

On the Electron Pair, the Single Bond C-C Rotational Energy Barrier and Other Molecular Mechanisms

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To find evidence of the electron pair has proven to be a very difficult task. Bader *et al.* tried to unsuccessfully find evidence of the electron pair in the topological analysis of the Laplacian of the electron density of molecules. By using electron localization functions, Silvi *et al.* pointed out where these pairs might be in the molecule and represented them as attractors. Still, to locate the electron pair does not give answers to different molecular mechanisms. For instance, the mechanism of hindered rotation about the carbon-carbon single bond in ethane, which is of great interest and controversy. This phenomenon is not yet explained by Silvi's most advanced molecular model (state of the art). A new alternative uses the relationship between the area of the electron density and the energy of the bond. This approach also provides the electron pair localization. Furthermore, by allowing the magnetic momenta of the bonding electrons to interact, an explanation of the rotational barrier appeared straightforwardly. Also, the model presented in this paper find bonding electrons not found by Silvi's model. The results agree and/or complement the state of the art.

1 Introduction

The valence theory of Lewis remains the basis for most modern ideas on the chemical bond. According to Lewis structures, there are bonding electron pairs in the valence shell of an atom in a molecule, and there are nonbonding electron pairs or lone pairs in the valence shell of many atoms in a molecule. From the topological analysis of the electron density, Bader *et al.* had extracted useful information about the bonding in a molecule. But, not much progress was made to reveal the location of these electron pairs [1].

According to Silvi *et al.* [2], the electron density alone does not easily reveal the consequences of the Pauli exclusion principle on the bonding. The work of several authors have produced a series of electron localization functions, which attempt to measure the Pauli repulsion by considering the Fermi hole. Hence, an alternative interpretation of these electron localization functions is to consider a system of fermions and a system of bosons with identical densities. The ground-state local kinetic energy of the non-interacting bosonic system is a lower bound to the local kinetic energy of the fermionic one. The excess local kinetic energy due to the Pauli principle is just the difference between the two. Where electrons are alone or form pairs of opposite spins, the Pauli principle has little influence on their behavior and they almost behave like bosons. In such regions the excess local kinetic energy has a low value. This identifies regions called attractors, every attractor consists of two electrons. There are three types: point, core and ring attractors. In this way, Silvi *et al.* is capable to locate and classify the electron pairs in organic molecules.

Nevertheless, in order to have this "non-interacting bosonic system", the magnetic momenta of the pairs of opposite spins are necessarily cancelling each other. Therefore, if the

rotational energy barrier for the single bond in ethane has a magnetic origin, Silvi's model would not be able to explain it. The need to understand this molecular mechanism had driven chemists away from Silvi's most advanced model to semi-empirical ones. Currently, the origin of a rotational barrier in a C-C single bond has a wide range of explanations. The barrier is often attributed to: 1) torsional strains in the molecule, 2) steric strains, 3) charge transfer, exchange or electrostatic and 4) hyperconjugative interactions [3].

This is of a foremost interest because it has been found that the rotational speed of the bond reduces in the presence of an external magnetic field [4].

In the model used in this paper*, covalent bonds, lone pairs and core electrons will be detected by using the structures observed in Fig. 1, namely: the two separated spheres (*ts*), the torus (*t*) and the sphere in a sphere (*ss*) [5]. In the case of a single C-C bond, the magnetic momenta of the two bonding electrons are left to interact between each other. The C-C double bond would be two single bonds that consequently are locked for rotation. The C-C triple bond presents a lone pair (a torus) around its double bond structure and benzene presents interacting toroidal lone pairs, which are responsible for aromaticity.

Full count and location of the electron pairs forming different bonds, as well as, lone pairs is achieved. This was comparable or better than Silvi's model (the state of the art) [2]. The model/method presented in this paper: 1) confirmed Silvi's model electron count for certain molecules, 2) produced more information about missed electrons, not accounted by Silvi's model and shed light on the possible mechanism behind rotational barrier and aromaticity.

*which has already been described in [5].

