

Topological Organic Chemistry. 11. Graph Theory and Reciprocal Schultz-Type Molecular Topological Indices of Alkanes and Cycloalkanes

Harry P. Schultz*,†

Department of Chemistry, University of Miami, Coral Gables, Florida 33124

Tor P. Schultz

Forest Products Laboratory, Mississippi State University, Mississippi State, Mississippi 39762

Received March 23, 1998

Various models of reciprocal and constant-interval reciprocal Schultz-type topological indices are described and illustrated with alkanes and cycloalkanes. The utility of the descriptors is briefly examined with quantitative–structural relationship studies.

INTRODUCTION

This paper extends the original study¹ of the Schultz index (S, MTI),

$$MTI = S = \sum_{i=1}^N [\nu(A + D)] \quad (1)$$

where A and D represent graph adjacency and distance matrices, and ν is the vector of all the vertex valences of a given graph, and invites attention to its reciprocal analogue (RS). Because interactions between atoms of a molecule decrease as their bond distances increase, Plavšić et al.² formulated an index (H), named in honor of Frank Harary, as a reciprocal analogue of the Wiener index (W).³

$$RW = H = (1/2) \sum_i \sum_j 1/[D]_{ij} = (1/2) \sum_i \sum_j [RD]_{ij} \quad (2)$$

Topological distance matrices (D) composed of reciprocal elements (RD), as just defined, instead of edge count integers, were examined in detail by, among others, Ivanciuc et al.⁴ and Diudea and Gutman.⁵ Diudea⁶ comprehensively reviewed and summarized research on reciprocal analogues of Wiener and Schultz indices, as well as extending applications of RD matrices.

The purpose of this present effort was to examine the use of RD matrices for deriving reciprocal Schultz (RS) and various modified reciprocal Schultz topological indices. Three objectives were sought with these experiments. Firstly, Bertz^{7,8} emphasized the desirability of increased topological index values of molecules as their complexities - chain lengths, branchings, cyclizations, etc. - increased. Prior studies¹ and reviews⁹ of the S indices of alkanes derived from D matrices displayed decreasing S index values as alkane isomer branchings increased. It was to be expected that related experiments using RD matrices for the generation of RS indices would effect a reverse trend; that is, an increase in index values with increase of molecular complexities (Table 1). Secondly, the utility of RS topological indices in reflecting quantitative–structural property relationships (QSPR) of the alkane sequence of ethane through the octane isomers was examined (Table 2). To this end, the boiling

5
|
1-2-3-4

(a)

| | | | | |
|------|------|------|------|------|
| 0 | 1 | 0.50 | 0.33 | 0.50 |
| 1 | 0 | 1 | 0.50 | 1 |
| 0.50 | 1 | 0 | 1 | 0.50 |
| 0.33 | 0.50 | 1 | 0 | 0.33 |
| 0.50 | 1 | 0.50 | 0.33 | 0 |

(c)

| | | | | |
|------|------|------|------|------|
| 0 | 1 | 0.67 | 0.33 | 0.67 |
| 1 | 0 | 1 | 0.50 | 1 |
| 0.50 | 1 | 0 | 1 | 0.50 |
| 0.33 | 0.67 | 1 | 0 | 0.33 |
| 0.67 | 1 | 0.67 | 0.33 | 0 |

(e)

| | | | | |
|---|---|---|---|---|
| 0 | 1 | 2 | 3 | 2 |
| 1 | 0 | 1 | 2 | 1 |
| 2 | 1 | 0 | 1 | 2 |
| 3 | 2 | 1 | 0 | 3 |
| 2 | 1 | 2 | 3 | 0 |

(b)

| | | | | |
|------|------|------|------|------|
| 0 | 1 | 0.67 | 0.33 | 0.67 |
| 1 | 0 | 1 | 0.67 | 1 |
| 0.67 | 1 | 0 | 1 | 0.67 |
| 0.33 | 0.67 | 1 | 0 | 0.33 |
| 0.67 | 1 | 0.67 | 0.33 | 0 |

(d)

| | | | | |
|------|------|------|------|------|
| 0 | 1 | 0.80 | 0.60 | 0.80 |
| 1 | 0 | 1 | 0.80 | 1 |
| 0.80 | 1 | 0 | 1 | 0.80 |
| 0.60 | 0.80 | 1 | 0 | 0.60 |
| 0.80 | 1 | 0.80 | 0.60 | 0 |

(f)

Figure 1. (a) 2-Methylbutane graph; (b) D matrix; (c) RD matrix; (d) CIRD matrix, matrix N_{\max} ; (e) CIRD matrix; vector N_{\max} ; (f) CIRD matrix, $N_{\max}5$.

point–descriptor (Table 3) and heat of formation–descriptor (Table 4) relationships were evaluated by regression studies. And finally, the degeneracy of indices obtained by use of RD matrices for the generation of various RS descriptors of both linear (Table 2) and cyclic (Table 5) alkanes was assessed.

These studies of RS topological indices were initiated in spite of the expectation of a possible flaw in the use of RD matrices from which to extract molecular topological indices.

