

ON THE ALMOST-ISOSPECTRALITY CONCEPT
for benzenoid systems

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Abstract

The recently proposed (Gutman and Markovic, Chem.Phys.Letters 185 (1991) 473) measure for almost-isospectrality (*aim*) of molecular graphs is examined and its definition is made more precise. It is found that there exist remarkably few pairs of almost-isospectral benzenoid systems ($aim < 0.01$). Some novel examples of this kind are reported.

Measuring almost-isospectrality

In a recent paper [1] two of the present authors proposed to measure the degree of coincidence between the spectra of two molecular graphs by means of a quantity *aim*. Two conjugated π -electronic systems for which *aim* is sufficiently small (tentatively $aim < 0.01$) are said to be almost-isospectral. The Hückel molecular orbital (HMO) energy levels of the respective two compounds will then almost coincide. Consequently, if we can trust in the HMO model, then we would have to ex-

pect that many of the physical and chemical properties of the conjugated molecules whose molecular graphs are almost isospectral differ insignificantly [1]. This especially applies to UV/visible and photoelectron spectroscopic features, ionization potentials and other MO-energy-related quantities.

Thus by studying the above mentioned measurable properties of conjugated molecules whose molecular graphs are almost isospectral we might be able to assay the HMO theory and to gain a direct experimental evidence for its accuracy, scope and limitations. Heilbronner and Jones [2] already performed such a test on the pair 1,3-divinylbenzene & 2-phenylbutadiene (whose molecular graphs are strictly isospectral) and came to the conclusion that the HMO model gives very poor results. In order to be able to extend such an analysis to benzenoid hydrocarbons (which are reasonably stable, planar conjugated systems without steric strain and for which the HMO model is believed to work particularly well) we need first to find isospectral or almost-isospectral Kekuléan benzenoid systems. Since pairs of isospectral Kekuléan benzenoids are - at the present moment - not known to exist [3-6], we directed our efforts towards almost-isospectral species [1].

If G and H are molecular graphs, each possessing n vertices and m edges [7], and if $x_1^G, x_2^G, \dots, x_n^G$ and $x_1^H, x_2^H, \dots, x_n^H$ are their eigenvalues [7], then

$$aim(G,H) = C \sum_{i=1}^n (x_i^G - x_i^H)^2 \quad (1)$$

where

$$C = \frac{n^2}{4m} \quad (2)$$

In eq. (1) it is assumed that the graph eigenvalues x_i^G and x_i^H are labeled in a non-decreasing order.

The criterion for choosing the normalization coefficient C in eq. (1) is that the numerical values of aim become as much as possible independent of the size of the graphs G and H (i.e. independent of the parameters n and m). In order to achieve this goal we calculated the expected value $\mathcal{E}[Z]$ of the quantity Z

$$Z = \sum_{i=1}^n (g_i - h_i)^2$$

in which g_i and h_i are random variables selected uniformly from a certain interval $[-a, +a]$. The value of a is determined from the conditions

$$\mathcal{E}\left[\sum_{i=1}^n (g_i)^2\right] = \mathcal{E}\left[\sum_{i=1}^n (h_i)^2\right] = 2m \quad (3)$$

Then the coefficient C in eq. (1) is chosen to be equal to $\mathcal{E}[Z]^{-1}$.

Now, in order to calculate $\mathcal{E}[Z]$ we need to know $\mathcal{E}[g_i]$ and $\mathcal{E}[h_i]$. In [1] it was stated without proof that

$$\mathcal{E}[g_i] = \mathcal{E}[h_i] = -a + 2ai/n - a/n \quad (4)$$

from which eq. (2) was deduced straightforwardly.

As a matter of fact, if the variables g_1, g_2, \dots, g_n and h_1, h_2, \dots, h_n are chosen from the interval $[-a, +a]$ randomly and uniformly, and then rearranged so as to form two non-decreasing sequences, then the respective expected values are given by [8]

$$\mathcal{E}[g_i] = \mathcal{E}[h_i] = -a + 2ai/(n+1) \quad (5)$$

At first glance the differences between eqs. (4) and (5) look insignificant. However, using (5) and bearing in mind (3) one computes $\mathcal{E}[Z] = 8m/(n+1)$. This result would force us to define the almost-isospetra- lity measure as

$$aim_0(G, H) = C_0 \sum_{i=1}^n (x_1^G - x_1^H)^2$$

where

$$C_0 = \frac{n+1}{8m} \quad (6)$$

By comparing eqs. (2) and (6) it is clear that with the increasing size of the molecular graphs G and H (i.e. with increasing n and m) the two almost-isospectrality measures will have completely different behaviors. In homologous series of benzenoid systems that differ only in their terminal fragments, we found that aim_0 is size-dependent, whereas aim is not size-dependent. An illustrative example is presented in Fig. 1; note that S_h and T_h are isoarithmic molecules [9], possessing coinciding sets of resonance structures, identical sextet polynomials etc. [10]. In view of these results we are inclined to consider aim as a somewhat better measure of almost-isospectrality of structurally similar benzenoid systems than aim_0 .

