Is the Chemical Bond Consistent with the Theory of Relativity?

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Abstract

An experimental non-model determination of the number of electron participating in a chemical bond has been achieved. This determination corroborates the valence theory of Lewis and coincides with current state of the art. The relationship between a normalized bond area and its bond energy is used to precisely characterize selected organic molecules. The mass fusion of bonding electrons with its mass loss or gain, is the probable origin of the chemical energy. A probable geometric meaning of thermodynamic functions is provided.

1 Introduction

Given the apparent divorce between special relativity and quantum mechanics, it is not known what changes in the molecule's mass after a chemical reaction has occurred. Special relativity said that regardless the kind of chemical bond, the energy released/absorbed is given by $\triangle E = \triangle m \cdot c^2$. Where $\triangle E$ is the chemical energy (in Kcal or KJ/mol) and $\triangle m$ is the molecule variation in mass between reactants and products. This chemical energy can be released (exothermic) or adsorbed (endothermic) during a chemical reaction, which means that the mass of the molecule will decrease or increase respectively. One clue about where to look is in the relationship between bond length and bond energy. This is because it is known that, generally, as the bond length get shorter, the energy of the bond becomes larger [1].

The bond length and area of the structure that occurs between bonding atoms is experimentally determined and shown in the contour map of the Laplacian of the electron density of the molecule [2]. However, the topological analysis of the electron density performed on this region is based on paths where bond critical points are found. This has made impossible to see any evidence of the electron pair [4]. In this regard, Silvi et. al. warn that the definition currently used to classify chemical bonds (in terms of bond order, covalency versus ionicity and so forth) are derived from approximate theories and are often imprecise. Then, these researchers offer a rigorous means of classification based on topological analysis of local quantum-mechanical functions related to the Pauli exclusion principle. With their method, they find "localization attractors". These attractors provide a basis for a well-defined classification of bonds, allowing an absolute characterization of covalency [5]. Nevertheless, a model based on a principle that will pair electrons artificially will be necessarily bias. Therefore, a non-model experimental verification is needed.

This paper shows a strong experimental evidence on the existence of Lewis electron pairs. Taking into account that the femtometer toroidal structures found in the atom nucleus [3] are also observed in the chemical bond [2], it was deduced that the bond is produced by the electron itself. In turns, this was the base for a non-model based method to count the number of electrons involved in a chemical bond and the revelation that the bond area is proportional to the bond energy [6]. In this paper, that method was applied to selected hydrocarbon molecules. It was found that: 1) the chemical bond is the result of the mass fusion of valence bonding electrons, 2) same number of valence bonding electrons can release different amounts of energy, occupying different areas and 3) more than two valence bonding electrons can be in the same spatial region. The valence bonding electrons change their masses after they fused. The mass defect product of such fusion is the origin of the chemical bond energy.

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 its silhouettes. These silhouettes were printed on paper and 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. 3 for the C-H bond, and in Fig. 4 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 between 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 is observed in Figs. 1 and 2. This method has been sufficiently described in ref. [6] and, in this paper, it was applied to 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 ref.[7]. Benzene C_6H_6 in [8] and C_2 is in [9].

