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Electron Localization Function as a Measure of Electron Delocalization and Aromaticity

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Abstract: The Electron Localization Function (ELF) has played in the last time an important role in understanding the special characteristics of the chemical bond. The chemical interpretation of the ELF as an indicator of the regions of the space where it is most probable to find a localized electron pair has been of great value in order to understand some complex chemical bonds. In this work, the ELF has been used to study the delocalization and aromatic character of a diversity of molecules. It is shown that whereas the analysis of the total ELF does not provide clear information about aromaticity, the separation of the function on its σ and π parts yields indeed valuable information about it. Moreover, it is possible to construct a quantitative scale of aromaticity. It is also shown that the use of the ELF to understand aromaticity is complementary to other methodologies. The study includes mono substituted benzene derivatives, cyclic organic compounds, borazine molecule and the mechanism of acetylene trimerization.

Keywords: Electron localization, ELF, Aromaticity.

INTRODUCTION

The electron delocalization in molecules is one of the most applied phenomena in organic chemistry [1]. The electron delocalization appears in different types of organic compounds, linear chains, planar rings or 3D structures [5, 6]. Associated to specific kind of compounds, empirical concepts such as aromaticity, homoaromaticity [7, 8], spherical or curved aromaticity [6] have been defined and studied. However, they cannot be experimentally measured. Continuous efforts have been made to give a sharp definition of these concepts and a way to quantitatively measure or calculate them [9-19].

The electron delocalization is associated with high stability, bond lengths intermediate between those of single and double bond, and in the case of cyclic systems, with the ring currents [20]. In the case of aromatic structures, benzene is the emblematic example and the description of its structure was an open problem during many years before the use of quantum mechanics described the structure through molecular orbital theory, the Huckel's rule description, valence bond theory and the identification of resonance forms. Since then, many methods have been proposed to evaluate or measure electron delocalization or aromaticity. Stabilization energies [21], magnetic properties [22, 23], delocalization indexes [24], Nucleus Independent Chemical Shift, NICS, with its extensions and modifications [12, 14], ACID (Anisotropy of the Induced Current Density) methodology [25], and recently, criterion based on properties of the electron density, which can be studied through the topological analysis of atoms in molecules or the electron localization function, ELF [26, 27, 28]. The ELF topological analysis has been used to determine aromaticity or to evaluate reactivity and selectivity in electrophilic aromatic substitutions [27]. Among many other applications of the ELF to evaluate reactivity it is worth to cite [27].

Recently, a scale based on the bifurcation values of a new function that include the σ and π components in separate way has been

used to quantify the electron delocalization in different polycyclic aromatic compounds [43, 44]. In the following, a short theoretical part about the origin and significance of the ELF will be outlined. After that, some interesting examples and applications will be shown and discussed.

ELF TOPOLOGICAL CONCEPTS

The ELF has been widely used to evaluate electron localization. It was initially introduced by Becke and Edgecombe [45] and its topological analysis was developed and implemented by Savin and Silvi [46, 47].

The ELF is defined in terms of the excess of local kinetic energy density due to the Pauli exclusion principle, $D(r)$, and the Thomas-Fermi kinetic energy density, $D_h(r)$.

$$\eta(\vec{r}) = \left[1 + \left[\frac{D(\vec{r})}{D_h(\vec{r})} \right]^2 \right]^{-1}$$

Where,

$$D(\vec{r}) = \frac{1}{2} \sum_{i=1}^N \left| \nabla \phi_i(\vec{r}) \right|^2 - \frac{1}{8} \frac{|\nabla \rho(\vec{r})|^2}{\rho(\vec{r})}$$

$$D_h(\vec{r}) = \frac{3}{10} (3\pi^2)^{\frac{2}{3}} \rho(\vec{r})^{\frac{5}{3}}$$

$$\rho(\vec{r}) = \sum_{j=1}^N \left| \phi_j(\vec{r}) \right|^2$$

and N is the number of electrons.

