

MATRIX INVERSE OF CHEMICAL GRAPHS

I. Ordering, Comparability and Similarity of
Benzenoid-alternant and Non-alternant
Hydrocarbons

Sherif El-Basil* and A. Hussein
Faculty of Pharmacy, Kasr El-Aini Street,
and Dept. of Mathematical Engineering,
Cairo University, Cairo - Egypt

(Received: August 1983)

ABSTRACT

Matrix inverses of seventeen polycyclic hydrocarbons are computed. The resulting matrices, \underline{A}^{-1} , are transformed into vectors, $\underline{V} = \underline{A}^{-1}\underline{X}$, where \underline{X} is a unit vector. Comparability conditions of Karamata are applied to the partial sums of the vector components and are used to order the hydrocarbons. Four molecular properties are studied including resonance energies, total pi-energies, ionization potentials and electron affinities. In general the results are in good agreement with the actual order of properties. Furthermore, the components of the vectors \underline{V} are used to construct a similarity matrix of the hydrocarbons. The resulting hierarchy distinguishes several topological features of the studied graphs.

While the adjacency (topological) matrix¹, \underline{A} is not invariant of the graph from which it is derived (because its form depends on the adopted numbering of the vertices), it seems that various powers of \underline{A} lead to counting various walks² characteristic of a given graph. The trace of \underline{A}^k matrices, $k = 1, 2, 3, \dots$ leads to numbers called spectral moments² which were found useful in ordering and characterization of graphs³. This communication considers the very special case where $k = -1$ i.e. the inverse of the adjacency matrix. The objective is to explore the

*Author to whom correspondence is made at: Faculty of Pharmacy, Kasr El-Aini Street, Cairo, Egypt.

potential of extracting informations from \underline{A}^{-1} matrix which might serve to code graphs of various topologies and thus apply comparability criteria⁴ to ordering⁵ molecules. Benzeneid alternants as well as non-alternant hydrocarbons are used as our substrates. The importance of the \underline{A}^{-1} matrix was recognized many years ago in connection with the relation between resonance theory and elementary MO theory⁶.

GRAPH-THEORETICAL METHOD

1. Matrix inverse of graph is obtained using standard sub-routine or a formula due to Heilbronner⁷.
2. A vector \underline{V}_i is associated with every \underline{A}_i^{-1} of graph G_i by the following transformation:

$$\underline{A}_i^{-1} \underline{X}_i = \underline{V}_i \quad (1)$$

where \underline{X}_i is a column vector whose components are all ones and which contains as many rows as \underline{A}_i does. I.e. the number of components in \underline{X}_i equals the number of vertices in G_i .

3. The components of \underline{V}_i are ordered descendingly. Thus, if these components are ordered: $C_{1i}, C_{2i}, \dots, C_{ni}$, then $C_{1i} \geq C_{2i} \geq \dots \geq C_{ni}$
4. Partial sums are formed from the ordered C's thus:

$$\begin{aligned} s_{1i} &= C_{1i}, \\ s_{2i} &= C_{1i} + C_{2i} \\ &\vdots \\ &\vdots \\ s_{ni} &= \sum_{j=1}^n C_{ji} \end{aligned} \quad (2)$$

The resulting sequence of partial sums $\{s_{1i}, s_{2i}, \dots, s_{ni}\}$ is the code of G_i .

5. Let $\{s_{1i}, s_{2i}, \dots, s_{ni}\}$ and $\{s_{1j}, s_{2j}, \dots, s_{mj}\}$ are codes of graphs G_i and G_j containing n and m vertices respectively. We say that G_i is comparable with G_j

if

$$\begin{aligned}
 s_{1i} &\geq s_{1j} \\
 s_{2i} &\geq s_{2j} \\
 &\vdots \\
 &\vdots \\
 \sum_{a=1}^n s_{ai} &\geq \sum_{b=1}^m s_{bj}
 \end{aligned}
 \tag{3}$$

i.e. if each partial sum in one graph is greater or equal (but not smaller) than the corresponding entry in the other graph. Conditions (3) are essentially those of Karamata⁸⁻¹⁰.