COMPUTATIONS

The study of the use of RD matrices for obtaining RS topological indices was initiated with reservation. Unlike with the D matrix integers, there are not constant reciprocal edge count intervals between adjacent vertices of graphs described with RD matrices. This disparity is illustrated with data presented in Table 6 where columns 1 and 2 list the integer edge counts and the corresponding constant differences between adjacent edge counts for a 10-unit representation. By contrast, the reciprocal vertex edge count intervals between vertices summarized in the data of columns 3 and

† Present address: P.O. Box 262, Big Horn, WY 82833.

Table 1. Descriptors Derived from Reciprocal (R) and Constant-Interval Reciprocal (CIR) Elements of D Matrices for Various Alkanes and Cycloalkanes

| no. | compound | descriptors | | | | | | | |
|-----|--------------------|-------------|-------|-------------------|-------|-------------------|-------|-------------|-------|
| | | R | | CIR | | | | | |
| | | | | N_{\max} matrix | | N_{\max} vector | | | |
| | | | | | | row sums | | column sums | |
| | | RS' | RS | CIRS' | CIRS | CIRS' | CIRS | CIRS' | CIRS |
| 1 | butane | 13.66 | 23.66 | 14.68 | 24.68 | 14.00 | 24.00 | 14.34 | 24.34 |
| 2 | methylpropane | 15.00 | 27.00 | 15.00 | 27.00 | 15.00 | 27.00 | 15.00 | 27.00 |
| 3 | cyclobutane | 20.00 | 36.00 | 20.00 | 36.00 | 20.00 | 36.00 | 20.00 | 36.00 |
| 4 | methylcyclopropane | 21.00 | 39.00 | 21.00 | 39.00 | 21.00 | 39.00 | 21.00 | 39.00 |
| 5 | bicyclobutane | 28.00 | 54.00 | 28.00 | 54.00 | 28.00 | 54.00 | 28.00 | 54.00 |
| 6 | tetrahedrane | 36.00 | 72.00 | 36.00 | 72.00 | 36.00 | 72.00 | 36.00 | 72.00 |

Table 2. *S* and *S'* Descriptors for the 39-Alkane Sequence Ethane Through the Octanes Derived from Reciprocal (R) and Constant-Interval Reciprocal (CIR) Elements of Distance Matrices