The ELF is a scalar function. Therefore, the analysis of its gradient vector enables to locate the attractors, and the volume enclosed by all gradient lines which end up at one attractor is called basin. The gradient analysis of the ELF divides the space in basins where electron pairs are most probable located. A localization domain is a volume formed at a given isosurface of the ELF and it may contain more than one attractor. In this case more than one basin is contained in this localization domain.

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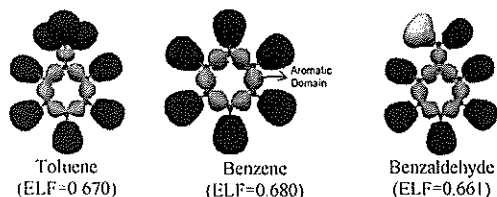


Fig. (1). Substituent effect on bifurcation ELF isosurfaces of mono-substituted benzene.

There are two kinds of basins, core basins surrounding a nucleus and valence basins that do not include a nucleus, with the exception of basins including a proton. The synaptic order is determined according to the number of connections between a given valence basin with core basins. A disynaptic valence basin corresponds to the classic two-center bond, a lone pair to a monosynaptic basin, whereas, a multicenter bond is characterized by a polysynaptic one. Different properties related to basins can be calculated by integrating the density or other quantities over the volume of each basin or evaluating the interaction between basins through the bifurcation analysis.

The ELF is mapped on the interval (0,1) which facilitates its analysis and interpretation. A region of the space with a high value of the ELF is interpreted as a region where is more probable to find an electron or a pair of localized electrons. At low values of ELF all basins are contained in one localization domain, but when the isosurface value increases, the basins begin to split and, finally, at some value of ELF the respective isosurface show all the basins separated. This process is conveniently followed by means of a bifurcation diagram [48-50]. The points of bifurcation have been interpreted as a measure of the interaction among the different basins and chemically, as a measure of electron delocalization. Various works using the concepts described before have been made to describe the electronic and structural characteristics of organic compounds, among others [29, 46-49].

APPLICATIONS

For example, the selectivity or orienting substituent effect in mono-substituted benzene derivatives was studied [27]. The effect of π -donor substituents (OH, NH_2 , F, CH_3 , C_6H_5 , Cl), and attractor substituents (CN, CHO, NO_2 , CF_3 and CCl_3) was analyzed using the bifurcation scheme of ELF. The contribution of the substituent on the electron delocalization in benzene was measure evaluating the bifurcation points in the aromatic domain of benzene and its changes due to the different substituents. The topological description of benzene contains six basins containing the protons and a distorted toroidal basin which is typical in this kind of compounds.

In the case of π -donor substituents, which have been classified as *ortho-para* orienting substituents, the aromatic domain is first opened at the substituted carbon and next around the vicinity of the

meta carbon. For attractor or *meta* orienting substituents, the aromatic domain bifurcates close to the *ortho* and *para* positions (see Fig. 1). Those results agree with the known orienting effects in the reactions of electrophilic aromatic substitution.

The ELF depends formally only on the density and it has no information about π and σ contributions in the bonds. The topological and population analysis, and the classical pictures of the ELF do not clearly describe the difference between both types of contributions. Hence, a new methodology using the topological analysis of a separated ELF formed only by the π -orbitals and the other one with the σ -orbitals have been recently proposed [43, 44]. In Fig. (2), it is possible to see the bifurcation points of the total, σ and π ELF of the benzene molecule.

This separation is possible because the kinetic energy is additive and can be decomposed in its π and σ parts. However, the basin descriptions of the total ELF do not correspond to the sum of the basins resulting from ELF_π and ELF_σ . Similar works based on orbital separation have been done for the *alpha* and *beta* spins contributions to the ELF [50]. Finally, using the bifurcation analysis of the separated ELF_π and ELF_σ was possible to characterize the π and σ delocalization in cyclic compounds and obtain a scale to quantify the electron delocalization, which is based on the average of the bifurcation values of π and σ systems. In this way, it was possible to evaluate the global aromatic character of a chemical system and the delocalization of each contribution individually.