6. A hierarchical diagram is constructed by connecting adjacent comparable graphs.

Results

Fig 1 is the hierarchy produced in step 6 i.e. when the comparability conditions (of Karamata⁸⁻¹⁰) are imposed on the partial sums of the vector components. The hierarchy involves 17 molecular graphs. Table 1 lists components and the corresponding partial sums of vectors given by eqn. 1. Four molecular properties are studied, viz., Resonance energies¹¹, RE's, total pi-energies¹², heats of atomizations¹³ and electron-affinities¹³ of the hydrocarbons.

Discussion of comparability results:

The resonance energies listed are based on method of Gomes¹¹ of counting all the conjugated circuits in all the Kekulé structures of the hydrocarbon. Total pi-energies are HMO values. It is clear that the partial sums of the components of the \underline{V}_i vectors (eqns 1, 2) succeed in partially ordering the molecular properties of the studied hydrocarbons. While naphthalene is non-comparable with

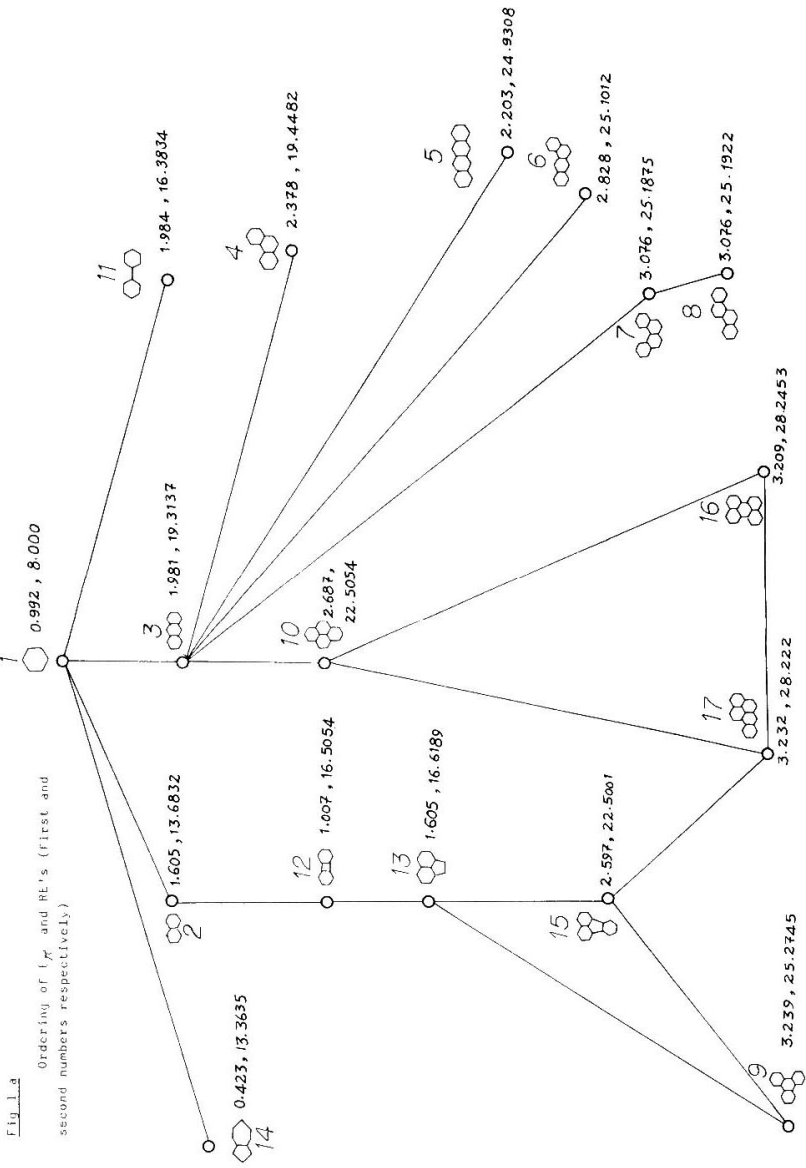
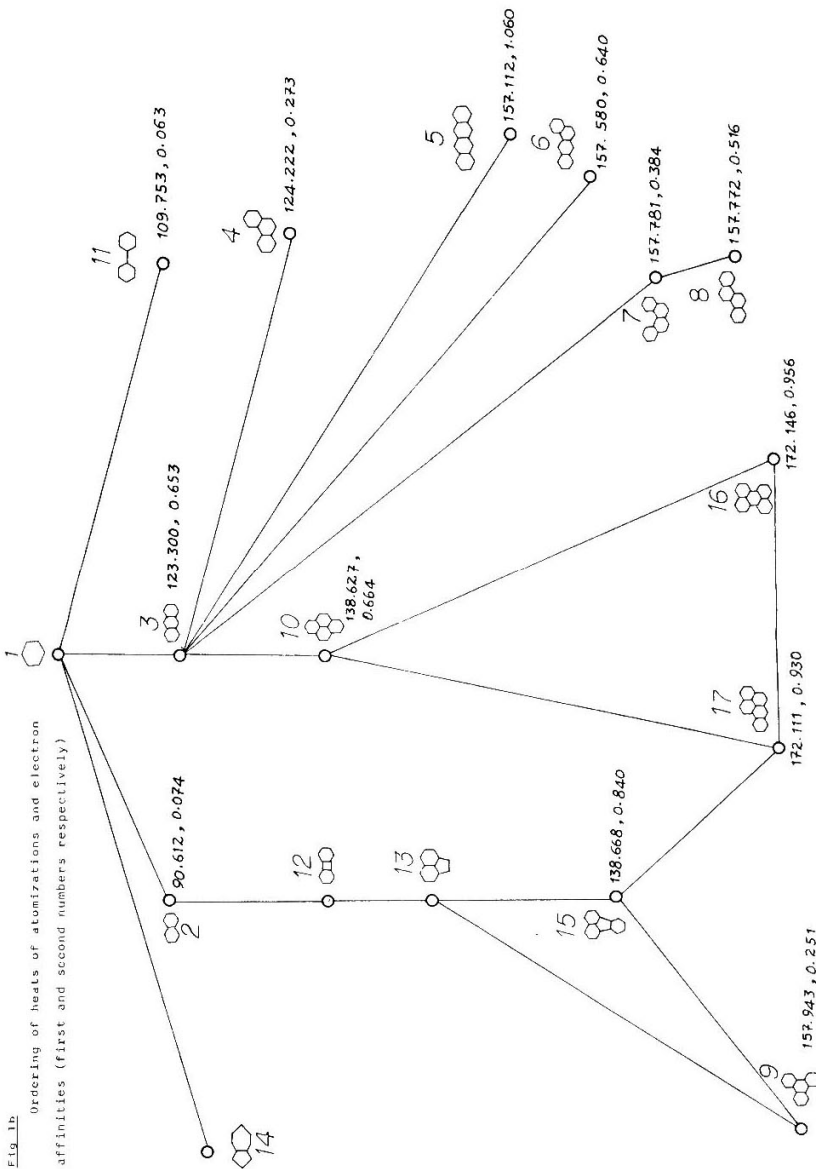