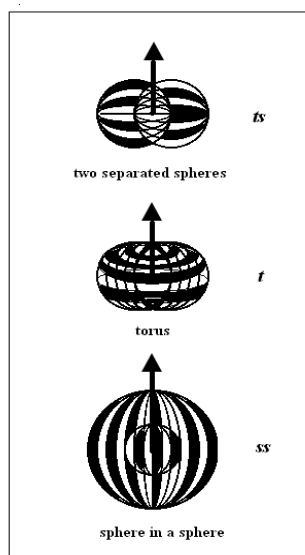


Fig. 1: Observables structures of the electron. The arrow represents its magnetic moment

2 Experimental

After observing the Laplacian of the electron density contour map of different hydrocarbon molecules, it was easy to identify C-C and C-H bonds and cut their silhouettes printed on paper. These silhouettes were weighted. The C-C or C-H bond lengths were used to calibrate the area measured in each bond. By this way, the bond area was calculated and it is reported in pm^2 . An example of this process is in Fig. 4 for the C-H bond, and in Fig. 8 for the C-C bond. Then, these areas were correlated with their respective bond energies. A linear correlation was possible after dividing the bond area by a whole number, n . This whole number is interpreted as the number of electrons participating in the bond and it is reported on the right side of the molecule formula. These are observed in Figs. 2 and 3. This method has been sufficiently described in [5] and, in this paper, it was applied to the hydrocarbon molecules: ethane, ethene, ethyne and benzene. The contour map of the Laplacian of the charge density for C-H and C-C bonds in ethane, ethene and ethyne molecules are in [6]. Benzene C_6H_6 in [7] and C_2 is in [8].

2.1 Electron count

Fig. 2 shows that with n very close to 2, the C-H bond area linearizes against the bond energy in the molecules: ethane C_2H_6 , 2; benzene C_6H_6 , 2.01 and ethyne C_2H_2 , 2. In the case of ethene C_2H_4 it is 1.824. Fig. 2 shows that n is exactly 2 in the case of C-C ethane and benzene, 8 in the case of dicarbon and 4 in the case of C-C ethyne. Ethene, however, presents 2.6 for the C-C bond in the plane of the molecule and 4 in the plane perpendicular to it and at the C-C axis.

The number of electrons involved in the C-H bond was very close to 2 regardless the class of C-H bond. The C-H

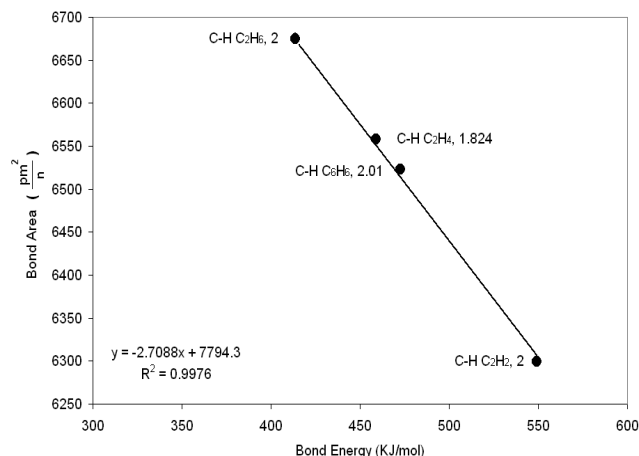


Fig. 2: Bond area vs. bond energy for C-H bonds in different molecules.

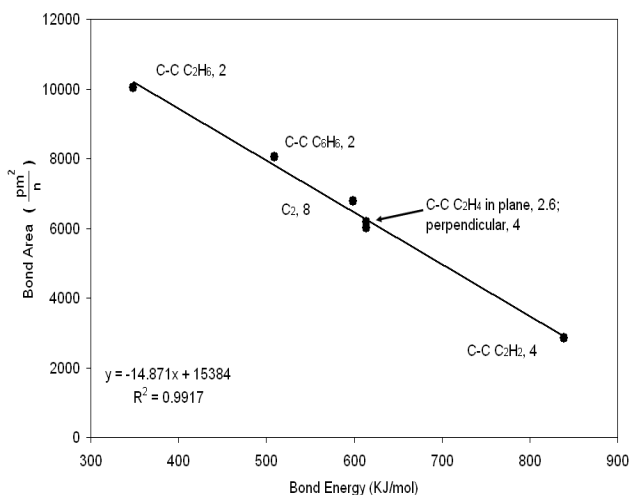


Fig. 3: Bond area vs. bond energy for C-C bonds in different molecules.