| no. | compound | bp, °C ^a | (-1) <i>H</i> _f (g), kJ/mol ^b | descriptors | | | | | | | |
|-----|---------------------------|---------------------|---|-------------|--------|-------------------|--------|-------------------|--------|-------------|--------|
| | | | | R | | CIR | | | | | |
| | | | | | | N_{\max} Matrix | | N_{\max} vector | | | |
| | | | | | | | | row sums | | column sums | |
| | | | | RS' | RS | CIRS' | CIRS | CIRS' | CIRS | CIRS' | CIRS |
| 1 | ethane | -88.6 | 83.45 | 2.00 | 4.00 | 2.00 | 4.00 | 2.00 | 4.00 | 2.00 | 4.00 |
| 2 | propane | -42.1 | 104.67 | 7.00 | 13.00 | 7.00 | 13.00 | 7.00 | 13.00 | 7.00 | 13.00 |
| 3 | butane | -0.5 | 125.66 | 13.66 | 23.66 | 14.68 | 24.68 | 14.00 | 24.00 | 14.34 | 24.34 |
| 4 | 2-methylpropane | -11.7 | 134.19 | 15.00 | 27.00 | 15.00 | 27.00 | 15.00 | 27.00 | 15.00 | 27.00 |
| 5 | pentane | 36.0 | 146.77 | 21.48 | 35.48 | 25.00 | 39.00 | 23.00 | 37.00 | 23.84 | 37.84 |
| 6 | 2-methylbutane | 27.8 | 153.68 | 23.32 | 39.32 | 25.36 | 41.36 | 24.17 | 40.17 | 24.85 | 40.85 |
| 7 | 2,2-dimethylpropane | 9.4 | 167.95 | 26.00 | 46.00 | 26.00 | 46.00 | 26.00 | 46.00 | 26.00 | 46.00 |
| 8 | hexane | 68.7 | 167.03 | 30.20 | 48.20 | 38.00 | 56.00 | 34.68 | 52.68 | 35.78 | 53.78 |
| 9 | 2-methylpentane | 60.2 | 174.8 | 32.30 | 52.30 | 38.00 | 58.00 | 34.91 | 54.91 | 36.34 | 56.34 |
| 10 | 3-methylpentane | 63.2 | 172.1 | 32.80 | 52.80 | 39.00 | 59.00 | 35.68 | 55.68 | 37.52 | 57.52 |
| 11 | 2,3-dimethylbutane | 57.9 | 178.3 | 34.64 | 56.64 | 38.04 | 60.04 | 36.00 | 58.00 | 37.36 | 59.36 |
| 12 | 2,2-dimethylbutane | 49.7 | 186.1 | 35.98 | 59.98 | 39.38 | 63.38 | 37.68 | 61.68 | 38.70 | 62.70 |
| 13 | heptane | 98.5 | 187.7 | 37.70 | 59.70 | 53.64 | 75.64 | 48.00 | 70.00 | 49.60 | 71.60 |
| 14 | 2-methylhexane | 90.0 | 194.6 | 41.92 | 65.92 | 53.20 | 77.20 | 48.48 | 72.48 | 50.20 | 74.20 |
| 15 | 3-methylhexane | 92.0 | 191.3 | 42.98 | 66.98 | 54.80 | 78.80 | 49.94 | 73.94 | 51.60 | 75.60 |
| 16 | 3-ethylpentane | 93.5 | 189.3 | 43.44 | 67.44 | 52.50 | 76.50 | 47.25 | 71.25 | 49.79 | 73.79 |
| 17 | 2,4-dimethylpentane | 80.4 | 201.7 | 44.28 | 70.28 | 52.50 | 78.50 | 47.98 | 73.98 | 50.34 | 76.34 |
| 18 | 2,3-dimethylpentane | 89.7 | 198.0 | 45.28 | 71.28 | 54.50 | 80.50 | 49.59 | 75.59 | 50.77 | 76.77 |
| 19 | 2,2,3-trimethylbutane | 80.8 | 204.5 | 45.96 | 75.96 | 54.06 | 84.06 | 51.17 | 81.17 | 53.21 | 83.21 |
| 20 | 2,2-dimethylpentane | 79.2 | 205.9 | 46.12 | 74.12 | 54.50 | 82.50 | 50.32 | 78.32 | 52.34 | 80.34 |
| 21 | 3,3-dimethylpentane | 86.0 | 201.2 | 47.12 | 75.12 | 56.50 | 84.50 | 51.70 | 79.70 | 53.54 | 81.54 |
| 22 | octane | 125.1 | 208.7 | 49.74 | 75.74 | 72.00 | 98.00 | 64.20 | 90.20 | 66.08 | 92.08 |
| 23 | 2-methylheptane | 117.6 | 215.4 | 50.62 | 78.62 | 70.96 | 98.96 | 63.39 | 91.39 | 65.69 | 93.69 |
| 24 | 3-methylheptane | 116.5 | 212.5 | 53.04 | 81.04 | 72.96 | 100.96 | 65.39 | 93.39 | 67.57 | 95.57 |
| 25 | 3-ethylhexane | 118.6 | 210.7 | 53.22 | 81.22 | 71.20 | 99.20 | 64.46 | 92.46 | 67.07 | 95.07 |
| 26 | 4-methylheptane | 117.7 | 212.0 | 53.30 | 81.30 | 73.64 | 101.64 | 65.40 | 93.40 | 67.74 | 95.74 |
| 27 | 2,5-dimethylhexane | 109.1 | 222.5 | 54.54 | 84.54 | 69.60 | 99.60 | 63.18 | 93.18 | 65.82 | 95.82 |
| 28 | 2,4-dimethylhexane | 109.5 | 219.2 | 55.56 | 85.56 | 72.00 | 102.00 | 65.22 | 95.22 | 67.77 | 97.77 |
| 29 | 2,3-dimethylhexane | 115.6 | 213.8 | 56.06 | 86.06 | 72.80 | 102.80 | 66.26 | 96.26 | 68.67 | 98.67 |
| 30 | 2,2-dimethylhexane | 106.8 | 224.6 | 56.64 | 88.64 | 72.00 | 104.00 | 65.88 | 97.88 | 68.22 | 100.22 |
| 31 | 3,4-dimethylhexane | 117.7 | 212.8 | 56.82 | 86.82 | 74.40 | 104.40 | 67.54 | 97.54 | 69.92 | 99.92 |
| 32 | 3-ethyl-2-methylpentane | 115.6 | 211.0 | 57.08 | 87.08 | 69.50 | 99.50 | 62.32 | 92.32 | 66.02 | 96.02 |
| 33 | 3,3-dimethylhexane | 111.9 | 220.0 | 58.16 | 90.16 | 75.20 | 107.20 | 68.70 | 100.70 | 70.92 | 102.92 |
| 34 | 2,3,4-trimethylpentane | 113.5 | 217.3 | 58.92 | 90.92 | 71.50 | 103.50 | 64.66 | 96.66 | 68.02 | 100.02 |
| 35 | 2,2,4-trimethylpentane | 99.2 | 224.0 | 59.26 | 93.26 | 70.50 | 104.50 | 64.55 | 98.55 | 67.84 | 101.84 |
| 36 | 3-ethyl-3-methylpentane | 118.2 | 214.9 | 59.42 | 91.42 | 72.50 | 104.50 | 65.27 | 97.27 | 68.54 | 100.54 |
| 37 | 2,2,3-trimethylpentane | 110.0 | 220.0 | 61.01 | 95.01 | 73.50 | 107.50 | 67.00 | 101.00 | 70.02 | 104.02 |
| 38 | 2,3,3-trimethylpentane | 114.8 | 216.3 | 61.26 | 95.26 | 74.50 | 108.50 | 67.61 | 101.61 | 70.54 | 104.54 |
| 39 | 2,2,3,3-tetramethylbutane | 106.4 | 225.3 | 64.94 | 102.94 | 72.08 | 110.08 | 68.00 | 106.00 | 71.06 | 109.06 |

^a CRC Handbook of Chemistry and Physics, 75th ed.; Lide, D. R., Ed.; CRC: Boca Raton, FL, 1995. ^b Clark, T.; McKervey, M. A. *Comprehensive Organic Chemistry*; Stoddart, J. F., Ed.; Pergamon: Oxford, 1979; Vol. I, p 69.

