part essentially is a depth-first search that for each pair of vertices $[(i,j)$, where $j = i, ..., n]$ traces the longest path from i to j by attaching a new vertex k to the string of vertices already lined up under a set of conditions. The conditions include, along with the conditions of path-tracing

k is a neighbor of the last vertex in the string,
k is not yet contained in the string,

the use of symmetry

the pair (i, j) is treated only if it is not equivalent by symmetry to a pair already treated,[14]

and the use of newly acquired information

Figure 2. Three graphs, their ω and ω' values, and the CPU times required to calculate them.

Table 1. Results of DETOUR for Some (Perhydro)fullerene Graphs[a]

fullerene	n	W	ω	ω'	CPU time, s	CPU time TOPSYM only, s
1 C_{20} (I_h)	20	500	3550[b]	3750[b]	0.02	0.01
2 C_{24} (D_{6d})	24	804	6330[b]	6618[b]	0.26	0.02
3 C_{26} (D_{3h})	26	987	8125	8463	0.57	0.03
4 C_{28} (T_d)	28	1194	10206	10598	0.48	0.04
5 C_{30} (D_{5h})	30	1435	12605[b]	13055[b]	2.63	0.04
6 C_{32} (D_3)	32	1687	15376	15888	5.75	0.07
7 C_{34} (C_{3v})	34	1971	18513	19091	8.75	0.07
8 C_{36} (D_{6h})	36	2292	22050	22693	13.47	0.07
9 C_{38} (D_{3h})	38	2651	26008[b]	26730[b]	69.70	0.10
10 C_{38} (C_{3v})	38	2629	26011	26733	48.38	0.11
11 C_{40} (T_d)	40	3000	30420	31220	30.59	0.09
12 C_{40} (C_{3v})	40	3000	30420	31220	133.38	0.13
13 C_{40} (D_{5d})	40	2990	30420	31220	24.18	0.10
14 C_{42} (D_3)	42	3390	35301	36183	195.78	0.14
15 C_{44} (T)	44	3830	40678	41646	217.88	0.15
16 C_{44} (D_{3h})	44	3818	40678	41646	185.71	0.14
17 C_{46} (C_3)	46	4281	46575	47633	1405.18	0.27
18 C_{48} (D_3)	48	4764	53016	54183	2396.68	0.24
19 C_{50} (D_{5h})	50	5275	60025	61275	597.88	0.20
20 C_{60} (I_h)	60	8340	104430	106230	4572.50	0.26

[a] Graphs appear in ref 17. [b] These values are *not* those of the corresponding complete graphs K_n.

as soon as for a pair (i, j) a path of a certain length l is found, for the same pair any further paths of length $\leq l$ are ignored,

in the case of a Hamiltonian cycle (containing all vertices, length n) being detected in the treatment of the first vertex (vertex pair (1,1)), for all other vertices a search for longest cycles is not required, and for all pairs (i, j) with i and j being neighbors along the Hamiltonian cycle and for all pairs equivalent by symmetry to them the length of the longest path is set to $n - 1$ without any path-tracing.

Many molecular structures of interest consist of a (poly)-cyclic core and tree-like attachments, and the core often contains a Hamiltonian cycle; for example, most graphs in refs 1, 7, and 15 are of this type. In order to use the Hamiltonicity also in these cases, the vertices in the tree-like attachments are initially recognized and marked as such. For these vertices, the diagonal elements of the detour matrix are at once set to zero. A Hamiltonian cycle in the core may then be found as a path from the first non-marked vertex to itself containing all non-marked vertices.

The output of the program for a given graph is (along with the Wiener index, W, a spin-off of the TOPSYM procedure) the detour matrix Δ (nonzero diagonal elements) and the detour index given in two variants, ω without (for comparison with published values) and ω' with inclusion of the nonzero diagonal elements. Optionally, the paths traced may be printed.