Fig. 1.a
Ordering of I_{R_i} and RE's (first and second numbers respectively)



its non-alternant isomer azulene, anthracene is comparable with its angular isomer, phenanthrene. Of the four isomeric non-branched cata-condensed benzenoid hydrocarbons, only, chrysene is comparable with its isoconjugate¹⁴, 3,4-benzphenanthrene. The three peri-condensed benzenoid hydrocarbons studied in this work, viz., 10, 16, 17 define the vertices of a triangle. Graphs 13 and 15 are adjacent and comparable. They both share the property of being non-alternant but their Kekulé VB structures contain conjugated circuits of type $4n+2$ only (n is an integer). Although the position of biphenylene, 12, is a discrepancy when its RE is compared with values of hydrocarbons 2 and 13 i.e. graphs preceding and proceeding it, yet its position predicts the correct relative value of pi-energy. It is interesting to observe that both molecules 2 and 13 have identical count of conjugation circuits and Kekulé structures. These two graphs are separated by biphenylene, 12. One observes, however, that \underline{V}_{13} is the only vector, in the studied set, with one negative component (C.f. Table 1), and thus if one applies the comparability conditions to the components¹⁵ (rather than to their partial sums) 13 becomes non-comparable with 12, since e.g. $C_{12}(\underline{V}_{13}) < C_{12}(\underline{V}_{12})$, but $C_8(\underline{V}_{13}) > C_8(\underline{V}_{12})$.