bond that was far from this behavior was C-H ethene with 1.824. This deviation will be further discussed later. Thus, two electrons are involved in the C-H bond in the cases of ethane, ethyne and benzene.

Given that Fig. 3 provides the number of electrons involved in each C-C bond for these molecules, one is ready to do the full count of electrons in each molecule.

2.1.1 Ethane, C_2H_6

Figs. 2 and 3 inform that the C-H and C-C bonds have two electrons each. Hence, as it is observed in Fig. 4a, ethane has the expected electron count for each bond. This electron distribution coincides with the one presented by Silvi et al. (Fig. 4b) where the black circles are point attractors with two electrons each. Silvi's model put these attractors at the mid-point of the C-C bond and towards the hydrogen atom in the C-H bond. This is probably due to electronegativity dif-

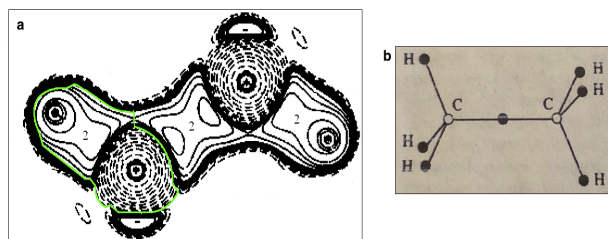


Fig. 4: **a)** Contour map of the Ethane molecule and its electron count. The green line shows how the C-H bond was cut. The C-C bond was also cut accordingly. Reprinted and adapted with permission from [6]. Copyright (1996) American Chemical Society. **b)** Silvi's et al. structure from [2]. It presents point attractors (black circles) alongside C-C and C-H bonds. It also shows core attractors (open circles) on the carbon atoms, used with permission of the publisher.

ferences between the bonding atoms. He also localized core attractors (open circles) on the carbon atoms. The model presented in this paper does not have that.

2.1.2 Rotational barrier

The ethane molecule presents one of the long standing problems in physical chemistry. This molecule has an energy barrier to its rotation. This barrier produces two types of conformers: the eclipsed and the staggered (see Fig. 5). The energy barrier between them is about 12 kJ/mol. Also, the C-C bond contracts from 153 pm in the staggered to 130 pm in the eclipsed conformer [3].

In between several explanations, the most favored ones are: 1) steric hindrance and 2) hyperconjugation. Although the steric effect is usually defined as the repulsion between C-H bonds or vicinal H atoms in the eclipsed conformation, the difference between torsional and steric strain is not clear. This is because they are not explicitly associated with a well-defined physical property.

Within the framework of natural bond orbital analysis, NBO, hyperconjugation is considered to be the source of the conformational preference of the molecule, by means of $\sigma_{C-H} - \sigma_{C-H}^*$ vicinal interactions, rather than the electrostatic contribution or Pauli repulsion.

Most other explanations in the literature are given either in terms of orbital interactions or based on an energetic analysis of the problem. The discussion is far from over [3].

In the model presented in this paper, the electron is observed as the size of the whole bonding region. Given that the electron is also a tiny magnet, the interaction of the magnetic momenta between the two bonding electrons of the C-C bond is directly the cause of this torsional barrier and the differences in the C-C length between conformers.

Fig. 5 presents the two configuration and the magnetic

momenta of the two bonding electrons. In the eclipse conformer, these magnetic momenta are at an angle of 180 degrees (maximum magnetic attraction). This shortens the C-C bond to 130 pm. Upon rotation of one of the carbon atoms, the angle between electron's magnetic momenta decreases. At $180 - 60 = 120^\circ$, a combination of distance between moments and the angle vanished this magnetic interaction. This lengthens the C-C bond (minimum magnetic attraction) in the staggered conformer.