The program was tested on all graphs appearing in refs 1, 7, and 15, and it reproduced all the detour index values published there.[16] The CPU times required were reasonably short. Thus, the graphs in Table 2 of ref 1 ($n \leq 10$) each required <0.01 s of CPU time on a SG Indigo workstation (150 MHz, R5000 coprocessor). Graphs G ($n = 6$), G_1 ($n = 18$), and G_2 ($n = 19$) (Figure 2) used <0.01, 0.02, and 0.06 s, respectively, on this computer, to be compared with 1.0, 25.7, and 123.5 s, respectively, reported earlier using the spanning-tree procedure on a HP-735 workstation.[1,9b] The largest bicyclic graph in ref 7 ($n = 26$) required 0.08 s, whereas the polycycle in Figure 1 ($n = 18$) required 0.23 s. The higher performance of the new procedure compared with existing ones allowed us to treat the (perhydro)fullerene graphs appearing in ref 17 ($20 \leq n \leq 60$); the results are given in Table 1. Note that the detour index is not a very discriminant topological index: for most (but not all) of the fullerenes in Table 1, the detour matrix and thus ω and ω' are identical to those of the corresponding complete graphs K_n.[18] The last column in Table 1 gives the CPU times required for the symmetry recognition by TOPSYM, demonstrating how efficiently this information is obtained.

APPLICATION

The detour index gained some interest recently because in combination with the Wiener index W it gave remarkable correlations with the boiling points (bps) of alkanes, notably including some cycloalkanes. Thus, for a sample of open-chain and monocyclic alkanes ($n = 1-10$), Lukovits[2] found a correlation of the type

$$\text{bp} = a(W\omega)^{0.125} + b$$
$$(r = 0.994, s = 6.4\ °C, N = 77) \quad (1)$$

to be significantly superior to the well-known correlation of bps with $n^{0.5}$ ($r = 0.986$, $s = 10.1$ °C, $N = 77$).

Trinajstić et al.,[1] using an almost identical sample of open-chain and monocyclic alkanes, obtained the nonlinear regression[19,20]

$$\text{bp} = a(W\omega)^c + b$$
$$(r = 0.9948, s = 6.2 \text{ for } c = 0.13066, N = 76) \quad (2)$$

We were intrigued by the fact that the aforementioned sample contained all open-chain alkanes from methane to the octanes, but only a few cycloalkanes, without a selection criterion being given. If the aforementioned correlation is real (i.e., reflects some underlying physics), then it should be generalizable.

Further, the best single topological descriptor for the bps of acyclic[21] as well as cyclic alkanes to date is Hosoya's Z index. In fact, Hosoya's pioneering study of the bps of acyclic and cyclic alkanes is still the standard against which any new development in the field should be tested.[22] Unfortunately, in that work neither r nor s values were given. The structures and bp values for the compounds considered, which are up to tricyclic, were also not given. For these reasons, we extracted from the Beilstein database all the mono- and polycyclic butanes through octanes for which a

bp at normal pressure is available. These additional 104 cyclic alkanes (i.e., those not contained in Trinajstić's sample,[1] including up to tetracyclic ring systems, spiro compounds and *bis*-monocyclic assemblies) are shown in Figure 3. The W, ω, Z, ω', and bp values of the additional alkanes are given in Table 2.

Many topological indices (TIs), such as W, ω, and Z strongly increase with increasing size of the molecule, just as do many properties, such as the bp. Therefore, the most critical test for a TI's correlation ability is how it behaves for a sample of compounds of constant n (e.g., the octanes). For his subsample of 18 acyclic and 11 monocyclic octanes, Lukovits[2] found the correlation

$$bp = a(W\omega)^{0.125} + b$$

$$(r = 0.790, s \text{ not given}, N = 29) \quad (3)$$

was superior to correlations with W or ω alone. We were able to reproduce this result,[19,20] obtaining

$$bp = a(W\omega)^{0.125} + b$$

$$(r = 0.771, s = 6.43, N = 28) \quad (4)$$

However, for the same sample, Z ($r = 0.897$, $s = 4.46$), $\log Z$ ($r = 0.866$, $s = 5.04$), and $(W\omega)^{1.0}$ ($r = 0.814$, $s = 5.86$) are more accurate single descriptors. The best two-variable linear regression uses Z and n_r (n_r = number of rings, $r = 0.932$, $s = 3.75$), as suggested by Hosoya's work.[22] Because this sample of octanes included the acyclic octanes (for which $\omega = W$ is known to be a poor descriptor for bps), it could be hoped that a regression analogous to eq 4 for the monocyclic octanes alone would perform better. This turned out to be the case, but only marginally so:

$$bp = a(W\omega)^{0.125} + b$$

$$(r = 0.908, s = 5.21, N = 10) \quad (5)$$

Again, Z ($r = 0.955$, $s = 3.70$) and $\log Z$ ($r = 0.950$, $s = 3.89$) are better single descriptors for this sample.

The 10 structures forming the latter sample are cyclopentane and cyclohexane derivatives along with cyclooctane itself. When the sample is broadened to all monocyclic octanes in our set (i.e., derivatives of cyclopropane, cyclobutane, and cycloheptane as well), the correlation deteriorates to

$$bp = a(W\omega)^{0.125} + b$$

$$(r = 0.783, s = 8.01, N = 32) \quad (6)$$

Here also, Z ($r = 0.881$, $s = 6.10$), $\log Z$ ($r = 0.876$, $s = 6.21$), and $(W\omega)^{1.0}$ ($r = 0.793$, $s = 7.84$) are better single descriptors.

Finally, broadening the sample to all acyclic, mono- and polycyclic octanes leads to

$$bp = a(W\omega)^{0.125} + b$$

$$(r = 0.739, s = 8.61, N = 76) \quad (7)$$

For this sample $(W\omega)^{1.0}$ is better ($r = 0.770$, $s = 8.15$), whereas $\log Z$ ($r = 0.687$, $s = 9.29$) and Z ($r = 0.674$, $s =$
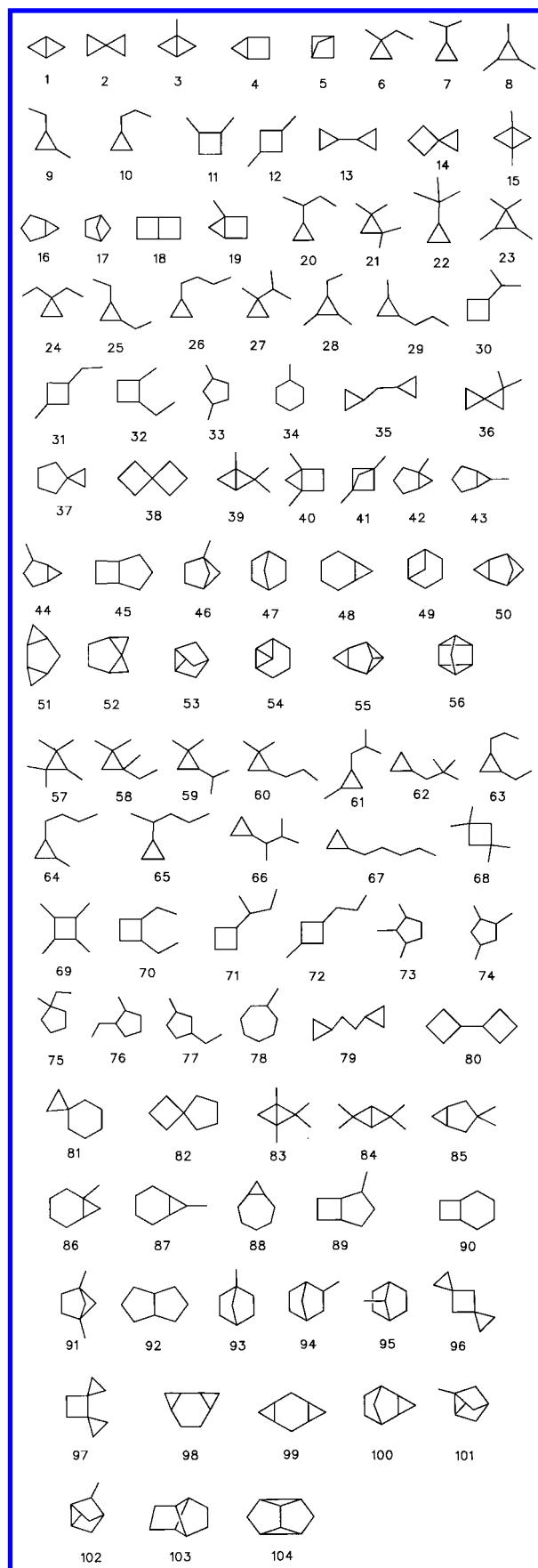
Figure 3. Structures of the compounds in Table 2.

