# The Characteristic Polynomial Does Not Uniquely Determine Molecular Topology

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**Examples of nonidentical pairs of molecular graphs for which connectivity characteristic polynomials are identical are given. A general method for constructing pairs of molecular graphs of this type is outlined. The potential number of these isomeric pairs is infinite. These circumstances preclude the unique coding of chemical structures by means of connectivity characteristic polynomials.**

The topology of any chemical structure can be unambiguously displayed with an atom connectivity matrix (ACM) or component connectivity matrix (CCM),[1–3] both illustrated below for propane. Expansion of either type of con-

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| C | 1 | | 1 | 1 | 1 | | | | | |
| 1 | C | 1 | | | | 1 | 1 | | | |
| | 1 | C | | | | | | 1 | 1 | 1 |
| 1 | | | H | | | | | | | |
| 1 | | | | H | | | | | | |
| 1 | | | | | H | | | | | |
| | 1 | | | | | H | | | | |
| | 1 | | | | | | H | | | |
| | | 1 | | | | | | H | | |
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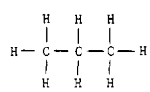
ACM




| | | |
|---|---|---|
| $CH_3$ | 1 | |
| 1 | $CH_2$ | 1 |
| | 1 | $CH_3$ |

CCM

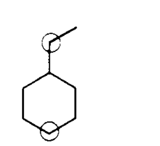
nectivity matrix leads to a characteristic polynomial (CP)* as given by eq 1 for the CCM–CP of propane. The ACM–

$$(CH_3)^2(CH_2) - 2(CH_3) = 0 \tag{1}$$

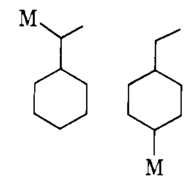
CP and the CCM–CP have recently received a vigorous advocacy by Kudo, *et al.*, as uniquely representing molecular topology.[3]

Of course, it is well-known that the CP of the adjacency matrix of a graph is in general not uniquely related to a single graphical structure.[4–7] The adjacency matrix is the (1,0) binary matrix $\mathbf{A} = [a_{ij}]$, where $a_{ij} = 1$ when points $i$ and $j$ are connected, and the CP is the expansion of the determinant of the matrix $\mathbf{A} - X\mathbf{I}$ where $\mathbf{I}$ is the identity matrix. Nonisomorphic graphs with identical CP's are called isospectral graphs and have the same spectrum of eigenvalues. Introduction of the variable diagonal terms as in the ACM is presumed to obviate the occurrence of conditions leading to isospectral graphs or molecules.[3]

Examples of isospectral open-chain and cyclic hydrocarbon systems that are of interest to organic chemists have been given in recent papers.[8,9] Methods for constructing pairs of isospectral molecules have been delineated based primarily on the use of the concepts of "isospectral points" and "induction points." Isospectral points in the styrene $\pi$-system graph are circled, and substitution of any graph M at the isospectral points in turn generates a pair of isos-

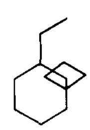


Isospectral points ○

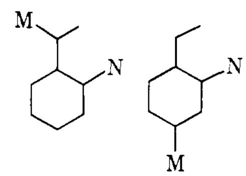



Isospectral graphs

pectral graphs.[8] Furthermore the square in the styrene graph designates an induction point.[9] Arbitrary substitu-



Induction point ◇



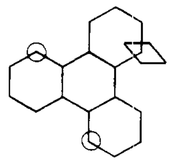
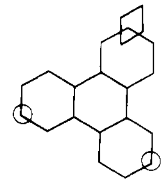

Isospectral graphs

tion at the induction point and further substitutions in turn at the isospectral points yield additional isospectral graphs. A proof that isospectral points must have identical absolute values of eigenvectors was also given.[9]

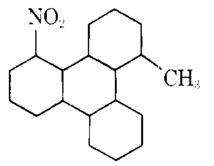
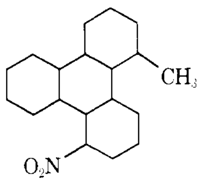
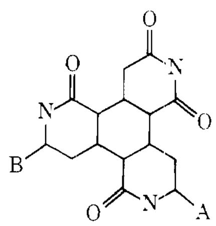
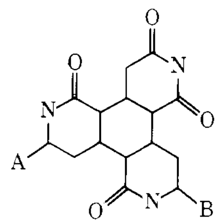
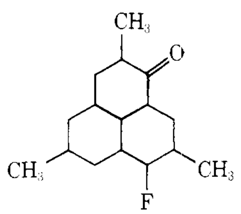
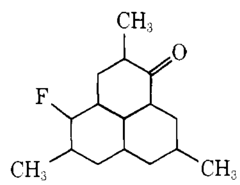
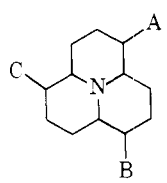
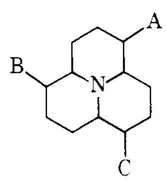
## ISOSPECTRAL MOLECULES WITH IDENTICAL ACM–CP

It is true that isospectral graphs based on the styrene isospectral points will have differing ACM–P or CCM–CP when the entire molecular structure is used to write the respective matrices. This is also true for all other examples of isospectral graphs previously given in the literature, contrary to an opinion of Balaban and Harary.[6] However, there is a particular large class of graphical or molecular structures that contain induction points for which the resulting pairs of isomeric structures have identical CP for every type of connectivity matrix. The genotype structure is a molecular graph with $n$-fold ($n > 2$) symmetry that contains equivalent points that are not related by a twofold element of symmetry. An example is provided by the triphenylene or perhydrotriphenylene graph in which isospectral and induction points are indicated by circles and squares, respectively.

* The characteristic polynomial is called the determinant polynomial and abbreviated DP in ref 3.

Since the designated points are related by symmetry, they must have equivalent absolute values of coefficients of eigenvectors. Since the reciprocal relationship of the induction point on the two isospectral points is also identical

from symmetry, substitution at the induction point has identical effects on the eigenvectors at the two isospectral points.[10] Substitution at the induction point destroys the structural equivalency of the circled points but does not affect their isospectrality. Pairs of isospectral molecular graphs generated by using these principles will have pairs of identical connectivity CP in any approximation. Some examples are given below, where the graphical figures are meant to include all attached hydrogen atoms.

Rather complicated structures with both real and abstract substituents are depicted in order to illustrate the great variety of possible molecular types. The structures can be saturated or unsaturated as long as the original threefold symmetry elements are maintained. It should be emphasized that pairs of molecules corresponding to graphs of this type are not geometric, diastereomeric, or enantiomeric isomers. They are structurally and topologically isomeric, as fundamentally different from each other as are the compounds 2-bromoheptane and 3-bromoheptane.

The fact that isomeric structures possess identical ACM–CP and CCM–CP shows that the presuppositions of Kudo, *et al.*, are incorrect. The total number of ACM–CP's is not equivalent to the total number of structural isomers and cannot be used to count unambiguously the number of structural isomers for a particular formula. I suggest that it is unlikely that any additional embellishments of molecular structural matrices will lead to characteristic polynomials that uniquely characterize each and every structure.


## ACKNOWLEDGMENT

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