Bond Length Equalization with molecular aromaticity—A new measurement of aromaticity

Chen-fei Shen, Zi-zhong Liu *, Hong-xia Liu, Hui-qing Zhang

Chemistry and Environment Science College, Inner Mongolia Normal University, Inner Mongolia Key Laboratory of Green Catalysis, Hohhot, Inner Mongolia 010022, China

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ABSTRACT

A new method to measure the amount of aromaticity is presented through the process of Bond Length Equalization (BLE). Degree of Aromaticity (DOA), a two-dimensional intensive quantity including geometric and energetic factors, as a new measurement of aromaticity is proposed. The unique characteristic of DOA and the formation of DOA will be displayed. The calculation of the geometrical optimization, DOA, Nucleus Independent Chemical Shifts (NICS) and Ring Stretching Vibration Raman Spectroscopy Frequency (RSVRSF) for the aromatic ring molecules – $G_nH_n^m$ (G = C, Si, Ge, n = 3, 5–8, m = +1, −1, 0, +1, +2) were calculated using the method of Density Functional Theory (DFT). The correlation between radius angle and molecular energy is absolute quadratic in the process of BLE. As the increasing of the number of ring atoms decreasing gradually, the value of DOA decreasing gradually, the aromaticity decreased gradually, which was a same conclusion as NICS and RSVRSF concluded.

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1. Introduction

In the history of molecular science, there were too many indexes presented to measure the amount of aromaticity. These indexes based on either molecular theory or the experimental data, including structural criteria (HOMA) [1], energetic criteria (ASE) [2] and magnetic criteria (NICS) [3] and experimental criterion (RSVRSF) [4] etc. Great contribution to the progress of chemistry when these indexes were doing, controversies were following [5].

In our point of view, those indexes share a common imperfection, they all view aromaticity as a mono-dimensional extensive quantity. On the side of "mono-dimensional", those indexes consider aromaticity in the only aspect of geometry, or in the only aspect of energy or in the only aspect of magnet, rather than a multi-dimensional quantity including two or more factors mentioned above. While on the side of "extensive", these index often only take some absolute value as a measurement of aromaticity [3,6], rather than their ratio, namely they fail to introduce some relative factors into consideration.

For example, experimental bond lengths were used to evaluate the HOMA (harmonic oscillator measure of aromaticity) index of aromaticity [7]. The HOMA is defined as a normalized sum of squared deviations of the individual experimental (or calculated) bond lengths and an optimal bond length [8]. A value of HOMA closer to 1 implies a larger aromaticity. But mono-dimensional geometrical HOMA cannot reflect the decreasing energy of Bond Length Equalization (BLE) [9]. Another example is Aromatic Stabilization Energy (ASE), an extensive energetic

physical quantity of aromaticity [2]. Traditional view of ASE is that a greater value of ASE implies a larger aromaticity. ASE shows the amount energy decreasing in the process of Bond Length Equalization (BLE). But ASE is only an absolute value of energy, rather than a ratio, with no relative factors inside. As we all know, a larger volume of water doesn't mean a larger density of water. The density of a cup of water is the same as the density of a barrel of water, because density is an intensive quantity, rather than an extensive quantity. We take aromaticity as an intensive quantity, so we think that traditional view of ASE may not be appropriate.

Not only should we take solvent mass into consideration, but also the solution mass, when we calculate the solution concentration. Similarly, not only should we take Bond Length Equalization Energy (E_{BLE}) into consideration, but also Delocalized Bond Energy (E_{DBE}), when we calculate the Degree of Aromaticity.

Schleyer and co-workers proposed the use of absolute magnetic shieldings, calculated at ring centers with available quantum mechanics programs, called nucleus-independent chemical shift (NICS), as a new aromaticity criterion [3]. NICS became popular because it can be easily calculated to characterize the aromatic degree of organic molecules [10], the inorganic aromatic molecules [11], all metal series [12] and sandwich aromatic matching molecules [13–15]. Significantly negative NICS values denote its diatropic ring currents and aromaticity, whereas positive values denote its paratropic ring currents and antiaromaticity. The zero NICS value denotes no-aromaticity [16]. But these absolute value means that NICS has no relative factor inside. They plot calculated NICSs vs ASEs for a set of aromatic ring molecules and their good linear correlation displayed [16]. NICS proves its validity upon ASE is another evidence explaining NICS as an extensive quantity, rather than an

* Corresponding author.
E-mail address: liuzz@imnu.edu.cn (Z. Liu).

intensive quantity. That is to say an inherent defect of ASE hasn't been removed.

Ring Stretching Vibration Raman Spectroscopy Frequency (RSVRSF) is a new aromatic criterion to determine the aromatic degree of the high symmetric molecules [4]. The bigger the RSVRSF, the bigger the aromatic degree is. Experimental trace of the aromatic degree can be achieved by RSVRSF [4]. But RSVRSF is still a one dimensional quantity of aromaticity.

Up to today, aromaticity hasn't been viewed as a multi-dimensional intensive quantity. Now, we study molecular aromaticity from a new angle of view, the process of Bond Length Equalization (BLE). Degree of Aromaticity (DOA), a two-dimensional intensive quantity including geometric and energetic factors, is defined as a novel measurement of aromaticity. In this paper, we first study the most typical aromatic molecule benzene (C_6H_6) from the process of its Bond Length Equalization (BLE). Then the concept of BLE will be generalized to $G_nH_n^m$(G = C, Si, Ge, n = 3, 5–8, m = +1, −1, 0, +1, +2). And the change rule in the process of BLE will be presented.