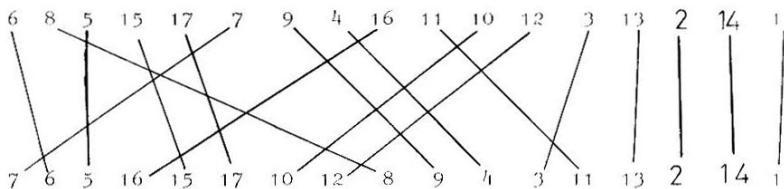
In general the predicted partial order of RE's, pi-energies and heats of atomizations of the hydrocarbons studied is quite satisfactory.

ON SIMILARITY OF GRAPHS¹⁶

The entries of the vectors \underline{V}_i are viewed as coordinates in multidimensional "structure" space. One then says that vectors which lie in the same region of space are similar. As a measure of the degree of similarity one may consider the familiar Euclidean metric¹⁶ between two graphs G_r and G_s defined as:

$$D(\underline{V}_R, \underline{V}_S) = \left[\sum_i (C_{ir} - C_{is})^2 \right]^{\frac{1}{2}} \quad (4)$$

where the summation is taken over all components in both vectors. Naturally singularity, i.e. $D = 0$ signifies identical systems. Thus, the smaller the value of $D(\underline{V}_R, \underline{V}_S)$ gets the more similar would be vectors \underline{V}_R and \underline{V}_S (defined by eqn. 1); and consequently the corresponding graphs G_R and G_S . Such similarity distances, given by eqn. 4, might be used to construct hierarchical ordering of structures. It turns out, however, that conclusions based on a comparison with a single standard may be deficient¹⁷. Thus if we calculate D values relative to benzene, e.g. the results may be biased towards measuring the peculiar property of \underline{V} (benzene) as having all its components being identical! It seems better, therefore, to compare structures not with a single structure but with two (or more) structures selected as standards. In the present study we arbitrarily selected hydrocarbons 6 and 7 as standards. Table 2 lists D values relative to these graphs. We arrive at the following orderings from the two standards:



The numbers correspond to graphs shown in Fig 1 and are ordered in descending similarity from left to right. Each crossing of lines indicates the structures which cannot be simultaneously be ordered with respect to both graphs 6 and 7, while any sequence not involving crossing of lines is an acceptable solution. Mathematically the problem is translated into search for all partial inequalities valid for

both selected reference graphs. For the case at hand we arrive at the following partial orderings which hold true for both 6 and 7.

