

A STOCHASTIC APPROACH TO THE TÜRKER ANGLES

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Abstract

Using a Monte Carlo method the average values of the Türker angles are calculated for graphs with n vertices and m edges, among which are the graphs representing isomeric conjugated hydrocarbons C_nH_{3n-2m} . The approach is extended to all values of m , $1 \leq m \leq n(n-1)/2$. The basic features of the dependence of the Türker angles on n and m are established. The results obtained shed new light on some fundamental properties of the total π -electron energy of conjugated molecules.

1. INTRODUCTION

The concept of the angle θ was introduced into the theory of total π -electron energy of unsaturated conjugated molecules by Lemi Türker [1], and was eventually elaborated both by the same author [2]-[5] and by others [6]-[8]. Recently, Türker defined [9] two more angles, denoted here by α and β . These, so-called "Türker angles" satisfy the condition

$$\alpha + \beta = \theta$$

and conform to the relations [7]-[9]:

$$\cos \theta = \frac{E}{\sqrt{2mn}} \quad (1)$$

$$\cos \alpha = \frac{E + n}{\sqrt{n(n + 2m + 2E)}} \quad (2)$$

$$\cos \beta = \frac{E + 2m}{\sqrt{2m(2m + n + 2E)}} \quad (3)$$

where E stands for the total π -electron energy (calculated within the HMO approximation and expressed in the units of the carbon-carbon resonance integral), and where n and m are the numbers of vertices and edges, respectively, of the corresponding molecular graph [10, 11]. In what follows a graph with n vertices and m edges will be referred to as an (n, m) -graph. Some of such graphs represent isomeric conjugated hydrocarbons with formula $C_n H_{3n-2m}$, provided, of course, $n - 1 \leq m < 3n/2$.

Originally [1, 9] the angles θ , α and β were considered only in the case of even alternant conjugated hydrocarbons. They, however, are easily extended to arbitrary π -electron systems or, more generally, to arbitrary (n, m) -graphs. This is achieved as follows.

Let G be an (n, m) -graph, and let X_1, X_2, \dots, X_n be its eigenvalues. It is well known that [10, 11]

$$E = |X_1| + |X_2| + \dots + |X_n| \quad (4)$$

and

$$X_1^2 + X_2^2 + \dots + X_n^2 = 2m. \quad (5)$$

Note that the relation (5) is valid for all graphs. Eq. (4) is the definition of the so called energy of the graph G and is, as such, also applicable to all graphs. In the case of the vast majority of chemically relevant graphs, E coincides with the HMO total π -electron energy (in β -units) of the underlying conjugated molecule; in a few cases this "graph energy" slightly deviates from the true HMO value. A detailed discussion of this matter can be found in the book [11].

Construct two n -dimensional vectors $\vec{A} = (1, 1, \dots, 1)$ and $\vec{B} = (|X_1|, |X_2|, \dots, |X_n|)$, and recall that by Eq. (4) their scalar product is just the energy of G :

$$\vec{A} \bullet \vec{B} = \sum_{i=1}^n (1 \cdot |X_i|) = \sum_{i=1}^n |X_i| = E. \quad (6)$$

On the other hand, the same scalar product is equal to $|\vec{A}| \cdot |\vec{B}| \cos \theta$ with θ being

the angle between the vectors \vec{A} and \vec{B} . The lengths of these vectors are:

$$|\vec{A}| = \sqrt{(1)^2 + (1)^2 + \cdots + (1)^2} = \sqrt{n}$$

and, in view of Eq. (5),

$$|\vec{B}| = \sqrt{(|X_1|)^2 + (|X_2|)^2 + \cdots + (|X_n|)^2} = \sqrt{2m}.$$

Whence,

$$\vec{A} \bullet \vec{B} = \sqrt{2mn} \cos \theta. \quad (7)$$

Combining Eqs. (6) and (7) we arrive at formula (1).

The quantities α and β are defined [9] as the angles between the vector $\vec{C} = \vec{A} + \vec{B}$ and the vectors \vec{A} and \vec{B} , respectively.

The geometric interpretation of the Türker angles θ , α and β is clear from Fig. 1. Knowing the lengths of the vectors \vec{A} , \vec{B} and \vec{C} , formulas (2) and (3) are deduced by standard trigonometric reasoning [7, 8].

