Violation of the Dewar-Longuet-Higgins Conjecture

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In 1952 Dewar and Longuet-Higgins have shown [1] that the product of all occupied Hückel energy levels (in β units) is equal to the number of Kekulé structures (K):

$$\prod_j^{\text{occ}} E_j = K \tag{1}$$

for benzenoid and acyclic polyenes. They have conjectured that the total π-electron energy

$$E_\pi = 2 \sum_j^{\text{occ}} E_j \tag{2}$$

is also proportional to K. In particular, if G and H are two isomeric hydrocarbons, the Dewar-Longuet-Higgins conjecture can be expressed as:

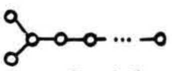
$$K(G) > K(H) \Rightarrow E_\pi(G) > E_\pi(H)\,. \tag{3}$$

Note that isomeric conjugated hydrocarbons have the same number of rings.

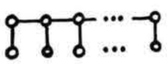
The rule (3) was extended later to cover non-benzenoid alternant [2] and non-alternant [3] conjugated systems and its validity has been demonstrated on numerous examples [4]. Recent graph-theoretical investigations of heterocyclic compounds [5] and conjugated polymers [6] give evidence that also these compounds fulfill the Dewar-Longuet-Higgins conjecture in many cases.

However, the offered [1–3] explanation for (3) that, if the product of a set of non-negative numbers is large (small), their sum is also large (small), is unsatisfactory. Nevertheless, no one violation from (3) has been reported yet.

In order to disprove the general validity of the Dewar-Longuet-Higgins conjecture (3) two classes of isomeric acyclic polyenes have been studied, their topologies [7] being represented by graphs **1** and **2**.



Graph **1**



Graph **2**

Obviously $K(\mathbf{1}) = 0$ and $K(\mathbf{2}) = 1$.

Rather simple analytical expressions for E_j and E_π could be derived for both **1** and **2**. Hence, for the graph **1**:

$$E_j(\mathbf{1}) = 2\cos\frac{(2j-1)\pi}{2n-2}\,,\quad j = 1, 2, \ldots, n-1\,,$$

$$E_n(\mathbf{1}) = 0\,, \tag{4}$$

$$E_\pi(\mathbf{1}) = \begin{cases} 2\,\mathrm{cotg}[\pi/(2n-2)] & \text{for even } n, \\ 2\,\mathrm{cosec}[\pi/(2n-2)] & \text{for odd } n. \end{cases} \tag{5}$$

For the graph **2**:

$$E_j(\mathbf{2}) = \cos[2j\pi/(n+2)] + \sqrt{1+\cos^2(2j\pi/n+2)}\,,\ j = 1, 2, \ldots, n/2;$$

$$E_{n/2+j}(\mathbf{2}) = \cos[2j\pi/(n+2)] - \sqrt{1+\cos^2[2j\pi/(n+2)]}\quad j = 1, 2, \ldots, n/2; \tag{6}$$

$$E_\pi(\mathbf{2}) = \sum_{j=1}^{n} \sqrt{1+\cos^2[2j\pi/(n+2)]} \tag{7}$$

where n denotes the number of vertices in **1** or **2**. Both expressions (5) and (7) become rapidly linear functions when n is increasing. Hence

$$E_\pi(\mathbf{1}) \approx 4/\pi\, n - 4/\pi = 1.273\,n - 1.273 \tag{8}$$

and

$$E_\pi(\mathbf{2}) \approx 1.216\,n - 0.396 \tag{9}$$

since [8]

$$\frac{1}{2\pi}\int_0^{2\pi} \sqrt{1+\cos^2 x}\,\mathrm{d}x = 1.216007\,. \tag{10}$$

Now, the slope of the line (8) is larger than that of (9) and therefore for n being large enough it must be

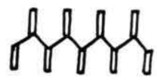
$$E_\pi(\mathbf{1}) > E_\pi(\mathbf{2}) \tag{11}$$

despite of $K(\mathbf{1}) < K(\mathbf{2})$. Calculations show that this occurs at $n = 18$, as indicated in the table

n	14	16	18	20
E_π (**1**)	16.471	19.029	21.583	24.136
E_π (**2**)	16.628	19.060	21.492	23.924

Thus

and



are the smallest pair of conjugated hydrocarbons which violate the Dewar-Longuet-Higgins conjecture.

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