Different cyclic aromatic and anti-aromatic compounds (see Table 1) were analyzed evaluating the bifurcation of the total ELF, the ELF_π , and the ELF_σ at which the complete bifurcation of the respective basins occurs [43]. The total ELF does not give information about electron delocalization and the separation between the aromatic and the antiaromatic systems could not be obtained. However, using the ELF_π the aromatic rings with high electron delocalization were clearly separated from those with localized bonds. The aromatic rings present bifurcation values ranging from 0.64 to 0.91 and the antiaromatic molecules have low values, between 0.11–0.35 [44]. In addition, the aromaticity was established in the correct way for molecules in which the number of ring is growing. The higher the number of rings the lower the electron delocalization and aromaticity. In molecules with the same number of rings, the planarity and linearity become the predominant factors as it is the case of anthracene and phenantrene, where the former has the highest delocalization. It is also important to mention the cyclohexatriene molecule which corresponds to one of the localized structures or one of the resonance structures of benzene. This system presents an ELF_π bifurcation of approximately half of the value of the π system of benzene, indicating the nonaromatic character of this system. It is interesting to mention that some of the molecules included in Table 1 were studied by the aromatic cyclic energy (ACE) [51] methodology and the obtained results agree with the ELF_π description of aromaticity.

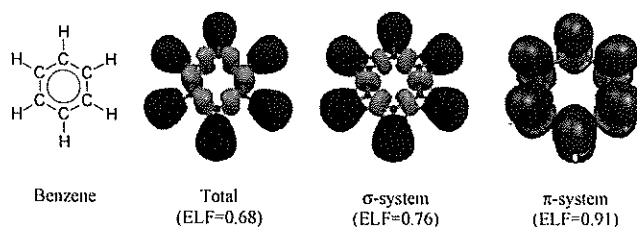


Fig. (2). ELF isosurfaces at the bifurcation point of the total, σ and π systems in benzene.

Table 1. Bifurcation Values of ELF_{π} , ELF_{σ} and Average of them in Different Cyclic Compounds


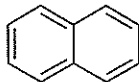
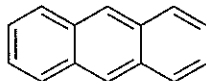
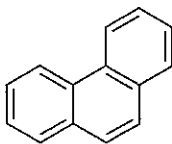
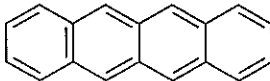
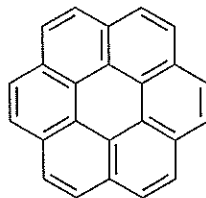

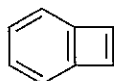
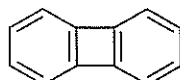
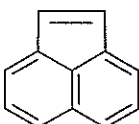
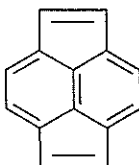
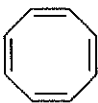

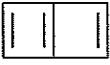
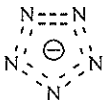
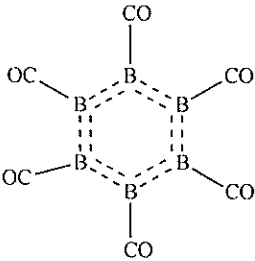
| System | ELF_{σ} | ELF_{π} | Average |
|---|----------------|-------------|---------|
|  | 0.76 | 0.91 | 0.84 |
|  | 0.76 | 0.78 | 0.77 |
|  | 0.77 | 0.70 | 0.74 |
|  | 0.75 | 0.64 | 0.70 |
|  | 0.74 | 0.69 | 0.72 |
|  | 0.76 | 0.75 | 0.76 |
|  | 0.75 | 0.82 | 0.79 |
|  | 0.76 | 0.72 | 0.74 |
|  | 0.76 | 0.74 | 0.75 |
|  | 0.76 | 0.75 | 0.76 |
|  | 0.77 | 0.71 | 0.74 |
|  | 0.73 | 0.35 | 0.54 |

Table 1. contd....

| System | ELF σ | ELF π | Average |
|---|--------------|-----------|---------|
|  | 0.79 | 0.11 | 0.45 |
|  | 0.78 | 0.15 | 0.47 |
|  | 0.81 | 0.78 | 0.80 |
|  | 0.68 | 0.85 | 0.77 |