4 of Table 6 are seen progressively to diminish with the increase in the integer vertex numbers of a graph. It was noted that the reciprocal edge count interval between vertices 1 and 2 (0.5) was larger than the sum of all the rest of the reciprocal edge count intervals from vertices 2 through 10

(0.4)! Elk¹⁰ recently wrote: "Let the distances between successive integers (of a math model) all be equal; similarly, let equal fractional parts be "uniformly" spaced."

Nonetheless, as a basis for creation of other variants of RS indices (vide infra), experiments were executed utilizing

Table 3. Regression Data Comparing Boiling Points Versus Reciprocal Index Data for the 39 Alkanes Ethane Through Octanes

| reciprocal index | bp, °C | r^2 | s | F |
|---------------------------------------|--|-------|-------|---------|
| RS' | $-123.017 + 31.452 \text{ RS}'^{1/2}$ | 0.935 | 12.67 | 534.20 |
| RS | $-134.300 + 26.376 \text{ RS}^{1/2}$ | 0.916 | 14.43 | 403.50 |
| CIRS', matrix N_{\max} | $-110.638 + 26.6312 \text{ CIRS}'^{1/2}$ | 0.974 | 7.980 | 1403.88 |
| CIRS, matrix N_{\max} | $-126.335 + 23.7195 \text{ CIRS}^{1/2}$ | 0.958 | 10.17 | 849.30 |
| CIRS', vector N_{\max} , row sum | $-115.636 + 28.5477 \text{ CIRS}'^{1/2}$ | 0.967 | 9.057 | 1081.67 |
| CIRS, vector N_{\max} , row sum | $-130.076 + 24.8690 \text{ CIRS}^{1/2}$ | 0.948 | 11.35 | 674.67 |
| CIRS', vector N_{\max} , column sum | $-113.702 + 27.7486 \text{ CIRS}'^{1/2}$ | 0.968 | 8.941 | 1110.69 |
| CIRS, vector N_{\max} , column sum | $-128.506 + 24.3918 \text{ CIRS}^{1/2}$ | 0.949 | 11.22 | 691.48 |

Table 4. Regression Data Comparing Heats of Formation Versus Reciprocal Index Data for the 39 Alkanes Ethane Through Octanes

| reciprocal index | $(-1)H_f(g)$, kJ/mol | r^2 | s | F |
|---------------------------------------|--|-------|-------|---------|
| RS' | $46.998 + 22.5525 \text{ RS}'^{1/2}$ | 0.984 | 4.403 | 2275.53 |
| RS | $37.277 + 19.1154 \text{ RS}^{1/2}$ | 0.985 | 4.334 | 2350.11 |
| CIRS', matrix N_{\max} | $59.563 + 18.5768 \text{ CIRS}'^{1/2}$ | 0.970 | 6.016 | 1201.96 |
| CIRS, matrix N_{\max} | $46.295 + 16.8141 \text{ CIRS}^{1/2}$ | 0.985 | 4.215 | 2486.99 |
| CIRS', vector N_{\max} , row sum | $54.987 + 20.074 \text{ CIRS}'^{1/2}$ | 0.978 | 5.124 | 1670.98 |
| CIRS, vector N_{\max} , row sum | $42.608 + 17.7524 \text{ CIRS}^{1/2}$ | 0.989 | 3.732 | 3182.10 |
| CIRS', vector N_{\max} , column sum | $56.429 + 19.500 \text{ CIRS}'^{1/2}$ | 0.978 | 5.166 | 1643.33 |
| CIRS, vector N_{\max} , column sum | $43.928 + 17.3883 \text{ CIRS}^{1/2}$ | 0.987 | 3.955 | 2829.39 |

RD matrices to compute reciprocal Schultz (RS) and modified reciprocal Schultz (RS') indices.

$$\text{RS} = \sum_{i=1}^n [\nu(\text{RD} + \text{A})] \quad (3)$$

$$\text{RS}' = \sum_{i=1}^n [\nu(\text{RD})] \quad (4)$$

The symbol ν is the valence vector of a graph of N vertices; RD represents the graph-theoretical, topological D matrix whose integer elements were transformed into the corresponding reciprocals; the adjacency (A) matrix has each element equal to unity if vertices i and j are adjacent; zero if not. Molecular graphs, hydrogen suppressed and with the interatomic C—C atom edge counts set at unity, were derived from the representative compounds listed in Tables 1, 2, and 5. The D matrices were derived in the usual fashion, then transformed into the individual element reciprocal (RD) matrices, the data being rounded to 2 decimal places for each number, as illustrated for 2-methylbutane in Figure 1a, 1b, and 1c. Columns 3 and 4 of Tables 1 and 5, and columns 5 and 6 of Table 2 list the RS' and RS data for the graphs studied. All molecular index data tabulated in this paper were invariant, hence descriptors.