9.44) are less suitable as single independent variables. The best three-variable linear regression uses Z, n_r, and ω' ($r = 0.892$, $s = 5.85$).

Table 2. Some TIs and Experimental Boiling Points of Mono- and Polycyclic Butanes through Octanes (as far as normal pressure bp data are available and the substances did not appear in Trinajstić's sample)

#	n_r	n	W	ω	Z	ω'	bp	#	n_r	n	W	ω	Z	ω'	bp
1	2	4	7	17	8	25.0	8.0	53	3	7	33	111	41	132.0	106.0
2	2	5	14	28	12	35.5	39.0	54	3	7	37	115	42	139.5	110.0
3	2	5	14	29	11	37.0	33.5	55	4	7	34	119	50	143.5	104.0
4	2	5	14	37	13	49.5	46.0	56	4	7	32	125	50	149.5	108.5
5	2	5	14	32	13	42.0	36.0	57	1	8	56	77	26	81.5	100.5
6	1	6	27	36	14	40.5	57.0	58	1	8	59	78	28	82.5	104.5
7	1	6	28	37	14	41.5	58.5	59	1	8	62	81	28	85.5	94.0
8	1	6	27	39	14	43.5	63.0	60	1	8	67	86	32	90.5	106.0
9	1	6	29	40	15	44.5	63.0	61	1	8	69	86	33	90.5	110.5
10	1	6	31	40	16	44.5	69.0	62	1	8	65	78	28	82.5	106.0
11	1	6	27	45	15	53.0	62.0	63	1	8	72	91	40	95.5	102.0
12	1	6	28	44	14	52.0	59.0	64	1	8	53	91	39	95.5	124.0
13	2	6	27	45	20	54.0	76.0	65	1	8	69	82	38	86.5	117.7
14	2	6	25	50	20	61.0	69.5	66	1	8	64	77	34	81.5	115.5
15	2	6	24	45	15	53.0	55.0	67	1	8	78	91	42	95.5	128.0
16	2	6	24	66	21	84.0	81.0	68	1	8	60	84	23	92.0	86.0
17	2	6	23	62	21	77.0	71.0	69	1	8	60	92	34	100.0	106.0
18	2	6	25	67	22	85.0	83.0	70	1	8	66	98	42	106.0	119.0
19	2	6	24	56	18	68.5	60.5	71	1	8	66	90	41	98.0	123.0
20	1	7	45	56	24	60.5	90.5	72	1	8	71	95	38	103.0	117.4
21	1	7	39	54	16	58.5	76.0	73	1	8	58	109	36	121.5	117.0
22	1	7	41	52	18	56.5	80.5	74	1	8	59	108	34	120.5	115.0
23	1	7	40	56	19	60.5	78.0	75	1	8	59	103	37	115.5	121.5
24	1	7	43	54	24	58.5	88.6	76	1	8	61	111	40	123.5	124.7
25	1	7	47	62	25	66.5	90.0	77	1	8	63	109	39	121.5	121.0
26	1	7	51	62	26	66.5	98.0	78	1	8	61	142	42	166.5	134.0
27	1	7	41	52	20	56.5	81.5	79	2	8	72	98	52	107.0	129.0
28	1	7	44	60	23	64.5	91.0	80	2	8	64	112	58	128.0	136.0
29	1	7	43	62	24	66.5	93.0	81	2	8	58	131	52	152.0	125.0
30	1	7	44	64	24	72.0	93.0	82	2	8	57	125	53	143.5	128.0
31	1	7	46	66	24	74.0	89.5	83	2	8	54	93	33	101.0	105.0
32	1	7	44	68	25	76.0	94.0	84	2	8	59	93	32	101.0	104.0
33	1	7	41	78	23	90.5	91.3	85	2	8	56	124	39	142.0	115.0
34	1	7	42	90	26	108.0	101.0	86	2	8	56	146	47	170.5	125.0
35	2	7	46	68	32	77.0	102.0	87	2	8	58	150	52	174.5	138.0
36	2	7	38	64	24	71.5	78.0	88	2	8	58	165	55	197.0	141.0
37	2	7	38	85	32	100.5	98.5	89	2	8	56	150	52	174.5	130.5
38	2	7	40	80	32	94.0	96.5	90	2	8	58	168	57	200.0	133.0
39	2	7	38	67	23	75.0	84.0	91	2	8	53	115	37	130.0	91.0
40	2	7	37	80	25	92.5	74.0	92	2	8	55	171	56	203.0	137.0
41	2	7	38	68	22	78.0	71.5	93	2	8	52	135	46	155.5	117.0
42	2	7	37	93	29	111.0	91.5	94	2	8	54	141	50	161.5	125.0
43	2	7	39	96	32	114.0	103.0	95	2	8	53	142	52	162.5	128.0
44	2	7	38	94	31	112.0	100.0	96	3	8	58	108	56	122.0	103.0
45	2	7	38	111	35	135.5	110.5	97	3	8	54	112	60	126.0	117.0
46	2	7	36	86	28	101.0	81.5	98	3	8	54	170	63	202.0	149.0
47	2	7	36	103	34	123.5	105.5	99	3	8	55	170	64	202.0	142.0
48	2	7	39	109	34	133.5	116.0	100	3	8	51	166	66	193.5	136.0
49	2	7	38	102	34	123.0	110.0	101	3	8	49	149	57	170.0	111.0
50	3	7	35	106	41	127.0	107.0	102	3	8	50	152	62	173.0	120.0
51	3	7	36	113	40	137.5	110.0	103	3	8	50	180	72	212.0	125.0
52	3	7	35	112	39	136.5	107.5	104	4	8	48	191	82	223.0	138.0