The analysis described before was extended to other cyclic molecules of interest in organic chemistry, B_6CO_6 and N_5^- . Both molecules showed electron delocalization lower than benzene, and were characterized as presenting global aromatic properties. The delocalization in the former specie is due to the isolobal character of the CH and BCO groups in the benzene and B_6CO_6 , respectively. In the case of the N_5^- ion, it has two contributions to the electron delocalization, the first one corresponding to the 6 π -electrons highly delocalized and the other one in the σ -system which was attributed to the interaction in the plane between the nitrogen lone pairs and the σ bonds of the cyclic structure.

The relation between topological analysis of ELF and magnetic properties such as NICS analysis has been studied in some works [52, 53]. The aromaticity in a series of propellanes formed by three-, four- and five-membered rings has been studied [52]. The NICS analysis found diatropic currents in the three-member σ -plane, which is characteristic of aromatic structures. The four-member rings support paratropic currents or antiaromatic properties and the five-member rings have moderated diatropic NICS values. The ELF analysis describes the electron population of the bridge-head carbon atoms in the propellanes and gives Lewis resonance structures by three-membered rings, which is in agreement with the aromatic character postulated with NICS analysis. The relation between bifurcation analysis and NICS values has been explored for a set of 4 cyclic molecules with different electronic characteristics that cover neutral, heteroatomic and charged systems [53]. The behavior of NICS and the bifurcation values of the ELF depend on the kind of cyclic structure. When charges or heteroatoms are introduced in the system, the correlation between the ELF and NICS indexes are affected, but the two schemes of analysis may give similar qualitative trends about the aromaticity of a molecular system.

A modification in the ELF bifurcation scheme of π -system has been done to analyze the $4n\pi$ and $(4n+2)\pi$ electrons all-carbon annulenes [54] and annulenyl-substituted olefins [55] with emphasis

on the aromaticity of $4n\pi$ -electron in their lowest triplet state. Planar conjugated rings containing $4n\pi$ electrons are anti-aromatic according to the Huckel's rule, but it is only applicable to singlet states. It is not directly extendable to triplet state where the Baird's rule based on Huckel's rule should be used [56]. Using perturbation molecular orbital theory has been showed that anti-aromatic systems in ground state become aromatic one in their lowest $\pi\pi^*$ triplet state [56] and it was confirmed using the bifurcation values of the ELF π , particularly, the ring-closure bifurcation values, RCBV(ELF π), and the span of bifurcation values, $\Delta BV(ELF\pi)$, in the annular system. RCBV(ELF π) should be as high as possible and $\Delta BV(ELF\pi)$ should be as low as possible, ideally zero. With these criteria was established the aromatic character of a variety of molecules in the triplet state.

Another example of electronic structure analysis using the separation of the ELF involves borazine, $(BH)_3(NH)_3$ [57]. In this specie, there are domains of the ELF with localized electron population in the B-H and N-H bonds being more localized in the boron atom. The ELF in the ring shows three separated localization domains corresponding to the three possible B-N-B fragments (See Fig. 3). These regions were identified as chemically meaningful domains exhibiting a strong although asymmetric electron delocalization which is produced by the electronegativity difference between boron and nitrogen atoms. Using the analysis of separated σ and π ELF functions was identified a weak σ interaction in the ring, about a half of the interaction of typical organic molecules, which is also due to the difference of electronegativity between B and N atoms.