Attention was next turned to devising an algorithm for the calculation of constant interval reciprocals (CIR) from D matrices

$$\text{CIR} = [N_{\max} - (N - 1)]/N_{\max} = [N_{\max} - N + 1]/N_{\max} \quad (5)$$

where N_{\max} is the largest integer in a given unit (matrix or vector); and N is the integer to be transformed into a CIR element. Table 6, columns 5 and 6, displays the CIR values and differences for the N_{\max} value of 10. Table 7 presents the CIR values for units based on N_{\max} values of 1 through 10. The parameter N_{\max} was based for these CIR studies within the entire matrix and also within each row vector, thus increasing the elasticity of the CIR topological index calculations. Figures 1d and 1e further exhibit the CIRD matrices for 2-methylbutane based on the matrix N_{\max} (Figure

1d) and each separate horizontal vector N_{\max} (Figure 1e). The CIR values may additionally be based upon even larger N_{\max} values, not studied at this time, such as the total number of vertices in a graph, as illustrated for a N_{\max} of 5 for the 5 vertices of 2-methylbutane in Figure 1f, or even any N_{\max} larger than the matrix maximum edge count. In the opposite direction, the use of any integer as its own maximum places the results back in the realm of the regular reciprocal. The operational elasticity of this concept for determining CIRD reciprocals and CIRS indices appears extensive. The same expressions already pictured for the computation of RS' and RS topological indices were also used to calculate CIRS' and CIRS topological indices from the corresponding CIRD matrices.

All of the CIR-matrix-based N_{\max} elements gave rise to symmetrical CIRD matrices, but the CIR-vector-based N_{\max} reciprocals gave unsymmetrical CIRD matrices in most instances. Only very small or very symmetric graphs, such as for ethane and propane and unsubstituted cycloalkanes, were represented by symmetric CIRD vector N_{\max} matrices. As a consequence of the unsymmetrical character of most of the CIRD vector N_{\max} matrices, CIRS' and CIRS topological indices derived therefrom exhibited slight differences, depending on whether the procedure of index calculation utilized row or column vector summation of the CIRD matrices in the operational sequences, as seen in Tables 1 and 5, columns 7–10, and Table 2, columns 9–12. The same indices were obtained by use of the vertical vectors as N_{\max} sources, but with the consequence that row summed results exchanged places with column summed results as in matrix transposition. Total row vector sums, however, always equaled total column vector sums.

RESULTS

The data gathered in Tables 1, 2, and 5 accomplished the three objectives of this study: (1) generating larger indices as molecular complexity increased; (2) examining index effectiveness for QSPR comparisons; and (3) assessing the uniqueness of each variant of the reciprocal descriptors. These ends tested the indices represented by the symbols RS' and RS; CIRS' and CIRS, matrix N_{\max} ; and CIRS' and CIRS, vector N_{\max} , summed by row and by column.

Table 5. Descriptors Derived from Reciprocal (R) and Constant Interval Reciprocal (CIR) Elements of D Matrices for Representative C_3 – C_{10} Cycloalkanes