We will introduce some necessary concept, such as ring radius, radius angle, single bond radius angle, double bond radius angle and so on, so that we can study the process of BLE. These concepts will be presented in detail in the Calculation Method part. With the help of those concepts above and quantum chemistry software, we can modify molecule to a new geometric structure to calculate its Bond Length Equalization Energy (E_{BLE}), Delocalized Bond Energy (E_{DBE}). We could deduce the formula of DOA from three quantities, namely ring radius (r), E_{BLE} and E_{DBE}. Finally, we will compare DOA with some traditional aromatic index, such as NICS, RSVRSF. Their quadratic correlations imply relationship among them and the validity of DOA.

2. Calculation Method

A. Software, functional method and basis sets

All quantities, including optimal structure, single point energy, Raman spectroscopy, Nuclear Independent Chemical Shift (NICS) were predicted by quantum software Gaussian 09. Bond distance and bond angles predicted with 6–311G(d,p) basis set. The Nuclear Independent Chemical Shift (NICS), calculated using B3LYP-GIAO/6–311 + G(d,p). First, we choose C_6H_6 as the system to be observed. How do these quantities of C_6H_6 change in the process of Bond Length Equalization (BLE) is the thing we want to know.

High symmetric aromatic ring molecules of C family $G_nH_n^m$(G = C, Si, Ge, n = 3, 5–8, m = +1, −1, 0, +1, +2) were geometrically optimized, simultaneously the optimal ring radius (r) and bond length of CH were determined. Change its radius angle, than its bond length of adjacent ring atoms would be different, which is on the contrary of the process of BLE (Fig. 1) [9].

B. Several necessary concepts to describe Bond Length Equalization process

Bond Length Equalization (BLE) is used to describe the process when bond length of adjacent ring atoms of the ring molecule becomes equal little by little. We called the longer bond as the single bond (BD_1), and the shorter bond as the double bond (BD_2) in the process of BLE. All single bonds are equal and decrease simultaneously, and all double bonds are equal and increase simultaneously, while the length of single bonds and double bonds are different except the end of BLE when all the bonds' length are equal (as C_6H_6 has three single bonds and three double bonds, and single bond, double bond arrange alternately (in detail, please see Fig. 1).

Ring radius is used to describe the distance from ring center to the ring atoms, were expressed by r. Radius angle is used to describe the angle of two adjacent radius, ring center is the vertex of the angle. We use θ to indicate radius angle; θ_1 represents the radius angle of single bond, while θ_2 represents the radius angle of double bond. BL_1 represents the single bonds' length, and BL_2 represents the double bonds' length.

From Fig. 1, we can see the left molecular structure, it is an unequal bond length structure, $\theta_1 > \theta_2$ and $BL_1 > BL_2$; the right molecular structure display a benzene molecule having a same ring radius with the left, while its $\theta_1 = \theta_2$ and its $BL_1 = BL_2$ which mean that the right molecular structure is the equalized bond length structure. The process of BLE is the moving from the left structure to the right.

We assume that the changes of radius angle trigger the process of BLE.

C. How to determine Bond Length Equalization Energy E_{BLE}

Experimentally, scientists put the enthalpy of a selected reaction to discover the amount of decreasing energy because of aromaticity [16]. Z. Mucsi, and coworkers put the enthalpy difference of two selected reactions, one is examined reaction another is reference reaction, to discover the amount of decreasing energy and its proportion because of aromaticity [17]. Now we want to evolve the work of Z. Mucsi. We will discover the amount of decreasing energy from the angle of its own structure changing rather than designed reactions.

E_{BLE} is the amount of energy that ring aromatic molecule decreased because of π electrons' delocalization; is the difference between two single point energy of a same molecular formula with different structure, one is the structure that all bonds' length of adjacent ring atoms is equal, another is the structure that bond length of adjacent ring atoms isn't equal, namely single bond and double bond arranged alternately.

Before the calculation of E_{BLE} of high symmetric D_{nh} aromatic molecules $C_nH_n^m$, we should reiterate that all discussed molecules are plane.

First, optimize and calculate single point energy of high symmetric D_{nh} aromatic molecules $C_nH_n^m$[n = 3, 5–8, m = +1, −1, 0, +1, +2]. Optimization could help us to determine the length of ring radius. This optimized molecule is one of the single point energy to be calculated. On the basis of the optimized structure, change the radius angle, not only single bond angles but also double bond angles, to get another
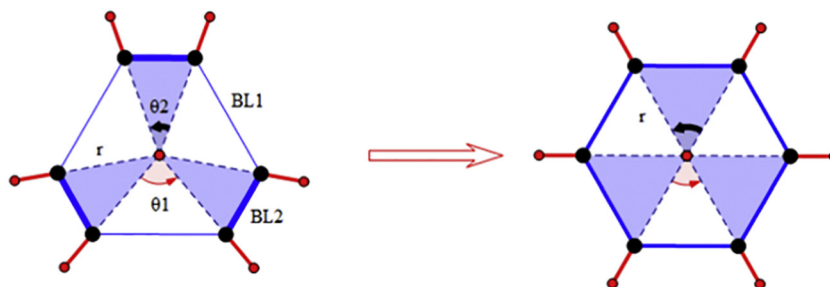

Fig. 1. An illustration of C_6H_6 in the process of Bond Length Equalization (BLE), its structure from left to right. Ring radius r, single bond radius angle θ_1, double bond radius angle θ_2, single bond length BL_1, double bond length BL_2.