$$6 < 5 < 15 < 17 < 9 < 4 < 3 \text{ (or 11)} < 13 < 2 < 14 < 1$$

$$6 < 5 < 15 < 17 < 10 < 12 < 3 < 13 < 2 < 14 < 1$$

$$6 < 8 < 9 < 4 < 11 \text{ (or 3)} < 13 < 2 < 14 < 1$$

$$6 < 8 < 11 \text{ (or 3)} < 13 < 2 < 14 < 1$$

$$6 < 5 < 16 < 10 < 12 < 3 < 13 < 2 < 14 < 1$$

$$6 < 5 < 16 < 11 \text{ (or 3)} < 13 < 2 < 14 < 1$$

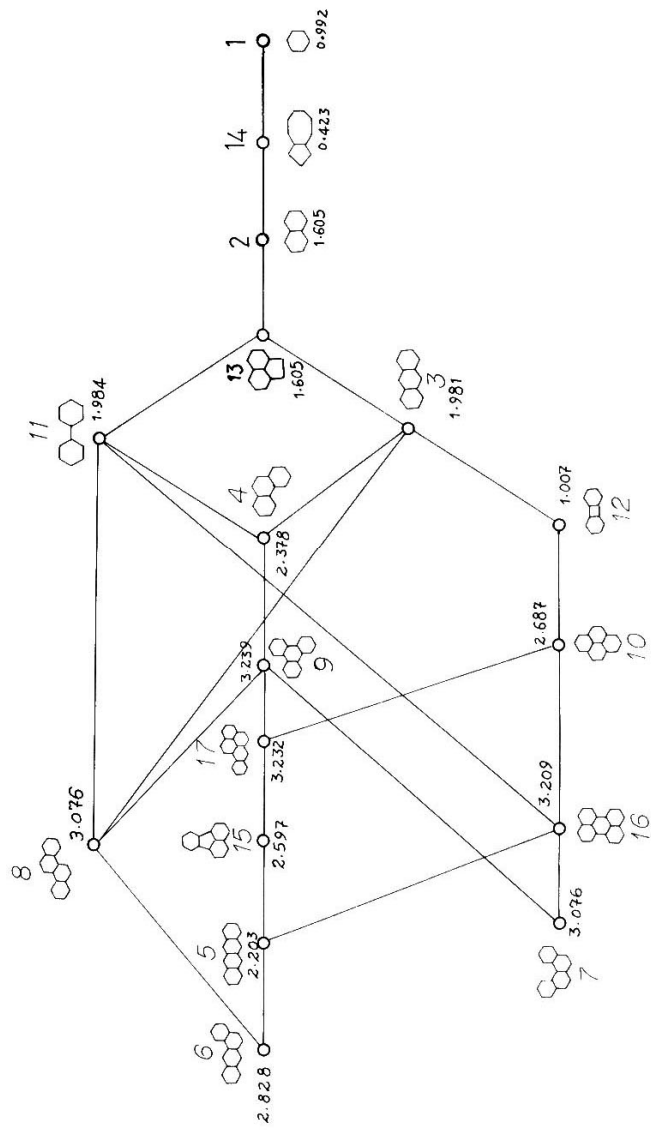
$$7 < 16 < 10 < 12 < 3 < 13 < 2 < 14 < 1$$

$$7 < 9 < 4 < 11 \text{ (or 3)} < 13 < 2 < 14 < 1$$

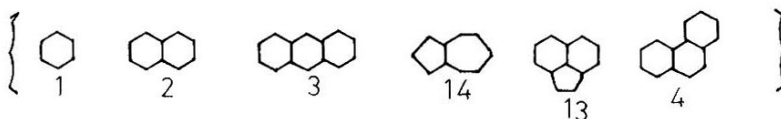
The above inequalities lead to the hierarchical diagram shown in Fig 2. It must be born in mind that the numbers used in constructing the similarity matrix (part of which is given in Table 2) are functions only of the connectivity of the graph and thus do not (or at least, are not expected to) feature the combinatorial aspects of the Kekulé structures which a particular graph represents. One, therefore, should distinguish the numerical values of properties and similarity of structures particularly when properties depend on factors beyond the simple connectivity of the graph. As an illustration we consider RE values derived from counting conjugated circuits in all Kekulé structures of the hydrocarbon. Such a property, therefore, has both topological i.e. purely structural and combinatorial elements. The elements of the \underline{A}^{-1} matrices preserve only the structural

Fig. 2.:

Ranking of hydrocarbons with respect to \bar{G} and \bar{I} , Numbers are RE's.

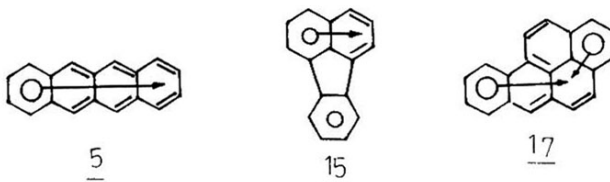


element i.e. graph connectivity. We might take a collection of graphs such as the set shown below