The π system in borazine has an electron delocalization lower than benzene, the archetypical aromatic molecule. It seems that the π density is highly localized over the nitrogen p-orbital, while the boron center has a lower electron density. Then, borazine was described as a molecule with some π aromatic character and with a weak σ interaction. However, globally, it is not considered as aromatic specie. The mean bifurcation values classify it as anti-

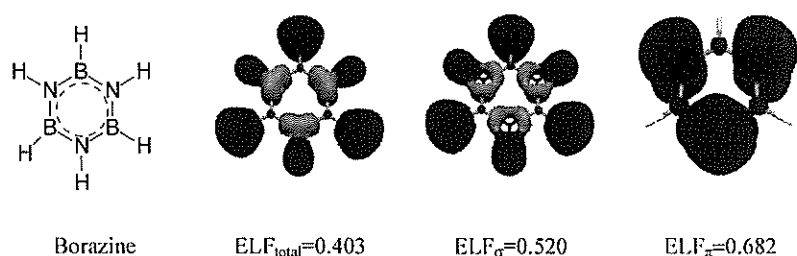
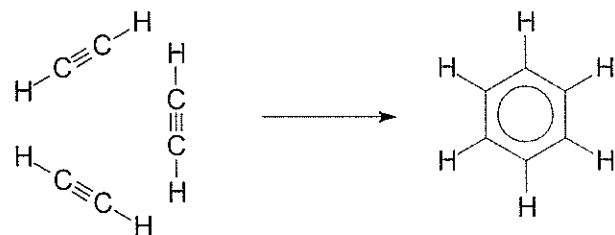


Fig. (3). ELF isosurfaces at the bifurcation point of the total, σ and π electronic systems of Borazine.

aromatic molecule with electron localization similar to cyclooctatetraene, cyclobutene, and bicycle (2,2,0)-hexatriene typical antiaromatic structures. The different electronegativity of B and N changes the chemical bonding and electron delocalization patterns due to the varying potential and the electronic system is not homogeneously delocalized as in benzene. The bonding characteristics obtained from the topological analysis of ELF describe three well-defined and weakly interacting fragments corresponding to the HB–NH–BH moieties. The bifurcation scheme analysis of σ – π separation reveals that borazine has not a global aromatic character despite its π aromaticity which is a consequence of the high accumulation of electron density at the nitrogen atoms avoiding an effective cyclic electron delocalization through boron.

The electron localization function (ELF) in combination with the catastrophe theory has also been used to evaluate molecular reaction mechanisms that yields aromatic products like the trimerization of acetylene (Scheme 1) [58]. The evolution of ELF basins along the reaction path allows identifying the points where change the number or type of ELF basins, and catastrophe theory characterizes these changes. The reaction coordinate can be divided in elementary steps which possess the same number and kind of basins and are named as domain of stability in the ELF topological analysis. The ELF separated functions provide us information about *in-plane* and *out-of-plane* electronic characteristics of a plane molecular system, and its bifurcation analysis provides a useful scheme to assess σ and π delocalization or aromatic character.



Scheme 1. Acetylene Trimerization.

Five domains of structural stability of ELF connected by four catastrophes were characterized along the IRC reaction path of acetylene trimerization as can be seen in Fig. (4). The domains are associated to different elementary chemical steps, first closed-shell repulsion between acetylene moieties, then transformation of the repulsion energy in mechanical deformation of the reactants leading to an approximation between acetylene units, after that a simultaneous (concerted) preparation of C–C bonds accompanied by a sharp increment of σ delocalization, followed by a formation of the C–C bonds, and finally, development of π -aromaticity or transformation of non-aromatic into aromatic benzene. The transition structure involved in this reaction does not show neither σ nor π aromatic character, only a low σ electron delocalization was found.

The approximation between acetylenes fragments is the most costly in terms of energy. A rearrangement of electron density between ELF basins was not found which indicates closed shell type