The equation that describe the interaction between the two electron magnets is,

$$F = \frac{3\mu_0}{4\pi} \frac{m_e^2}{r^4} \cos \theta \quad (1)$$

where μ_0 is the permeability of the free space, m_e is the electron magnetic moment, r is the distance between magnetic moments and θ is the angle between them. Mimicking the magnitude of the Ehrenfest forces acting on the C atoms, Fe(C) for different C-C distances presented in [3]. The change in magnetic force, equation (1), needed to explain the barrier at different C-C distances is presented in Fig. 6.

Given that there are no other energy barrier, it is believed that the bond rotation occurs in step between the carbon atoms in the bond. This means that once one carbon reached the weakening angle, the other rotates to reach 180° again. This mechanism would be consistent with a reduction in the rotation speed in the presence of an external magnetic field, which has been experimentally detected [4]. Silvi's model is simply incapable to reproduce this interaction because the bonding electrons' magnetic momenta are not free to interact in this way.*

2.2 Ethene, C₂H₄

Fig. 7a shows so far, the electron count extracted from the results in Figs. 2 and 3. Since $4(1.824) + 2.6 \approx 10$, a deficit of two electrons remains unexplained. However, the C-C electron count in the plane perpendicular to the molecular plane at the C-C axis gives exactly 4 (see Figs. 3 and 7b). This is, even though no indication of localization in this region is observed and these 4 electrons look to be in the same region of space (fused). This count probably means that the C-H electron count on the molecular plane, 1.824 is 2 in the plane perpendicular to it. Thus, a full electron count of this molecule is obtained. Coincidentally, Silvi's model presents same electron count and localization. Two point attractors (4 electrons) at the plane perpendicular to the molecular plane for ethene: one over and the other under the molecular plane and point attractors (2 electrons each) for the four C-H bonds in the molecular plane (see Fig. 7c).

The C-C single bond results, already described for ethane, provide a way to understand the double bond. Simply, after

*they are cancelling each other, completely coupled to obey the Pauli principle.

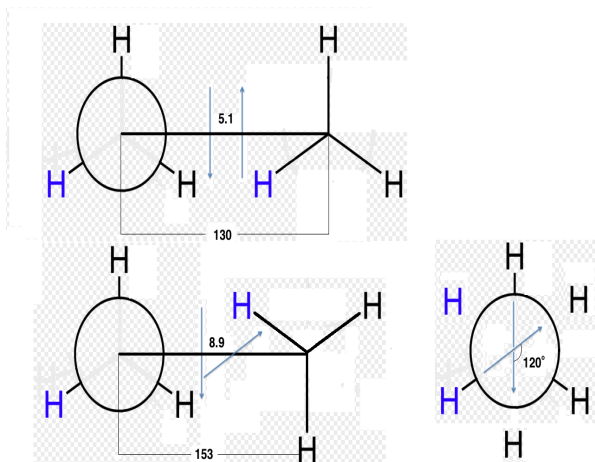


Fig. 5: Eclipsed (top) and Staggered (down) ethane conformers. The eclipsed conformer present the maximum magnetic attraction and shorter C-C bond length. Whereas, the staggered conformer has the lowest magnetic attraction and the longest C-C bond length. The extra projection shown down right is to present the angle between the two bonding electrons magnetic momenta in the staggered conformer. All distances are in pm.