For the combined sample (all acyclic alkanes from methane to the octanes plus all cyclic alkanes with known bp values from cyclopropane to a tetracyclooctane plus the few cyclic nonanes and decanes included in Trinajstić's sample, altogether 180 structures) we obtained

$$bp = a(W\omega)^c + b$$
$$(r = 0.987, s = 7.17 \text{ for } c = 0.12972, N = 180) \quad (8)$$

However, $(W\omega)^{0.125}$ is almost as good ($r = 0.987$, $s = 7.19$). In terms of s, this is slightly worse than eq 2 for the earlier subsample, but still remarkable for this large number of compounds of rather diverse structure. In fact, this correlation is better than those using $n^{0.5}$ ($r = 0.966$, $s = 11.4$) or log Z ($r = 0.953$, $s = 13.5$) as a single independent variable.

Having aimed at a sample of compounds as comprehensive as possible in the $n = 1-8$ range, we next tried to obtain a sample of compounds with bps as reliable as possible. Using the Beilstein database and the primary literature, we therefore excluded all those compounds whose bps had not been reported concordantly by at least two independent research groups (difference <4 °C). The bps of 37 structures in Table 2 were deemed unreliable by this criterion (#1, 3, 5, 19, 22, 28, 32, 36, 38, 40, 41, 44, 46, 49, 50, 52, 56, 57, 59−66, 69, 71, 84, 89, 91, 95−98, 102, 104), whereas those of Trinajstić's sample[1] were all found reliable (after correction of errors[20]). For the sample of acyclic and mono- and polycyclic octanes with reliable bps we obtained

$$\mathrm{bp} = a(W\omega)^{0.125} + b$$

$$(r = 0.782,\ s = 7.26,\ N = 56) \quad (9)$$

to be compared with eq 7. Again $(W\omega)^{1.0}$ gives a better regression ($r = 0.809$, $s = 6.85$), and $\log Z$ ($r = 0.774$, $s = 7.37$) and Z ($r = 0.751$, $s = 7.68$) give less precise regressions.

