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On the Türker Angles in the Theory of Total π-Electron Energy

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The Türker angles θ, α and β are quantities invented by Lemi Türker, and are used in the theory of total π-electron energy (E) of unsaturated conjugated hydrocarbons. We report here expressions for θ, α and β in terms of E and the parameters n (= half the number of carbon atoms) and e (= the number of carbon-carbon bonds). The forms of these expressions are remarkably similar. Numerical calculation performed on a representative set of benzenoid hydrocarbons reveals that the dependence of the angles α and β on molecular structure is very similar, and that their ratio is almost constant ($\alpha/\beta \approx 1.564 \pm 0.015$).

Introduction

In the theory of total π-electron energy (E) of unsaturated conjugated molecules[1–3] it is well known that the two main structural factors determining E are the number of carbon atoms ($2n$) and the number of carbon-carbon bonds (e). In 1971 McClelland[4] established that the expression E_M,

$$E_M = 2(ne)^{1/2} \tag{1}$$

is an upper bound for E, which means that the ratio E/E_M is necessarily less than unity. In 1992 Türker[5] arrived at the ingenious idea of interpreting this ratio as the cosine of a certain angle, namely

$$E/E_M = \cos\theta \tag{2}$$

i.e.,

$$E = 2(ne)^{1/2}\cos\theta.$$

The parameter θ should justly be called *the Türker angle* of the total π-electron energy.

The Türker angle θ has proven to be a useful novel concept in the theory of total π-electron energy, and it has found numerous applications[5–10]. Recently, Türker has introduced[11] two more angles, closely related to θ. These are conceived as follows.

First of all, recall that if $X_1, X_2, \ldots, X_n$ are the positive eigenvalues of the molecular graph of an alternant hydrocarbon, then[1–3,5,11]

$$2\sum_{i=1}^{n} X_i = E \quad \text{and} \quad \sum_{i=1}^{n} X_i^2 = e. \tag{3}$$

Let $\vec{A} = (1, 1, \ldots, 1)$ and $\vec{B} = (X_1, X_2, \ldots, X_n)$ be two vectors in the n-dimensional Euclidean space. Their lengths are

$$|\vec{A}| \equiv [\vec{A} \bullet \vec{A}]^{1/2} = \left[\sum_{i=1}^{n}(1 \cdot 1)\right]^{1/2} = \sqrt{n} \tag{4}$$

and

$$|\vec{B}| \equiv [\vec{B} \bullet \vec{B}]^{1/2} = \left[\sum_{i=1}^{n}(X_i \cdot X_i)\right]^{1/2} = \sqrt{e} \tag{5}$$

and the angle between them is θ. Their scalar product simultaneously satisfies the conditions[5]

$$\vec{A} \bullet \vec{B} = |\vec{A}|\,|\vec{B}| \cos\theta = (ne)^{1/2} \cos\theta = \frac{1}{2} E_M \cos\theta$$

and

$$\vec{A} \bullet \vec{B} = \sum_{i=1}^{n}(1 \cdot X_i) = \frac{1}{2} E$$

leading to Eq. (2). The above relations hold for all alternant hydrocarbons.

In a recent paper[11] Türker considers the vector $\vec{C} = \vec{A} + \vec{B}$ and defines two new angles:

α- the angle between $\vec{C}$ and $\vec{B}$, and

β- the angle between $\vec{C}$ and $\vec{A}$.

In what follows, α and β are also referred to as *Türker angles*. Clearly,

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

An illustration of the above definitions is found in Figure 1 of Türker's paper[11].

Expressions for the Türker Angles

The length of the vector $\vec{C}$ is equal to

$$|\vec{C}| \equiv [\vec{C} \bullet \vec{C}]^{1/2} = \left[\sum_{i=1}^{n}(1 + X_i)^2\right]^{1/2}$$

which because of Eq. (3) becomes

$$|\vec{C}| = (n + e + E)^{1/2}. \tag{6}$$

In addition, the scalar products between $\vec{C}$ and $\vec{A}$ as well as between $\vec{C}$ and $\vec{B}$ are readily calculated:

$$\vec{C} \bullet \vec{A} = \sum_{i=1}^{n}(1 + X_i) \cdot 1 = n + E/2 \tag{7}$$

$$\vec{C} \bullet \vec{B} = \sum_{i=1}^{n}(1 + X_i) \cdot X_i = E/2 + e \tag{8}$$

By definition, the angle α between vectors $\vec{C}$ and $\vec{B}$ satisfies

$$\vec{C} \bullet \vec{B} = |\vec{C}|\,|\vec{B}| \cos\alpha$$

and by Eqs. (5), (6) and (8),

$$\cos\alpha = (E/2 + e)[e(n + e + E)]^{-1/2}.$$

In a fully analogous manner, from Eqs. (4), (6) and (7),

$$\cos\beta = (E/2 + n)[n(n + e + E)]^{-1/2}.$$

Define now an auxiliary quantity Y as

$$Y = [(E - E_M)(E + E_M)]^{1/2}$$

where E_M is given via Eq. (1). Then, in view of the trigonometric identity

$$\tan x = (1 - \cos^2 x)^{1/2} \cos^{-1} x$$

we obtain

$$\tan\alpha = Y/(E + 2n); \quad \tan\beta = Y/(E + 2n); \quad \tan\theta = Y/E.$$

Thus our final expressions for the Türker angles read

$$\alpha = \arctan[Y/(E + 2n)] \tag{9}$$

$$\beta = \arctan[Y/(E + 2e)] \tag{10}$$

$$\theta = \arctan[Y/E]. \tag{11}$$

Formulas (9)-(11) are the main result of this paper. One should observe the remarkable formal similarity between them. These formulas are mathematically exact and enable the calculation of the Türker angles, provided that the parameters E, n, e are known. Formulas (9)-(11) make it possible - at least in principle - to examine the dependence of the Türker angles on the structure of the underlying conjugated molecule. Some results along these lines are reported in the subsequent section.

Numerical Work and Discussion

The Türker angles α, β and θ were computed for benzne and the set of 105 Kekuléan benzenoid hydrocarbons from the book HMO Energy Characteristics by Zahradnik and Pancir[12]. For benzene $\alpha = 11.422°, \beta = 8.049°, \theta = 19.471°$, and for naphthalene $\alpha = 13.588°, \beta = 9.114°, \theta = 22.703°$. For all other (polycyclic) benzenoid molecules α, β and θ fall in relatively narrow intervals $(14.021°, 15.982°)$, $(9.142°, 10.212°)$ and $(23.187°, 25.748°)$, respectively. The average values of α, β and θ (benzene and naphthalene excluded) are $15.005°, 9.596°$ and $24.601°$, respectively, and the standard deviations are $0.381°, 0.206°$ and $0.577°$, respectively. Thus, the angles depend only slightly on the details of the molecular structure; all three angles show a tendency to increase with the increasing size of the molecule.

The most remarkable observation made is that the ratio between α and β is almost constant. For benzene and naphthalene this ratio is equal to 1.4189 and 1.4909, respectively, whereas for all other benzenoid systems examined its value falls in the interval (1.5205, 1.6126). The average of the ratio α/β (without benzene and naphthalene) was found to be 1.564 with a standard deviation of only 0.015. This constancy of the α/β ratio is an unexpected feature of the Türker angles. Finding an explanation of this phenomenon remains a challenging task for the future.

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