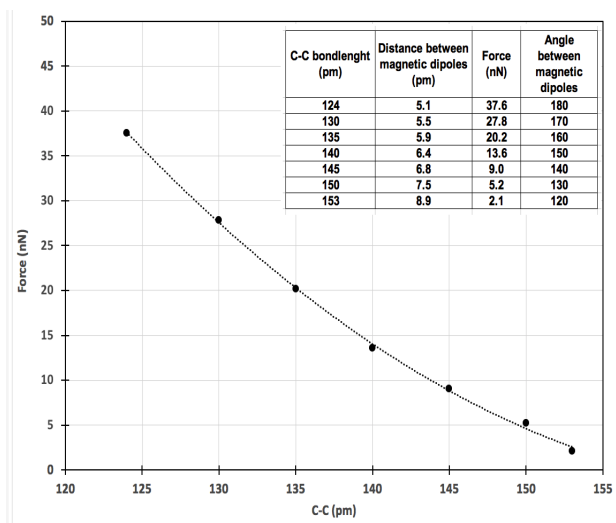


Fig. 6: Magnetic force between carbon atoms in the C-C bond for different C-C distances. The insert present the force values, distance between magnetic dipoles and angle assigned to each C-C distance. The integral of the curve is 12 kJ/mol.

the first single bond occurs, a second single bond in the C-C bond will lock any possibility for rotation. This is concurrent in both models presented here. Furthermore, Silvi's model does not present a point attractor in the line between the two carbons. Thus, the double bond looks like two out of line sigma bonds.

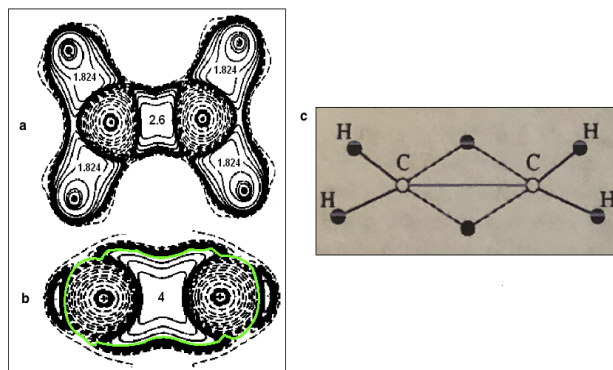


Fig. 7: Contour map of the Ethene molecule and its electron count. The C-C bond electron count at the plane of the nuclei (a) is different from the count at the perpendicular plane (b). The green line shows how the C-C bond was cut. Reprinted (adapted) with permission from [6]. Copyright (1996) American Chemical Society. c) Silvi's et al. structure from [2] used with permission of the publisher.

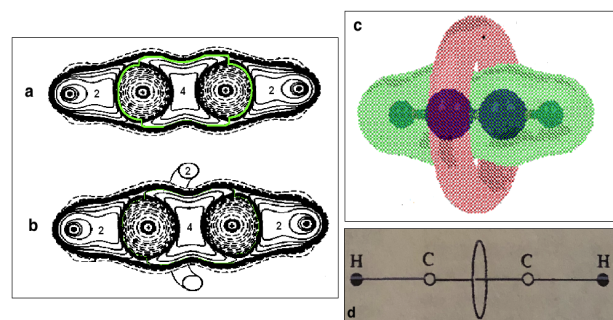


Fig. 8: a) Contour map of the ethyne molecule and its electron count, there is a lack of two electrons. The green line shows how the C-C bond was cut. b) These two electrons are fused in a toroidal lone pair around the C-C bond. Reprinted (adapted) from [6]. Copyright (1996) American Chemical Society. c) This structure has been observed in the molecular electrostatic potential of ethyne. This is from [9] used with permission of the publisher. d) Silvi's et al. structure from [2] used with permission of the publisher.

2.3 Ethyne, C_2H_2

Fig. 2 presents that C-H bond has two electrons in ethyne, Fig. 3 shows that the C-C bond has 4. Therefore, Fig. 8a presents a lack of two electrons. These two electrons will be bonded outside of the ethyne's C-C bond and at its midpoint, completely fused, producing a lone pair with a toroidal shape (see Fig. 8b). This has been observed in the molecular electrostatic potential of this molecule (see Fig. 8c [9]). This toroidal shape has also been noticed as a "ring attractor" in the electron localization function, $\eta(\mathbf{r})$, of this molecule in [6]. Concurrently, Silvi's structure also presents this ring attractor (2 electrons) and the point attractors for the C-H bonds, see Fig. 8d. But, it misses the other four electrons in the C-C bond. Fig. 8b depicts the complete electron count for the