| no. | compound | descriptors | | | | | | | |
|-----|----------------------------------|-------------|--------|-------------------|--------|-------------------|--------|-------------|--------|
| | | R | | CIR | | | | | |
| | | | | N_{\max} matrix | | N_{\max} vector | | | |
| | | | | | | row sums | | column sums | |
| | | RS' | RS | CIRS' | CIRS | CIRS' | CIRS | CIRS' | CIRS |
| 1 | cyclopropane | 12.00 | 24.00 | 12.00 | 24.00 | 12.00 | 24.00 | 12.00 | 24.00 |
| 2 | cyclobutane | 20.00 | 36.00 | 20.00 | 36.00 | 20.00 | 36.00 | 20.00 | 36.00 |
| 3 | methylcyclopropane | 21.00 | 39.00 | 21.00 | 39.00 | 21.00 | 39.00 | 21.00 | 39.00 |
| 4 | cyclopentane | 30.00 | 50.00 | 30.00 | 50.00 | 30.00 | 50.00 | 30.00 | 50.00 |
| 5 | ethylcyclopropane | 29.98 | 51.98 | 32.04 | 54.04 | 30.83 | 52.83 | 31.17 | 53.17 |
| 6 | methylcyclobutane | 30.49 | 52.49 | 33.04 | 55.04 | 31.17 | 53.17 | 31.68 | 53.68 |
| 7 | 1,2-dimethylcyclopropane | 31.66 | 55.66 | 34.04 | 58.04 | 32.34 | 56.34 | 33.36 | 57.36 |
| 8 | 1,1-dimethylcyclopropane | 33.00 | 59.00 | 33.00 | 59.00 | 33.00 | 59.00 | 33.00 | 59.00 |
| 9 | cyclohexane | 39.96 | 63.96 | 44.04 | 68.04 | 44.04 | 68.04 | 44.04 | 68.04 |
| 10 | cycloheptane | 51.24 | 79.24 | 56.00 | 84.00 | 56.00 | 84.00 | 56.00 | 84.00 |
| 11 | 1-cyclopropylbutane | 49.48 | 79.48 | 61.60 | 91.60 | 56.88 | 86.88 | 57.50 | 87.50 |
| 12 | 1-cyclopropyl-2-methylpropane | 51.94 | 83.94 | 60.50 | 92.50 | 55.98 | 87.98 | 57.50 | 89.50 |
| 13 | 1-ethyl-1,2-dimethylcyclopropane | 57.12 | 93.12 | 67.50 | 93.50 | 62.29 | 98.29 | 64.55 | 100.55 |
| 14 | ethylcyclopentane | 53.12 | 83.12 | 64.00 | 94.00 | 59.11 | 89.11 | 60.45 | 90.45 |
| 15 | 1,2-dimethylcyclopentane | 55.62 | 87.62 | 62.08 | 94.08 | 59.02 | 91.02 | 60.38 | 92.38 |
| 16 | propylcyclobutane | 50.38 | 80.38 | 64.20 | 94.20 | 59.09 | 89.09 | 60.27 | 90.27 |
| 17 | methylcyclohexane | 53.02 | 83.02 | 64.25 | 94.25 | 59.62 | 89.62 | 60.29 | 90.29 |
| 18 | 2-cyclopropylbutane | 53.10 | 85.10 | 63.00 | 95.00 | 58.09 | 90.09 | 59.09 | 91.09 |
| 19 | isopropylcyclobutane | 53.61 | 85.61 | 63.75 | 95.75 | 58.51 | 90.51 | 60.61 | 92.61 |
| 20 | 1-ethyl-2-methylcyclobutane | 53.86 | 85.86 | 64.00 | 96.00 | 59.01 | 91.01 | 61.11 | 93.11 |
| 21 | 2-methyl-1-propylcyclopropane | 52.18 | 82.18 | 65.20 | 97.20 | 59.89 | 91.89 | 61.74 | 93.74 |
| 22 | 1,1-dimethylcyclopentane | 56.96 | 90.96 | 63.42 | 97.42 | 59.34 | 93.34 | 60.70 | 94.70 |
| 23 | 1-methyl-1-propylcyclopropane | 54.28 | 88.28 | 63.50 | 97.50 | 59.32 | 93.32 | 60.50 | 94.50 |
| 24 | tertiary butylcyclopropane | 56.94 | 92.94 | 62.04 | 98.04 | 59.15 | 95.15 | 60.85 | 96.85 |
| 25 | 1,2-diethylcyclopropane | 52.84 | 84.84 | 66.40 | 98.40 | 60.22 | 92.22 | 62.82 | 94.82 |
| 26 | 1,3-dimethylcyclopentane | 55.12 | 87.12 | 66.50 | 98.50 | 60.88 | 92.88 | 62.56 | 94.56 |
| 27 | 1-ethyl-3-methylcyclobutane | 53.10 | 85.10 | 66.60 | 98.60 | 60.77 | 92.77 | 62.82 | 94.82 |
| 28 | 1-isopropyl-1-methylcyclopropane | 57.28 | 93.28 | 62.72 | 98.72 | 59.83 | 95.83 | 61.53 | 97.53 |
| 29 | 1-isopropyl-2-methylcyclopropane | 54.94 | 88.94 | 65.00 | 99.00 | 59.50 | 93.50 | 62.44 | 96.44 |
| 30 | 1-ethyl-2,3-dimethylcyclopropane | 55.28 | 89.28 | 65.50 | 99.50 | 60.27 | 94.27 | 63.11 | 97.11 |
| 31 | 1,1,2-trimethylcyclobutane | 57.79 | 93.79 | 63.74 | 99.74 | 60.85 | 96.85 | 62.55 | 98.55 |
| 32 | 1,1-diethylcyclopropane | 55.44 | 89.44 | 66.00 | 100.00 | 60.36 | 94.36 | 62.88 | 96.88 |
| 33 | 1-ethyl-1-methylcyclobutane | 55.70 | 89.70 | 66.25 | 100.25 | 61.21 | 95.21 | 62.63 | 96.63 |
| 34 | 1,2,3-trimethylcyclobutane | 55.95 | 89.95 | 66.75 | 100.75 | 61.03 | 95.03 | 63.04 | 97.04 |
| 35 | 1-ethyl-2,2-dimethylcyclobutane | 56.62 | 92.62 | 66.50 | 102.50 | 61.43 | 97.43 | 64.11 | 100.11 |
| 36 | 1,1,3-trimethylcyclobutane | 56.79 | 92.79 | 66.75 | 102.75 | 60.49 | 96.49 | 63.18 | 99.18 |
| 37 | 1,1,2,3-tetramethylcyclopropane | 59.30 | 97.30 | 65.42 | 103.42 | 61.00 | 99.00 | 64.06 | 102.06 |
| 38 | 1,1,2,2-tetramethylcyclopropane | 60.64 | 100.64 | 66.76 | 106.76 | 62.68 | 102.60 | 65.40 | 105.40 |
| 39 | cyclooctane | 62.56 | 94.56 | 76.00 | 108.00 | 76.00 | 108.00 | 76.00 | 108.00 |
| 40 | cyclononane | 74.88 | 110.88 | 90.00 | 126.00 | 90.00 | 126.00 | 90.00 | 126.00 |
| 41 | cyclodecane | 87.20 | 127.20 | 116.00 | 156.00 | 116.00 | 156.00 | 116.00 | 156.00 |