A definition of aim

In order to avoid the difficulties mentioned in the previous section we need to slightly modify the original definition of aim . This can be done in the following manner.

Divide the interval $[-a, +a]$ into n equal parts i.e. consider the intervals $I_i = [-a + 2a(i-1)/n, -a + 2ai/n]$, $i = 1, 2, \dots, n$. Choose the variables g_i and h_i randomly and uniformly from the interval I_i and impose the conditions (3). Observe that in this case the orderings $g_1 \leq g_2 \leq \dots \leq g_n$ and $h_1 \leq h_2 \leq \dots \leq h_n$ are automatically obeyed.

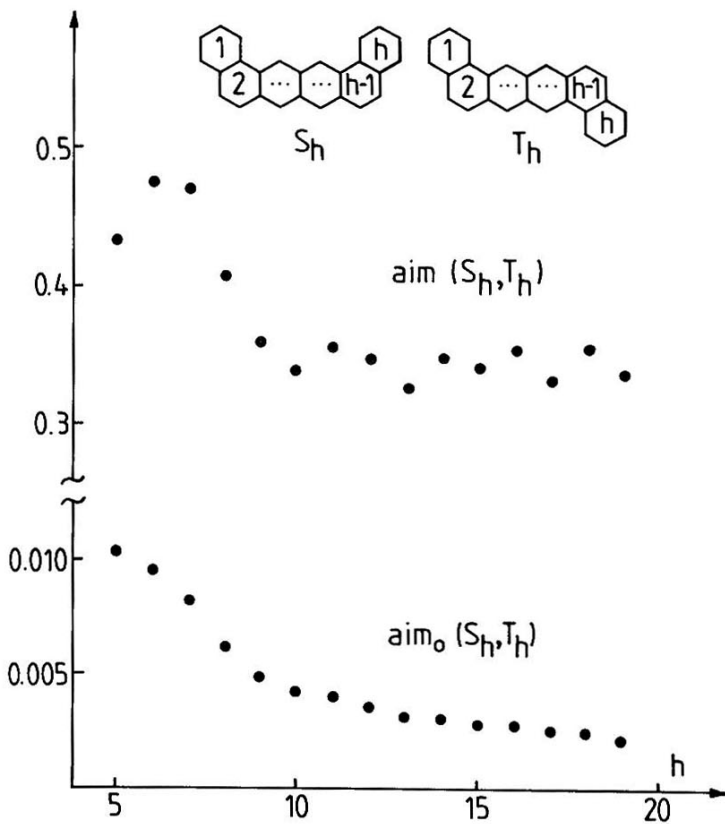


Fig. 1. The two almost-isospectrality measures as functions of the numbers of hexagons (h) of the benzenoid isomers S_h and T_h ; observe that for $h \geq 9$ $aim(S_h, T_h)$ is essentially independent of h , namely the respective points are scattered along a horizontal line; $aim_o(S_h, T_h)$ monotonically decreases with increasing h and is thus evidently size-dependent

Since the probability density of the variables g_1 and h_1 is now

$$\Gamma_1(x) = n/2a \quad \text{for } x \in I_1 \\ 0 \quad \text{for } x \notin I_1 \quad (7)$$

we have

$$\mathcal{E}[g_1] = \mathcal{E}[h_1] = \int_{-\infty}^{+\infty} x \Gamma_1(x) dx$$

which after elementary integration yields eq. (4). Further,

$$\mathcal{E}[(g_1)^2] = \mathcal{E}[(h_1)^2] = \\ = \int_{-\infty}^{+\infty} x^2 \Gamma_1(x) dx = (a/n)^2 [(n+1-2l)^2 + 1/3] .$$

By substituting this relation back into eq. (3) and performing a lengthy calculation we obtain $a = (6m/n)^{1/2}$, the same formula as reported in [1].

Hence $\mathcal{E}[Z] = 4m/n^2$ is a mathematically exact result provided the probability distribution of the random variables g_i and h_i is given by eq. (7), $i = 1, 2, \dots, n$. Consequently, the almost-isospectrality measure, as given by eqs. (1) and (2), has to be defined via the probability density function (7).

A theorem on aim

Measuring the degree of coincidence of two graph spectra by means of *aim*, we may ask whether it would be possible to relabel the eigenvalues $x_1^H, x_2^H, \dots, x_n^H$ so as to decrease the value of the right-hand side of eq. (1). The answer to this question is negative:

Theorem. Let $x_1^G \leq x_2^G \leq \dots \leq x_n^G$. Then among the possible orderings of the eigenvalues of the graph H , the ordering $x_1^H \leq x_2^H \leq \dots \leq x_n^H$ corresponds to the minimum value of *aim*, as defined by means of eq. (1).