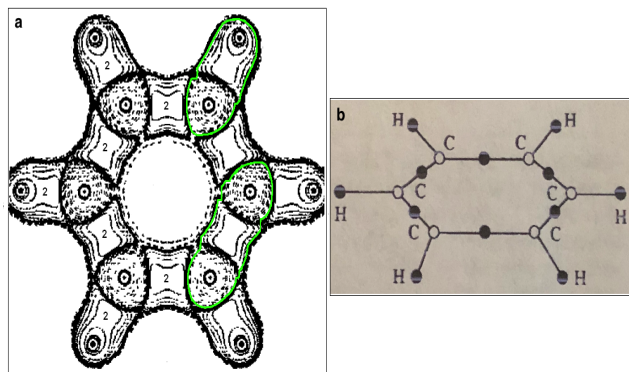


Fig. 9: a) Contour map of the Benzene molecule and its electron count. There is a lack of six electrons. These electrons are fused in two lone pairs at both sides of the C_6 ring. The green line shows how the bonds were cut. This is from [7] used under Creative Commons license. b) Silvi's et al. structure from [2] used with permission of the publisher.

ethyne molecule.

The evidence shows that the triple bond is a double bond with a lone pair. Also, the availability of two more bonding electrons would make this lone pair to disappear into a quadruple bond, which has been observed in dicarbon [5].

2.4 Benzene, C_6H_6

Figs. 2 and 3 show that the C-H and C-C bond in benzene have two electrons each. Fig. 9a presents the electron count for benzene. Silvi's structure (Fig. 9b) also depicts the same C-H and C-C electron count. None of these structures inform the whereabouts of the six remaining electrons. It is believed that they will go to two fused toroids (three electrons each) on both sides of the C_6 molecular plane. This is because that has been observed in the molecular electrostatic potential of benzene [9] (see Fig. 10). The aromatic stabilization energy for benzene is 120 kJ/mol [10], which is comparable to a weak chemical bond (for example F-F with 155 kJ/mol [5]). Thus, it is believed that these lone pairs act as such.

2.4.1 Aromaticity

In the customary view of aromaticity, an external magnetic field induces a molecular plane ring current in the delocalized π electrons of the aromatic ring. This current will produce its own magnetic field, which will go against the external magnetic field. This effect will deshield protons outside of the molecular plane. According to Fig. 10, there are three electrons in each toroidal lone pair; two of them are magnetically coupled and the third one will be uncoupled. The same structure occurs on the other side of the molecular plane. Therefore, they will magnetically attract across such plane (see Fig. 10). When an external magnetic field is imposed on the benzene molecule, these toroidal lone pair

structures will align their magnetic momenta against the external magnetic field naturally resisting to lose its original and more stable configuration. As in the customary explanation, this effect will deshield the protons outside of the molecular plane.

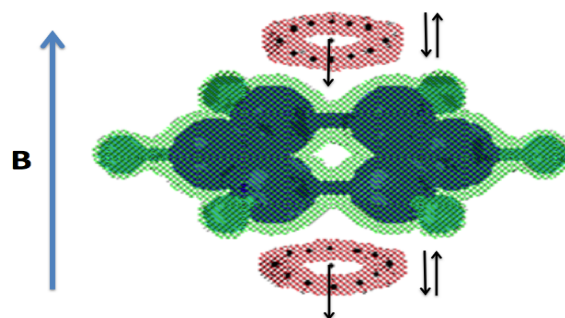


Fig. 10: Molecular electrostatic potential of benzene. The arrows depict the coupling of the three electrons in each lone pair. When an external magnetic field B is imposed, the magnetic moments of the two odd electrons aligned against it as shown. This is from [9] used with permission of the publisher.

3 Conclusions

A new experimental method to find the number of electrons shared in a chemical bond has been applied to selected hydrocarbon molecules. The information obtained is comparable and/or complements the state of the art. The total distribution of electrons in four fundamental hydrocarbons has been achieved. The long standing mystery of the ethane rotational barrier has been explained. The interaction between bonding electron magnets presents itself as fundamental to understand organic molecules.

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