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# ISOSPECTRAL MOLECULES

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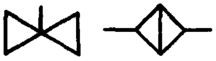
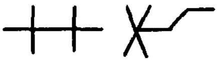
The adjacency matrix of a graph is identical to the Hückel molecular orbital (HMO) secular matrix for the electronic system isomorphic to the graph.[1-4] This congruity has led several investigators to devise methods for writing out the algebraic terms of the characteristic polynomial from inspection of the graph of a molecular system.[1,5-10] Structure-reactivity relationships with the polynomial coefficients have been established.[11-15] Finally, the easily obtained solutions (factorization and/or Newton's method) to the characteristic polynomials are the eigenvalues of the delocalized electronic species.

In graph theory, the set of eigenvalues for the adjacency matrix is called the spectrum of the graph. At a meeting of the American Mathematical Society, Harary conjectured that the characteristic polynomial of the adjacency matrix characterizes the graph.[16,17] In other words, a graph would possess its unique characteristic polynomial, and hence a unique spectrum of eigenvalues. A counter-example was immediately provided and many are now known. It has even been established that almost all non-cyclic graphs (tree graphs) have an isospectral mate.[18] The smallest pair of connected isospectral graphs is shown in **1**,[17] and the two smallest tree graphs are given in **2**.[19]

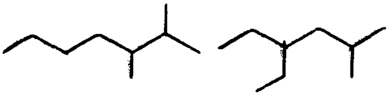


**1**

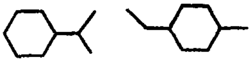


**2**

It is of interest to identify those pairs of possible molecular structures that are isospectral. Neither **1** nor **2** fit in this category, although the second structure in **1** could represent dimethylbicyclobutane or the dimethylenebicyclobutadiene π-system. The graphs shown in **3** and **4** are the smallest possible pairs in which both structures could correspond to molecular hydrocarbon species. I think it is intriguing that the formally more localized 2-phenylallyl radical π-system must have exactly the same HMO delocalization energy as the fully conjugated 4-vinylbenzyl system.

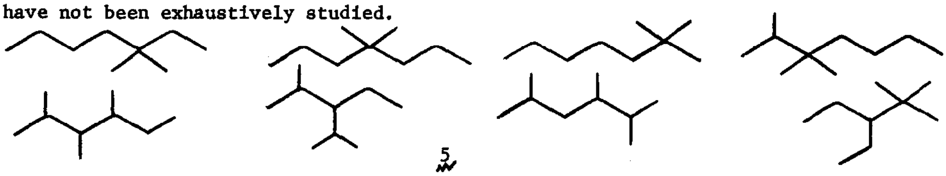


**3**



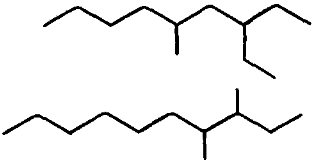
**4**

Since the graphs in **3** or **4** can represent either π or carbon-skeleton σ-systems one notes that 2,3-dimethylheptane and 4-ethyl-2-methylhexane would have identical energy levels within a carbon-carbon bond orbital theoretical approach.[20-22] There are four other pairs of 9-vertex isospectral graphs that can represent saturated hydrocarbon systems shown in **5**.[23] Only four isospectral tree graph pairs can be written for 10-vertex systems,[23] and larger graphs have not been exhaustively studied.

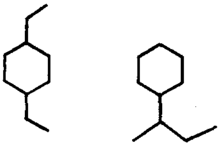


**5**

The molecules depicted in **6** and **7** are the smallest pairs of stable ground-state π-structures that are isospectral. One notes again that formally through-conjugated systems

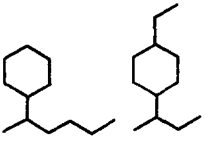


**6**

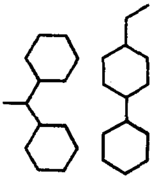


**7**

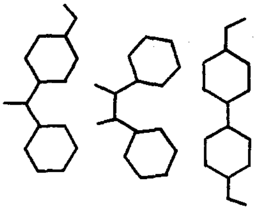
are isospectral to cross-conjugated systems. Within HMO approximations both molecules of each pair would be expected to absorb at the same wavelength. The classical effect of cross-conjugation is therefore not a general effect as is usually presupposed.[24,25] Further examples are given by the pairs of isospectral molecules in **8** and **9** and the trio of isospectral compounds shown in **10**.



**8**

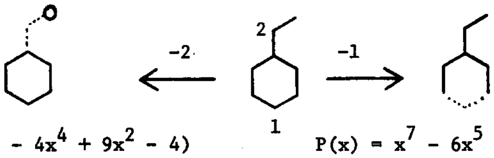


**9**



**10**

No completely general algorithms can be deduced for constructing pairs of isospectral molecules. However, in an extended graph-theoretical study of the HMO secular polynomials of $\pi$-systems I discovered that the styrene graph contains within itself two different vertices that can be excised to leave residual systems that are isospectral. This means, because of



$$P(x) = (x)(x^6 - 4x^4 + 9x^2 - 4) \qquad P(x) = x^7 - 6x^5 + 9x^3 - 4x$$

well-known recursive formulae for polynomials,[7,18] that any graph R may be attached to styrene graph at positions 1 and 2 to yield two different isospectral graphs. The isospectral $\pi$ graphs in **4**, and **7**-**10** were assembled making use of this principle, and infinite numbers of isospectral pairs are obtainable using the "isospectral points" of styrene graph. A search for isospectral points in other molecular graphs has so far not been successful.

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