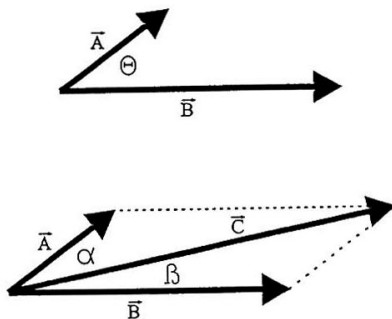


Fig. 1. Geometric interpretation of the Türker angles

In the study of the Türker angles the question to be asked first is how these quantities depend on various structural features of the conjugated molecule under consideration, i. e., on the structure of the underlying molecular graph. The simplest among these questions is how θ , α and β depend on the parameters n and m . In this work we offer a partial answer to it.

2. A MONTE CARLO APPROACH TO THE TÜRKER ANGLES

Following a recently elaborated technique [12, 13], we calculated the average Türker angles by a Monte-Carlo type computer experiment. Using the Haas random number generator [14] we constructed labeled graphs with n vertices and m edges, uniformly at random. This was done by fixing a value of n , starting with the n -vertex graph without edges and adding to it new edges one-by-one, uniformly at random: thus the number of edges varies between $m = 1$ and $m = n(n-1)/2$. For the (n, m) -graph thus obtained the energy was calculated and then, by using Eqs. (1)-(3), the three Türker angles. Typical results are shown in Figs. 2, 3 and 4.

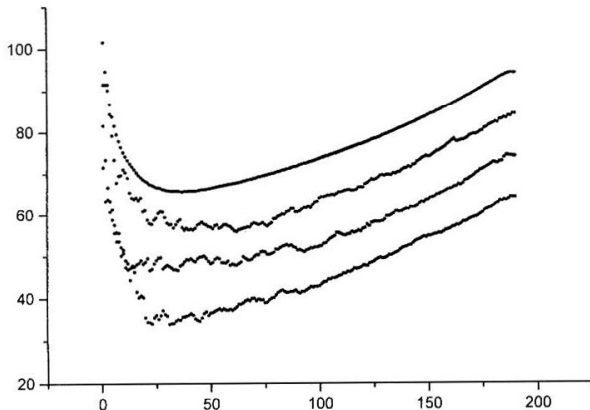


Fig. 2. The Türker angle θ (in degrees) calculated for $n = 20$ and $m = 1, 2, \dots, 190$; the three bottom curves are results of three consecutive Monte Carlo experiments, the top curve is the average value of 250 repeated Monte Carlo experiments; the second, third and fourth curves are shifted upwards by 10, 20 and 30 degrees, respectively

It should be noted that the present procedure generates symmetric graphs less frequently than those asymmetric, and thus somewhat distorts the average values obtained. We believe that these discrepancies are not too significant, especially in view

of the fact that, as the number of vertices is increasing, the vast majority of the graphs encountered in our study has a trivial automorphism group. Nevertheless, efforts are being made to upgrade our analysis by employing graph generators that produce (n, m) -graphs (not labeled graphs!) uniformly at random. The results obtained along these lines will be communicated elsewhere.

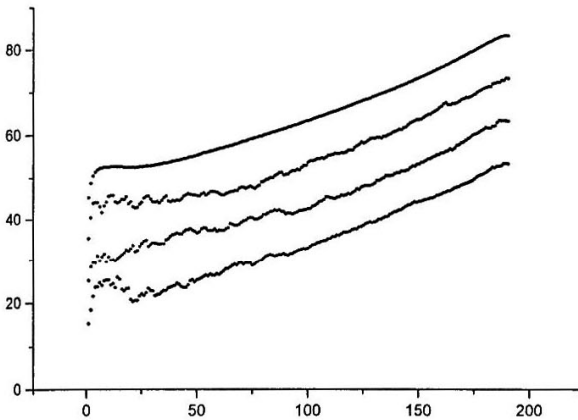


Fig. 3. The Türker angle α (in degrees) calculated for $n = 20$ and $m = 1, 2, \dots, 190$; other details are same as in Fig. 2

Whereas the individual Monte Carlo results vary significantly (cf. the three lower curves in Figs. 2, 3 and 4), after averaging over a sufficiently large number of repeated runs an almost perfectly smooth curve is obtained (cf. the top curve in Figs. 2, 3 and 4). Empirically we found that 250 repetitions are sufficient for obtaining a smooth and reproductive (n, m) -dependence of the Türker angles.