There were relatively few sequence differences noted among the various reciprocal S' and S sets of data of Tables 1, 2, and 5. Table 1, whose essence was initially presented by Bertz,^{7,8} illustrated the increase in all of the kinds of descriptors, an increase that paralleled the increase in complexity of the linear and cyclic 4-carbon-atom-saturated hydrocarbons. Each of the compounds of Table 1, except butane, is very symmetrical and has all the same values for the varied indices. Bertz^{7,8} has stated that the parallelism between index and increasing complexity of molecules is a desirable circumstance, opposite to the sequence of index values observed in most other papers (except, most notably, the Balaban J index), including that of S(MTI) indices reported and reviewed in earlier studies.^{1,9} Table 2 presents data for the 39-alkane sequence of ethane through the octanes. The data reflect the increasing complexities of the pictured alkanes, with a few compounds displaying slightly different sequences of the variant indices. A discerning measure of complexity order of the six isomers of the dimethylhexanes succinctly summarizes all of the data of

Table 6. Comparisons of Edge Counts (EC) and Edge Count Intervals (Δ EC) for Graphs and Matrices Using Integers, Reciprocal Edge Counts (REC), and Constant Interval Reciprocal Edge Counts (CIREC) for a 10-Unit Construct

| | EC | Δ EC | REC | Δ REC | CIREC | Δ CIREC |
|----|----|-------------|--------|--------------|--------|----------------|
| 1 | | | 1.0000 | | 1.0000 | |
| 2 | | 1 | 0.5000 | 0.5000 | 0.9000 | 0.1000 |
| 3 | | 1 | 0.3333 | 0.1667 | 0.8000 | 0.1000 |
| 4 | | 1 | 0.2500 | 0.0833 | 0.7000 | 0.1000 |
| 5 | | 1 | 0.2000 | 0.0500 | 0.6000 | 0.1000 |
| 6 | | 1 | 0.1667 | 0.0333 | 0.5000 | 0.1000 |
| 7 | | 1 | 0.1429 | 0.0238 | 0.4000 | 0.1000 |
| 8 | | 1 | 0.1250 | 0.0179 | 0.3000 | 0.1000 |
| 9 | | 1 | 0.1111 | 0.0139 | 0.2000 | 0.1000 |
| 10 | | 1 | 0.1000 | 0.0111 | 0.1000 | 0.1000 |

Table 7. Constant Interval Reciprocal (CIR) Values for Units of N maximum of 1–10 Vertices

| N_{max} | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| 1 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 2 | | 0.5000 | 0.6667 | 0.7500 | 0.8000 | 0.8333 | 0.8571 | 0.8750 | 0.8889 | 0.9000 |
| 3 | | | 0.3333 | 0.5000 | 0.6000 | 0.6667 | 0.7143 | 0.7500 | 0.7778 | 0.8000 |
| 4 | | | | 0.2500 | 0.4000 | 0.5000 | 0.5714 | 0.6250 | 0.6667 | 0.7000 |
| 5 | | | | | 0.2000 | 0.3333 | 0.4286 | 0.5000 | 0.5556 | 0.6000 |
| 6 | | | | | | 0.1667 | 0.2857 | 0.3750 | 0.4444 | 0.5000 |
| 7 | | | | | | | 0.1429 | 0.2550 | 0.3333 | 0.4000 |
| 8 | | | | | | | | 0.1250 | 0.2222 | 0.3000 |
| 9 | | | | | | | | | 0.1111 | 0.2000 |
| 10 | | | | | | | | | | 0.1000 |

Table 8. Sequences of Increasing Complexities of x,x -Dimethylhexanes

| | | | | | | |
|---|------|------|------|------|------|------|
| Bertz ¹¹ | 2, 5 | 2, 4 | 2, 3 | 3, 4 | 2, 2 | 3, 3 |
| Balaban, J ¹¹ | 2, 5 | 2, 4 | 2, 2 | 2, 3 | 3, 4 | 3, 3 |
| Schultz, S (MTI) ⁹ | 2, 5 | 2, 2 | 2, 4 | 2, 3 | 3, 4 | 3, 3 |
| RS | 2, 5 | 2, 4 | 2, 3 | 3, 4 | 2, 2 | 3, 3 |
| CIRS, N_{max} , matrix | 2, 5 | 2, 4 | 2, 3 | 2, 2 | 3, 4 | 3, 3 |
| CIRS, N_{max} , vector, row sum | 2, 5 | 2, 4 | 2, 3 | 3, 4 | 2, 2 | 3, 3 |
| CIRS, N_{max} , vector, column sum | 2, 5 | 2, 4 | 3, 4 | 2, 3 | 2, 2 | 3, 3 |
| differences, CIRS values, above 2 rows | 2, 5 | 2, 4 | 2, 3 | 3, 4 | 2, 2 | 3, 3 |

Table 2, presented in Table 8 in the format devised by Medeleanu and Balaban.¹¹ The first two rows of Table 8 repeat those of the reference;¹¹ the third row is ordered on the review data of the S(MTI) indices tabulated by Mihalić and Trinajstić;⁹ the remaining rows derive from the data of this paper. All rows agree that 2,5-dimethylhexane is the least and 3,3-dimethylhexane is the most complex of the 6 dimethylhexane isomers of octane! Table 5 presents descriptor data for the same series of cycloalkanes to which an earlier study¹² of the S index was dedicated. The molecular indices confirm that an increase in size and/or substitution of a cycloalkane increases its complexity.