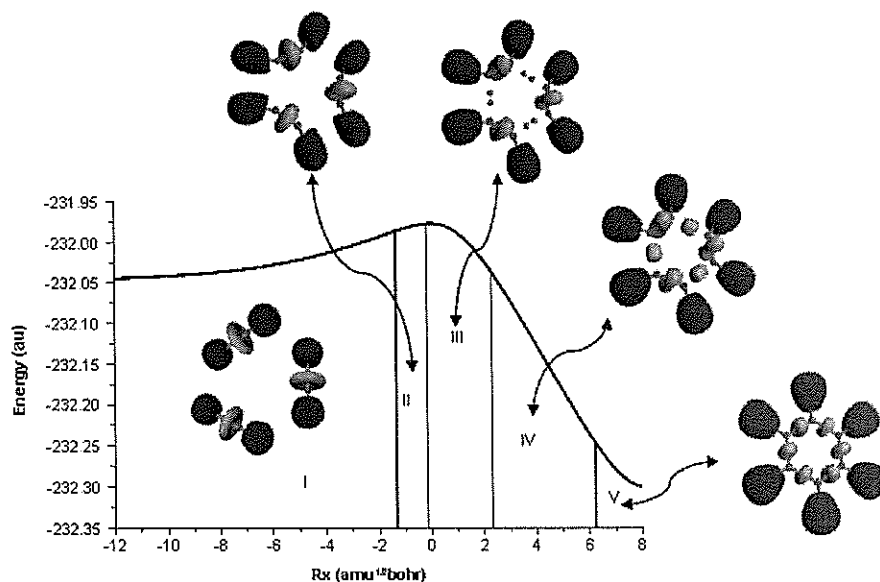


Fig. (4). ELF localization domains in the characterized steps along the IRC of the trimerization of acetylene.

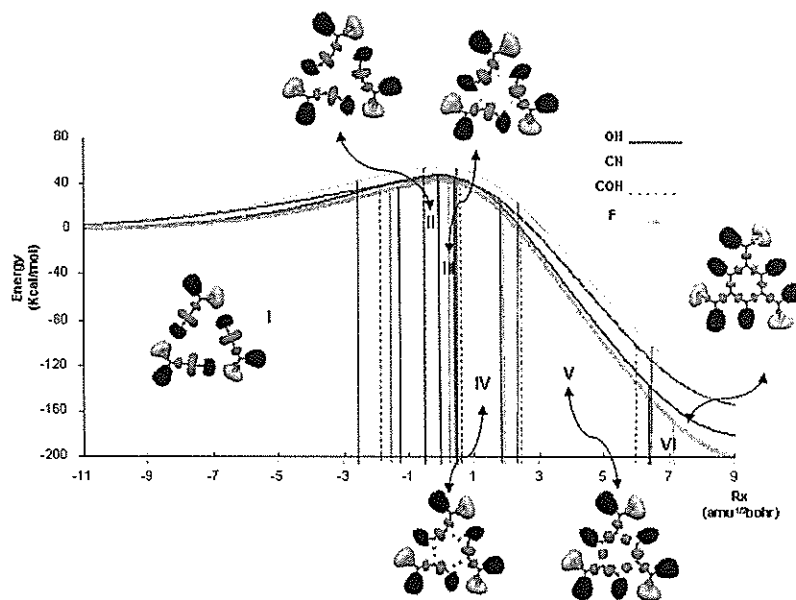


Fig. (5). ELF localization domains along the IRC path of the mono-substituted acetylene trimerization.

interaction between acetylene moieties. Two kinds of interactions were determined, repulsive closed shell interaction and the distortion of acetylene reactants.

The second step of the reaction corresponds to the transformation of the triple bonds in resonance structures with intermediate characteristics between triple and double bond. It includes a through-space electron delocalization to the adjacent hydrogen atoms.

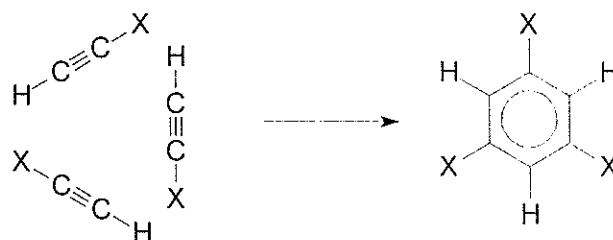
In the third region of the reaction there is a symmetric accumulation of charge over the six carbon atoms with electron charge transfer from the C-C and C-H bonds. The new structure generates a σ delocalization, which has been associated with the formation of central paratropic σ current determined through magnetic analysis.

The region number IV corresponds to the formation of a six-membered ring where three new C-C single bonds are formed. The population of the new formed basins is coming from the former triple bond. The new cyclic structure shows an increasing delocalization of the π system which corresponds to the formation of a diatropic π current as observed by magnetic analysis [59]. However, the bifurcation analysis of the ELF does not reveal aromaticity.