We might pose the question: "Which graph in the above set is least similar to naphthalene?" Intuitively, one might guess that graph 13 is least similar to naphthalene. If one examines Fig 2, one can easily see that 2 and 13 are in fact "very similar"! In fact they have identical values of RE's (See Fig 1). Again if one wonders which two graphs in the above set are most similar to benzene, it might be intuitively guessed that naphthalene 2 and phenanthrene 4, are such two graphs, based on the fact that the subset (1, 2 and 4) are all belong to all-benzenoid cata-condensed benzenoid hydrocarbons. (An all-benzenoid hydrocarbon is characterised by having full sextets in one of its Kekulé structures). Such a conclusion is again erroneous from the point of view of the hierarchical ranking of graphs shown in Fig 2: Although anthracene is not an all-benzenoid hydrocarbon, it is more similar to benzene than phenanthrene is! The same holds for molecular properties. Unexpectedly azulene, 14, a nonalternant lies as close to benzene as naphthalene does. One must recall, however, that both naphthalene and azulene are similar from the point of view of the type of conjugated circuits in their VB structures. In fact both contain only $4n+2$ type. Some encouraging observations of hierarchical ranking of Fig 2 are the following: (a) Graphs (2, 8, 7, 4 and 11) represent all-benzenoid hydrocarbons¹⁸. Such graphs lie on adjacent points, with triphenylene, 2, at the center. (b) Graphs (10, 16, 17) are pericondensed structures, again lie on adjacent points. (c) The fact that perylene, 16, is

adjacent to biphenyl, 11, needs a comment. The fact that they are adjacent means a high degree of similarity (which might not have been forecasted). Indeed the length of the bond between the two rings in biphenyl is 1.50 Å which is almost the value for a single bond¹⁸. Similarly the two *central bonds* in perylene have a length of 1.50 Å¹⁸. The two hydrocarbons are very similar in the sense that both are built from two almost non-interacting units¹⁸. Biphenylene, 12, which is the next nearest neighbour to perylene, has its two central bonds essentially single, their length being 1.52 Å¹⁸. A detailed description of the similarity among these three hydrocarbons, 16, 11 and 12 might be found in reference 19. (d) Fluoranthene, 15 is closer to 17 than 5 is which is not what one might anticipate. However, this is no longer unexpected if one realizes that both 15 and 17 has two sextets, in the Clar¹⁹ representation, yet 5 has only one:



A detailed justification of the above representations is available in reference 20. It might be worthy of observation that 15 contains only $4n+2$ type conjugated circuits.

References:

- (1) F. Harary, Graph Theory, Reading, Mass. Addison-Wesley, 1972.
- (2) M. Randić, J. Comput. Chem. 1, 586 (1980).
- (3) S. El-Basil and A. Shalabi, Math.Chem 14, 191 (1983)

- (4) Comparability criteria were initiated by Muirhead: R.F. Muirhead, Proc. Edinburgh Math. Soc. 19, 36 (1901); 21, 144 (1903); 24, 45 (1906). Muirhead's restriction to integral parameterization was later removed: J. Karamata, Publ. Math. Univ. Belgrade 1, 145 (1932).
- (5) Ordering of structures has been considered in both mathematical and chemical literature, c.f. M. Randić and C.L. Wilkins, Chem. Phys. Letters, 63, 332 (1979).
- (6) N.S. Ham and R. Ruedenberg, J. Chem. Phys. 29, 1215 (1958).
- (7) Heilbronner's formula is restricted only to graphs containing hexagons and/or linear fragments: E. Heilbronner, Helv. Chim. Acta, 45, 1722 (1962).
- (8) M. Randić, Internat. J. Quantum Chem.: Quantum Biology Symposium, 5, 245 (1978).
- (9) M. Randić, Chem. Phys. Letters, 55, 547 (1978).
- (10) E.F. Beckenbach and R. Bellman, Inequalities (Ergebnisse der Mathematik und ihre Grenzgebiete, Neu Folge, Heft 30) Springer Verlag, Berlin (1961).
- (11) Resonance energies, RE's, reported in this work are based on counting all conjugated circuits in all Kekulé structures, C.f., J.A.N.F. Gomes, Theoret. Chim. Acta (Berlin), 59, 333 (1981).
- (12) HMO pi-energies are compiled from C.A. Coulson and A. Streitwieser, Jr., Dictionary of pi Electron Calculations (Pergamon, Oxford, 1965).
- (13) Heats of atomizations and electron-affinities are quoted from M.J.S. Dewar, J.A. Hashmall and N. Trinajstić, J. Am. Chem. Soc., 92, 5555 (1970).