For the combined sample of all alkanes with reliable bps from methane to acyclic and polycyclic octanes plus the few cyclic nonanes and decanes included in Trinajstić's sample, we obtained

$$\mathrm{bp} = a(W\omega)^{c} + b$$

$$(r = 0.992,\ s = 6.12 \text{ for } c = 0.12941,\ N = 143) \quad (10)$$

to be compared with eq 8. Again $(W\omega)^{0.125}$ is almost as good ($r = 0.992$, $s = 6.16$). So, in the samples with reliable bps, the s values are lower by more than one degree than in the samples including unreliable bps. For the same sample ($N = 143$), the best five-variable multilinear regression found in this work uses ω, ω', $\log Z$, n_r, and $(W\omega)^{0.125}$ ($r = 0.996$, $s = 4.28$). Use of ω' instead of ω resulted in slightly poorer statistics in most cases.

CONCLUSION

The detour index ω in combination with the Wiener index W proved to be useful for regression of bps in a large combined sample of acyclic, monocyclic, and polycyclic alkanes. However, for a sample of constant n (the octanes), the detour index is inferior to Z or variants thereof.

EXPERIMENTAL SECTION

The program DETOUR, written in FORTRAN 77, is obtainable from the authors, as is a list of the regression coefficients in eqs 4−10. Experimental bps given are averages if more than one measurement is reported in the literature. In the case of stereoisomers, the bp given is an average over the available values of stereoisomers. Regression analyses were performed using the statistics software SAS.

REFERENCES AND NOTES

(1) For a leading reference see Trinajstić, N.; Nikolić, S.; Lucić, B.; Amić, D.; Mihalić, Z. The Detour Matrix in Chemistry. *J. Chem. Inf. Comput. Sci.* **1997**, *37*, 631−638.

(2) Lukovits, I. The Detour Index. *Croat. Chem. Acta* **1996**, *69*, 873−882.

(3) Randić, M. On Characterization of Cyclic Structures. *J. Chem. Inf. Comput. Sci.* **1997**, *37*, 1063−1071.

(4) (a) Historical note: Harary, when introducing the detour matrix, did not explicitly define its diagonal elements.[5] Instead, he gave as an example the detour matrix of one graph. This graph happened to be a directed graph in which actually a closed circuit did not exist for any vertex. The main diagonal entries given were all zeros. Subsequent authors interpreted these zeros as zeros by definition. (b) In ref 3 for cyclic graphs a matrix D/DD is defined, an element of which is the quotient of a distance matrix element and the corresponding detour matrix element. The definition of Δ proposed here avoids the problem of division by zero in the main diagonal of this matrix.

(5) (a) Harary, F. *Graph Theory*; Addison-Wesley: Reading, MA, 1969. (b) Buckley, F.; Harary, F. *Distance in Graphs*; Addison-Wesley: Reading, MA, 1990.

(6) Müller, W. R.; Szymanski, K.; Knop, J. V.; Trinajstić, N. An Algorithm for Construction of the Molecular Distance Matrix. *J. Comput. Chem.* **1987**, *8*, 170−173.

(7) Lukovits, I.; Razinger, M. On Calculation of the Detour Index. *J. Chem. Inf. Comput. Sci.* **1997**, *37*, 283−286.

(8) For early computer realizations of path- and ring-tracing see references given in ref 11 and the following: Zamora, A. An Algorithm for Finding the Smallest Set of Smallest Rings. *J. Chem. Inf. Comput. Sci.* **1976**, *16*, 40−43. Randić, M.; Brissey, G. M.; Spencer, R. B.; Wilkins, C. L. Search for All Self-Avoiding Paths for Molecular Graphs. *Comput. Chem.* **1979**, *3*, 5−13, and references cited therein.

(9) (a) Nikolić, S.; Trinajstić, N.; Jurić, A.; Mihalić, Z. The Detour Matrix and the Detour Index of Weighted Graphs. *Croat. Chem. Acta* **1996**, *69*, 1577−1591. (b) Trinajstić, N.; Nikolić, S.; Mihalić, Z. On Computing the Molecular Detour Matrix. *Int. J. Quantum Chem.* **1997**, *65*, 415−419.