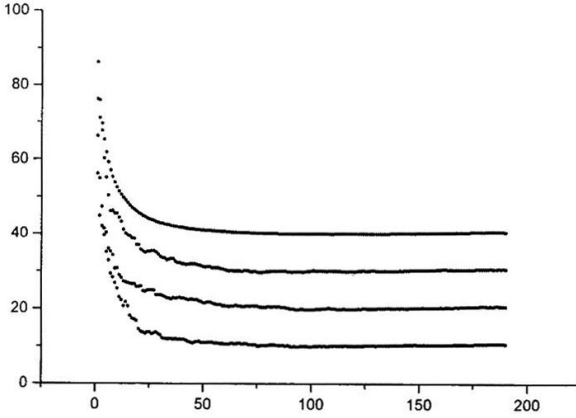


Fig. 4. The Türker angle β (in degrees) calculated for $n = 20$ and $m = 1, 2, \dots, 190$; other details are same as in Fig. 2

3. PROPERTIES OF AVERAGE TÜRKER ANGLES

The basic features of the (n, m) -dependence of the Türker angles are seen from Figs. 2-5.

The Angle θ

For a fixed value of n the average $\theta = \theta(m)$ curve decreases, has a minimum and then monotonically increases. The value m_{min} of m at which θ is minimal linearly increases with n . A least-squares fitting of the data for $n = 5, 6, \dots, 30$ gave

$$m_{min} = (2.33 \pm 0.05)n - (9.0 \pm 0.9)$$

with correlation coefficient $R = 0.995$.

Curiously, however, the minimal value of θ is practically independent of n and is found to be 35.5 ± 0.8 degrees.

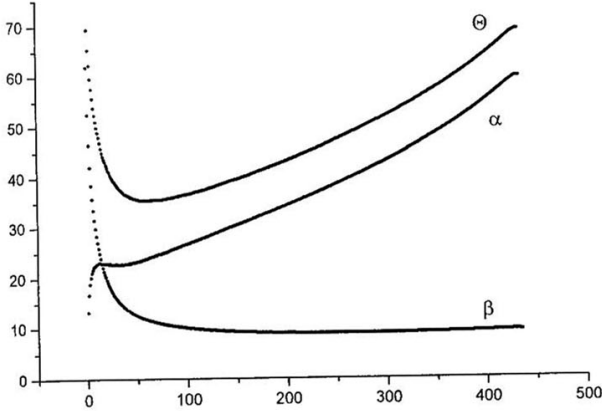


Fig. 5. The m -dependence of the three average Türker angles (in degrees) for $n = 30$; the curves are averages of 250 repeated Monte Carlo calculations; $m = 1, 2, \dots, 435$

The Angle α

For a fixed value of n the average $\alpha = \alpha(m)$ curve first rapidly increases, attains a maximum and very near to it a minimum, and then monotonically increases. In this latter region the $\alpha(m)$ and $\theta(m)$ curves run practically parallel to each other, a consequence of the fact that β is nearly constant (see below).

Both the maximum and the minimum on the $\alpha(m)$ curve are quite shallow and (especially for smaller values of n) are located so close to each other that are difficult to observe. With increasing n the position of the maximum is only slightly shifted towards larger values of m . The same is true for the separation between the maximum and the minimum. Thus, for $n = 10$, $\alpha_{max} = 22.2^\circ$ at $m = 4$ and $\alpha_{min} = 21.7^\circ$ at $m = 6$, whereas for $n = 20$, $\alpha_{max} = 22.7^\circ$ at $m = 14$ and $\alpha_{min} = 22.5^\circ$ at $m = 20$.

The Angle β

For a fixed value of n the average $\beta = \beta(m)$ curve first rapidly decreases and then attains an almost constant value. This constant value is weakly dependent on n . For

instance, for $n = 10, 20, 30$ it is equal to 12.3, 10.3 and 9.0 degrees, respectively. A closer inspection reveals that $\beta(m)$ has a very shallow minimum, whose depth does not exceed 0.5° , and which in Figs. 4 and 5 cannot be noticed.

* * *

We believe that by means of the above described stochastic approach we established the fundamental characteristics of the dependence of the Türker angles on the parameters n and m . We examined this dependence in the entire range of m , that is for $1 \leq m \leq n(n-1)/2$. By this we extended the study of the angles to graphs having more edges than it is possible in the case of molecular graphs. We consider this as an advantage: some of the above specified properties of θ , α and β would hardly ever be discovered if their study would be restricted to molecular graphs.

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