- (14) Isoconjugate molecules are defined in M. Randić, *Tetrahedron*, 33, 1907 (1977).
- (15) C.f. Ju. A. Schreider, *Equality, Resemblance and Order*, (Mir Publishers Moscow, 1975), Chapter IV.
- (16) For mathematical formalism, see, F. Fratev, O.E. Polansky, A. Meihorn and V. Monev, *J. Mol. Struct.* 56, 245 (1979).
- (17) C.L. Wilkins and M. Randić, *Theoret. Chim. Acta* (Berlin), 58, 45 (1980); M. Randić and C.L. Wilkins, *Internat. J. Quantum Chem.: Quantum Biology Symposium* 6, 55 (1979).
- (18) E. Clar, *The Aromatic Sextet*, John Wiley & Sons (1972). Chapter 11.
- (19) Ref. 18, pp. 76, 96.
- (20) Ref 18 Chapters 14 ,21

TABLE 1

Vectors, $\underline{V}_i = \underline{A}_i^{-1} \underline{X}_i$ where \underline{X}_i is a unit vector conformable with \underline{A}_i^{-1} . The components of the vectors are ordered descendingly and their partial sums are given below each vector in parentheses.

<u>No.</u> *	<u>\underline{V}_i and Partial Sum</u>
1	0.5, 0.5, 0.5, 0.5, 0.5, 0.5 (0.5, 1.0, 1.5, 2.0, 2.5, 3.0)
2	0.667, 0.667, 0.667, 0.667, 0.333, 0.333, 0.333, 0.333, 0.333, 0.333 (0.667, 1.334, 2.001, 2.668, 3.001, 3.334, 3.667, 4.00, 4.333, 4.666)
3	0.5, 0.5, 0.5, 0.5, 0.5, 0.5, 0.5, 0.5, 0.5, 0.5, 0.5, 0.5, 0.0, 0.0 (0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 6.0, 6.0)
4	0.8, 0.8, 0.6, 0.6, 0.6, 0.6, 0.4, 0.4, 0.4, 0.4, 0.2, 0.2, 0.2, 0.2 (0.8, 1.6, 2.2, 2.8, 3.4, 4.0, 4.4, 4.8, 5.2, 5.6, 5.8, 6.0, 6.8, 7.0)
5	0.6, 0.6, 0.6, 0.6, 0.6, 0.6, 0.4, 0.4, 0.4, 0.4, 0.4, 0.4, 0.4, 0.4, 0.2, 0.2, 0.2, 0.2 (0.6, 1.2, 1.8, 2.4, 3.0, 3.6, 4.0, 4.6, 5.0, 5.4, 5.8, 6.2, 6.6, 7.0, 7.4, 7.8, 8.0, 8.2, 8.4, 8.6)
6	0.8, 0.8, 0.714, 0.6, 0.6, 0.571, 0.571, 0.428, 0.428, 0.428, 0.428, 0.400, 0.400, 0.286, 0.286, 0.2, 0.2, 0.2, 0.143. (0.8, 1.6, 2.314, 2.914, 3.514, 4.085, 4.656, 5.084, 5.512, 5.940, 6.34, 6.74, 7.026, 7.312, 7.512, 7.712, 7.912, 8.055)