Proof. Let $aim^\dagger(G,H)$ correspond to the ordering $x_1^H \leq x_2^H \leq \dots \leq x_n^H$ and $aim^\ddagger(G,H)$ to some other ordering of the eigenvalues of the graph H. Without loss of generality we may assume that this latter ordering is obtained by exchanging x_r^H and x_s^H . Then

$$aim^\ddagger(G,H) - aim^\dagger(G,H) = \left[(x_r^G - x_s^H)^2 + (x_s^G - x_r^H)^2 \right] - \left[(x_r^G - x_r^H)^2 + (x_s^G - x_s^H)^2 \right] .$$

Direct calculation gives now

$$aim^\ddagger(G,H) - aim^\dagger(G,H) = 2 (x_r^G - x_s^G)(x_r^H - x_s^H) . \quad (8)$$

Because $x_r^G \geq x_s^G \iff x_r^H \geq x_s^H$, the right-hand side of (8) cannot become negative-valued. Consequently, $aim^\ddagger(G,H) \leq aim^\dagger(G,H)$ with equality if and only if $x_r^G = x_s^G$ or $x_r^H = x_s^H$. ■

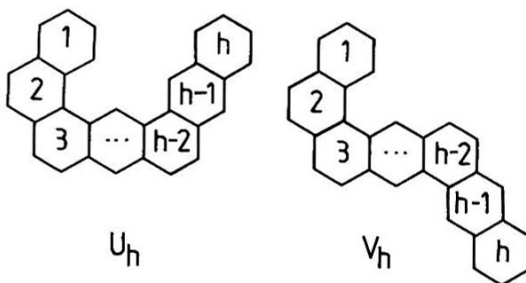
Search for almost-isospectral benzenoid systems

In [1] the condition $aim < 0.01$ was established as a criterion for almost-isospectrality of a pair of benzenoid isomers. An extensive examination (which is described in due detail in the present section) revealed that this seems to be a very restrictive requirement and that the actual number of almost-isospectral benzenoids happens to be surprisingly small.

Isospectral benzenoid systems (for which $aim = 0$) have recently been discovered by one of the present authors and a general method for their construction has been put forward [4]. This procedure, however, necessarily produces odd pericondensed isospectral species [4,5], which, consequently, cannot possess Kekulé structures. The smallest

such example corresponds to hydrocarbon radicals whose formulas are $C_{33}H_{17}$ i.e. to benzenoid systems composed of nine hexagons ($h = 9$) [6]. Bearing this in mind we decided to examine the structurally most similar $h = 9$ Kekuléan $C_{32}H_{16}$ and $C_{34}H_{18}$ benzenoids [11-13], hoping to detect among them cases with low values of *aim*. However, among the 46 possible $C_{32}H_{16}$ isomers and the 333 possible $C_{34}H_{18}$ isomers there is not a single almost-isospectral pair. The minimal *aim*-values found were 0.222 (for $C_{32}H_{16}$) and 0.029 (for $C_{34}H_{18}$).

There are 118 catacondensed $C_{30}H_{18}$ benzenoid isomers ($h = 7$) and 411 $C_{34}H_{20}$ benzenoid isomers ($h = 8$) [13]. Among them only two pairs were found to be almost-isospectral, namely U_7, V_7 and U_8, V_8 ;
 $aim(U_7, V_7) = 0.00522$, $aim(U_8, V_8) = 0.00516$.



Because of this result we determined the *aim*-values also for the higher members of the U_h, V_h series. These are depicted in Fig. 2. For $h = 11$ and $h = 18$, $aim(U_h, V_h) = 0.00181$ and 0.00157 , respectively, which are the smallest *aim*-values found by us so far.

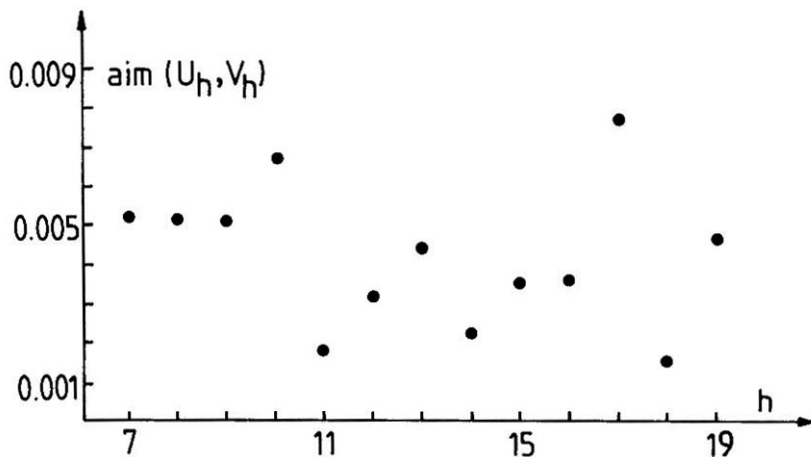


Fig. 2. The *aim*-values for the homologous series U_h, V_h ; observe the apparent absence of any periodicity and regularity

The examples presented in Figs. 1 and 2 clearly illustrate that the dependence of *aim*(G,H) on the structure of the molecular graphs G and H is very complicated and apparently fails to follow any reasonable pattern. In particular, we don't know how to design almost-isospectral benzenoid systems (except by brute-force search). Examination of the structure-dependency of *aim* is under way in our laboratory.

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