The second objective of this study was to determine the utility of the reciprocal S indices in reflecting QSPR relationships for the various alkane descriptors recorded in Table 2. No attempt was made to analyze QSPR data for the compounds in Table 5. The requisite information for some Table 5 compounds was not available in the literature; others of the cycloalkanes presented the problem of diastereoisomerism, with consequent differing physical properties. Two sets of physical properties - boiling points and heats of formation - were used in these QSPR studies. The boiling points of the alkanes descend with the increasing complexity of the various alkane isomers, and hence also with the increase of corresponding molecular indices; heats of formation exhibit the opposite relationships. As these QSPR comparisons are presented it is well to keep in mind the admonishment of Mihalić and Trinajstić⁹ that regression studies of properties versus descriptors should possess values above $r = 0.99$ ($r^2 = 0.98$) to be useful.

The regression equations and accompanying statistical data involving boiling point relationships with the various reciprocal indices are listed in Table 3 in the same order as presented in columns 5–12 of Table 2. None of the r^2 values attains the standard of $r^2 > 0.98$ established by Mihalić and Trinajstić.⁹ At best, the average r^2 value of all data based on the various CIR indices ($r^2 = 0.961$) is greater than that derived from use of ordinary reciprocal indices ($r^2 = 0.926$). Mihalić and Trinajstić⁹ ascertained an r^2 value of 0.9964 from the regression data derived from their review of the regular

S(MTI) indices versus boiling points for the same set of alkanes listed in this presentation, without methane.

The data of Table 2, which compared heats of formation with the various reciprocal S indices listed in columns 5–12, were also subjected to regression analysis. The equations and corresponding statistical data are listed in Table 4, with more acceptable results than were just reported in the study involving boiling points. The average r^2 value for the QSPR relationships based on ordinary reciprocals was slightly better ($r^2 = 0.985$) than the average value calculated for results based on constant interval reciprocals ($r^2 = 0.981$).

Finally, the descriptors listed in Tables 1, 2, and 5 were observed to be almost, but not quite, entirely unique. Of all the data in all the tables, only one pair of topological indices was degenerate - the CIRS matrix N_{max} indices (104.50) for 2,2,4-trimethylpentane and 3-ethyl-3-methylpentane (Table 2, 35 and 36). Mihalić and Trinajstić⁹ reported two pairs of duplicates among the S(MTI) indices they recorded in their summary of the same list of alkanes as in Table 2. And, in an earlier paper that reported the S(MTI) indices of the same cycloalkanes as tabulated in Table 5, Schultz et al.¹² reported 13 replicate index values.

REFERENCES AND NOTES

- (1) Schultz, H.P. Topological Organic Chemistry. 1. Graph Theory and Topological Indices of Alkanes. *J. Chem. Inf. Comput. Sci.* **1989**, 29, 227–228.
- (2) Plavšić, D.; Nikolić, S.; Trinajstić, N.; Mihalić, Z. On the Harary Index for the Characterization of Chemical Graphs. *J. Math. Chem.* **1993**, 12, 235–250.
- (3) Wiener, H. Structural Determination of Paraffin Boiling Points. *J. Am. Chem. Soc.* **1947**, 69, 17–20.
- (4) Ivanciuc, O.; Balaban, T. S.; Balaban, A. T. Reciprocal Distance Matrix; Related Local Vertex Invariants and Topological Indices. *J. Math. Chem.* **1993**, 12, 309–318.
- (5) Diudea, M. V.; Gutman, I. Wiener-Type Topological Indices. *Croat. Chem. Acta* **1998**, 71, 21–51.
- (6) Diudea, M. V. Indices of Reciprocal Properties or Harary Indices. *J. Chem. Inf. Comput. Sci.* **1997**, 37, 292–299, and references cited therein.
- (7) Bertz, S. H. The Bond Graph. *J. Chem. Soc. Chem. Comm.* **1981**, 818–820.
- (8) Bertz, S. H. Branching in Graphs and Molecules. *Disc. Appl. Math.* **1988**, 19, 65–83.
- (9) Mihalić, Z.; Trinajstić, N. A Graph Theoretical Approach to Structure-Property Relationships. *J. Chem. Educ.* **1992**, 69, 701–712.
- (10) Elk, S. B. Orismology (the Science of Defining Words) and the Geometrical Foundations of Chemistry. 5. The Heuristics of Primacy. *J. Chem. Inf. Comput. Sci.* **1997**, 37, 835–840.
- (11) Medeleanu, M.; Balaban, A. T. Real Number Vertex Invariants and Schultz-Type Indices Based on Eigenvectors, accepted for publication in *J. Chem. Inf. Comput. Sci.*
- (12) Schultz, H. P.; Schultz, T. P. Topological Organic Chemistry. 6. Graph Theory and Molecular Topological Indices of Cycloalkanes. *J. Chem. Inf. Comput. Sci.* **1993**, 33, 240–244.
- (13) Diudea, M. V.; Randić, M. Matrix Operator, W (M_1 , M_2 , M_3), and Schultz-Type Indices. *J. Chem. Inf. Comput. Sci.* **1997**, 37, 1095–1100, and references cited therein.