The final region corresponds to the formation of benzene. An equalization of C-C distances is observed. There is a high energetic stabilization which closely resembles the transformation of a non-aromatic system into an aromatic one. The ELF population analysis describes the electron density flowing from former double bonds to the single ones to reach the same population in all bonds. Further, the bifurcation analysis shows the increase in electron delocalization reaching the typical aromatic behavior of benzene.

The effect of substituent over mono-substituted acetylene trimerization has also been studied using the ELF analysis [60]. The substituent groups were F, CN, COH and OH as it is indicated in the scheme 2.

The main difference in the topological analysis with respect to the acetylene trimerization is the appearance of a new step. The third region described before is splitted in two steps which takes into account the asymmetric structure introduced by substituent. Hence, six domains of structural stability were determined in the mono-substituted acetylene trimerizations which can be seen in Fig. (5).



Scheme 2. Monosubstituted Acetylene trimerization (X=F, CN, COH and OH).

The width of the first step in all reactions is different being wider for CN substituent. This step was also the most costly of the activation energy barrier being higher for OH substituted acetylene. The electron withdrawing substituents decrease the energy barrier in comparison to acetylene trimerization. The second step includes the TS for acetylene with F and OH substituents while for compounds with COH and CN substituents, the end of the second step is located before the TS. The third step corresponds to the formation of three new monosynaptic basins. The position and population transfer depends on the substituent. For fluoroacetylene trimerization this step was the shortest of all analyzed systems, and the new basins are formed over unsubstituted carbon atoms of acetylene. For systems with COH, CN and OH, the formation of new monosynaptic basins occurs over substituted carbon atoms. In all cases, the population of new basins comes from the disynaptic basins that describe the initial C-C triple bond.

The fourth step contains the formation of three new monosynaptic basins at carbon atoms. The electron population increase along the step and it is transferred from both the C-C and C-H bonds. In the fifth step, three bonds are formed from the accumulation of charge of monosynaptic basins previously formed. The new bonds generate a six-membered ring with alternating single and double bonds. This step has the largest stabilization energy in the energy profile which was attributed to change of hybridization due to the substituent effect. At the final step, the formed bonds change to an intermediary single-double bond, there is a shortening of bond lengths and the electron population increases by transference from the double bond. All electronic rearrangements are produced

in the plane of the molecular system where the effects of σ system are more important than those of π systems. Therefore systems with σ electron withdrawing substituents show higher stabilization energy in the trimerization. The last step corresponds to the transformation or generation of six totally delocalized bonds, where the bond distances and electron population of the final basins are equalized going from non-aromatic to an aromatic structure. Hence, the aromatization is higher for systems bearing substituents with π contributions (COH, CN and OH).

Finally, it is possible to notice that the formyl substituent presents the most relevant modification of the reaction mechanism. At the beginning, it promotes reactant stabilization by hydrogen interaction, next it decreases close shell interactions and increases the distortion energy generating the highest stabilization by aromaticity. This is due to the high electron delocalization of the π system into both the ring and the substituent. The 1,3,5-trifluorobenzene shows the lowest stabilization of the π system by aromatization, the main effect of the fluorine is due to the σ inductive character provided by the high electronegativity. However, it does not contribute to the delocalization in the out of plane electron system. The nitrile and hydroxyl substituents produce similar effects in the delocalization by aromaticity. The π electron withdrawing characteristic in nitrile substituent is compensated in the hydroxyl group by the π electron releasing and σ inductive capacities.

CONCLUSIONS

It has been shown that the ELF beside many other applications it is also a useful function to understand and predict the aromatic character or electron delocalization of a molecular system. The benefits of the ELF function are based on its simplicity of analysis and the relationship between the ELF division of molecular space with chemical concepts such as core, valence, bonding, and non-bonding regions. The interaction between these regions can be measured through a bifurcation scheme and interpreted in terms of electron delocalization giving a solid framework to assess this property.

ACKNOWLEDGMENTS

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