(10) Nikolić, S.; Trinajstić, N.; Jurić, A.; Mihalić, Z.; Krilov, G. Complexity of Some Interesting (Chemical) Graphs. *Croat. Chem. Acta* **1996**, *69*, 883−897.

(11) Rücker, G.; Rücker, C. Nomenclature of Organic Polycycles Out of the Computer − How to Escape the Jungle of the Secondary Bridges. *Chimia* **1990**, *44*, 116−120.

(12) Klin, M.; Rücker, C.; Rücker, G.; Tinhofer, G. *Algebraic Combinatorics in Mathematical Chemistry. Methods and Algorithms. I. Permutation Groups and Coherent (Cellular) Algebras. Technical Report*, Technical University Munich, 1995.

(13) (a) Rücker, G.; Rücker, C. Computer Perception of Constitutional (Topological) Symmetry: TOPSYM, a Fast Algorithm for Partitioning Atoms and Pairwise Relations among Atoms into Equivalence Classes. *J. Chem. Inf. Comput. Sci.* **1990**, *30*, 187−191. (b) Rücker, G.; Rücker, C. On Using the Adjacency Matrix Power Method for Perception of Symmetry and for Isomorphism Testing of Highly Intricate Graphs. *J. Chem. Inf. Comput. Sci.* **1991**, *31*, 123−126. (c) Rücker, G.; Rücker, C. Isocodal and Isospectral Points, Edges, and Pairs in Graphs and How to Cope with Them in Computerized Symmetry Recognition. *J. Chem. Inf. Comput. Sci.* **1991**, *31*, 422−427.

(14) Another use of symmetry information is the following: vertex k is attached to a vertex string only if its relations to the vertices already in the string and to vertex j are not equivalent by symmetry to those of a previously tried vertex k'. Such a test, however, in most cases does not pay in terms of CPU time and therefore is not routinely performed in DETOUR.

(15) Amić, D.; Trinajstić, N. On the Detour Matrix. *Croat. Chem. Acta* **1995**, *68*, 53−62.

(16) Exceptions were graph 24 in ref 15, in which case DETOUR found the correct ω value (41) instead of the erroneous one (37) given there and not detected in ref 7, and the bicyclus with "$k = 15$, $m = 6$, $n = 3$" in ref 7, whose correct ω value is 2823 instead of the published 3658.

(17) Laidboeur, T.; Cabrol-Bass, D.; Ivanciuc, O. Determination of Topological Equivalence Classes of Atoms and Bonds in C_{20}-C_{60} Fullerenes Using a New Prolog Coding Program. *J. Chem. Inf. Comput. Sci.* **1996**, *36*, 811−821.

(18) Randic, M.; DeAlba, L.; Harris, F. E. Graphs with the Same Detour Matrix. *Croat. Chem. Acta* **1998**, *71*, 53−68.

(19) One compound not fitting the inclusion criteria ("cyclohexane, 1,2-dimethylene") in Lukovits's sample was left out in Trinajstić's and our studies.

(20) Lukovits's and Trinajstić's data sets contain several incorrect bps. The most important corrections made in the present study are as follows (°C): methane, −161.5; 2,2-dimethylpentane, 79.2; 2,3-dimethylpentane, 89.7; isopropylcyclohexane, 154.8; 1,2,4-trimethylcyclohexane, 144.8; methylcyclopropane, 0.7; 1,1,3-trimethylcyclopentane, 104.9.

(21) Gao, Y.; Hosoya, H. Topological Index and Thermodynamic Properties. IV. Size Dependence of the Structure-Activity Correlation of Alkanes. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 3093−3102. See also Randić, M. Comparative Regression Analysis; Regressions Based on a Single Descriptor. *Croat. Chem. Acta* **1993**, *66*, 289−312.

(22) Hosoya, H.; Kawasaki, K.; Mizutani, K. Topological Index and Thermodynamic Properties. I. Empirical Rules on the Boiling Point of Saturated Hydrocarbons. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 3415−3421.