- 7 0.75, 0.75, 0.5, 0.5, 0.5, 0.5, 0.5, 0.5, 0.5, 0.5, 0.5,
0.5, 0.5, 0.5, 0.25, 0.25, 0.25, 0.25, 0.0
(0.75, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5,
6.0, 6.5, 7.0, 7.25, 7.5, 7.75, 8.0, 8.0)
- 8 0.875, 0.875, 0.75, 0.75, 0.625, 0.625, 0.625, 0.625,
0.375, 0.375, 0.375, 0.375, 0.25, 0.25, 0.125, 0.125,
0.125, 0.125
(0.875, 1.75, 2.5, 3.25, 3.875, 4.5, 5.125, 5.75,
6.125, 6.5, 6.875, 7.25, 7.5, 7.75, 7.875, 8.00,
8.125, 8.25)
- 9 0.667, 0.667, 0.667, 0.667, 0.667, 0.667, 0.333,
0.333, 0.333, 0.333, 0.333, 0.333, 0.333, 0.333,
0.333, 0.333, 0.333, 0.333
(0.667, 1.334, 2.001, 2.668, 3.335, 4.002, 4.335,
4.668, 5.001, 5.334, 5.667, 6.0, 6.333, 6.666, 6.999,
7.333, 7.666, 8.0)
- 10 0.5, 0.5, 0.5, 0.5, 0.5, 0.5, 0.5, 0.5, 0.5, 0.5,
0.5, 0.5, 0.5, 0.5, 0.0, 0.0
(0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0,
5.5, 6.0, 6.5, 7.0, 7.0, 7.0)
- 11 0.75, 0.75, 0.5, 0.5, 0.5, 0.5, 0.5, 0.5, 0.25, 0.25,
0.25, 0.25
(0.75, 1.50, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 4.75, 5.0,
5.25, 5.5)
- 12 0.667, 0.667, 0.667, 0.667, 0.333, 0.333, 0.333,
0.333, 0.333, 0.333, 0.333, 0.333
(0.667, 1.334, 2.001, 2.668, 3.001, 3.334, 3.667,
4.0, 4.333, 4.666, 5.0, 5.333)
- 13 0.667, 0.667, 0.667, 0.667, 0.555, 0.555, 0.444,
0.444, 0.333, 0.333, 0.333, -0.111
(0.667, 1.334, 2.001, 2.668, 3.223, 3.778, 4.222,
4.666, 4.999, 5.332, 5.665, 5.554)

- 14 1.00, 0.5, 0.5, 0.5, 0.5, 0.5, 0.5, 0.5, 0.0, 0.0
(1.00, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 4.5, 4.5)
- 15 0.667, 0.667, 0.667, 0.667, 0.555, 0.555, 0.444,
0.444, 0.333, 0.333, 0.333, 0.333, 0.333, 0.333,
0.333, 0.111
(0.667, 1.334, 2.001, 2.668, 3.223, 3.778, 4.222,
4.666, 4.999, 5.332, 5.665, 5.998, 6.333, 6.666,
7.00, 7.111)
- 16 0.667, 0.667, 0.555, 0.555, 0.5, 0.5, 0.5, 0.5, 0.5,
0.5, 0.5, 0.5, 0.5, 0.444, 0.444, 0.333, 0.333,
0.333, 0.111, 0.0
(0.667, 1.334, 1.889, 2.444, 2.944, 3.444, 3.944,
4.444, 4.944, 5.444, 5.944, 6.444, 6.944, 7.388,
7.832, 8.165, 8.498, 8.831, 8.942, 8.942)
- 17 0.667, 0.667, 0.667, 0.667, 0.667, 0.555, 0.555,
0.555, 0.444, 0.444, 0.333, 0.333, 0.333, 0.333,
0.333, 0.333, 0.333, 0.333, 0.111, 0.0
(0.667, 1.334, 2.001, 2.668, 3.335, 3.89, 4.445, 5.0,
5.444, 5.888, 6.221, 6.554, 6.887, 7.22, 7.553,
7.886, 8.219, 8.552, 8.663, 8.663)
-

* Numbers correspond to graphs shown in Fig 1

TABLE 2

Part of similarity table based on the components of the vectors $\underline{V} = \underline{A}^{-1} \underline{X}$. (\underline{X} is a unit vector).

<u>No.</u> *	<u>6</u>	<u>Z</u>
1	1.30826	1.4577
2	0.9369	1.11215
3	0.77167	0.79056
4	0.52978	0.73824
5	0.39328	0.4743
6	0.000	0.4376
7	0.43757	0.000
8	0.32706	0.6374
9	0.4920	0.6775
10	0.72351	0.6124
11	0.70602	0.8660
12	0.75283	0.6283
13	0.80526	1.0192
14	1.096	1.2747
15	0.42219	0.5629
16	0.57655	0.4817
17	0.4226	0.5892

* Numbers correspond to graphs shown in Fig 1.