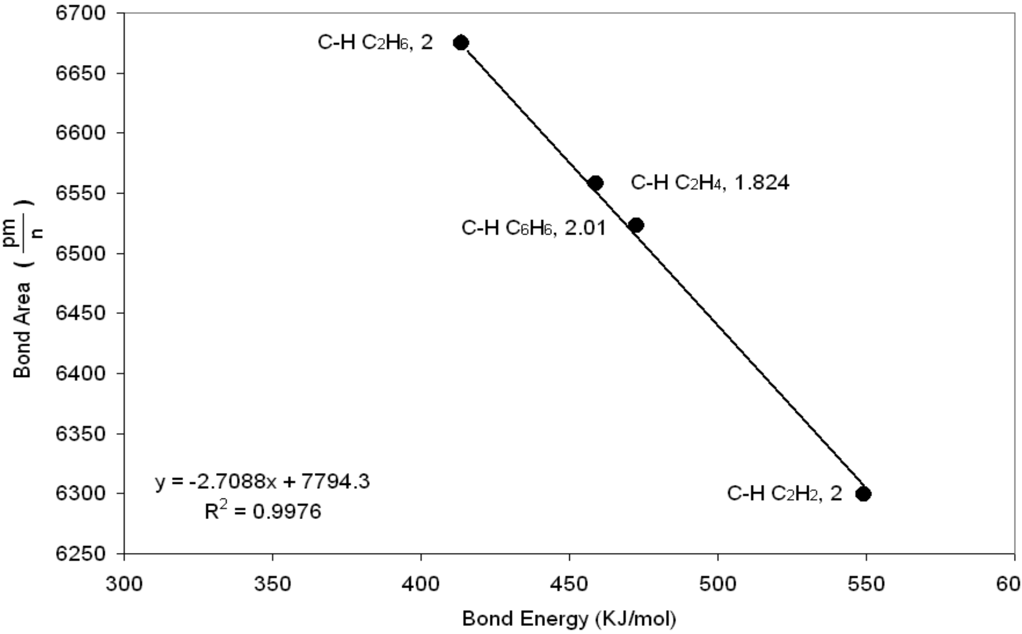

Figure 1: Bond area vs. bond energy for C-H bonds in different molecules.

3 Electron Counting

Figure 1 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.

Figure 2 shows that **n** is exactly 2 in the case of C-C ethane and benzene, 8 in the case of dicarbon as reported in [6] 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 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 Figure 2 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:

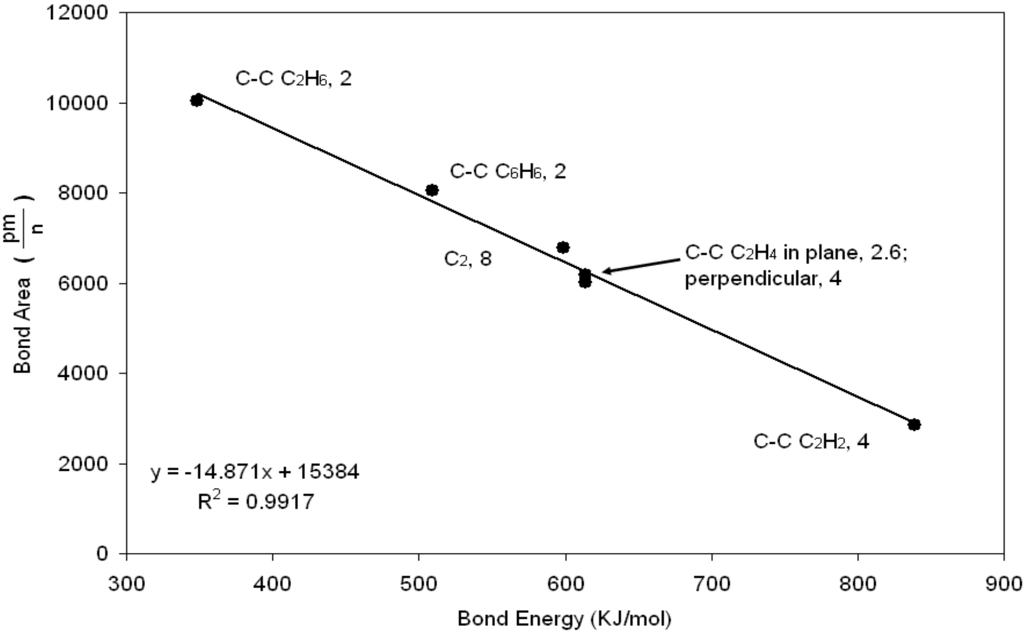

Figure 2: Bond area vs. bond energy for C-C bonds in different molecules.

3.1 Ethane, C_2H_6

From Figure 2, there are also two electrons involved in its C-C bond. Hence, as it is observed in Figure 3 ethane has the expected electron count for each bond.

3.2 Ethyne, C_2H_2

Figure 4 presents a lack in the electron counting. There are two electrons in each C-H bond and just 4 in the C-C bond, clearly presenting a deficit of two more electrons. These two electrons would be bonded outside of the ethyne's C-C bond and at its midpoint, completely fused, producing a lone pair with a toroidal shape. This toroidal shape has been noticed as a "ring attractor" in the electron localization function, $\eta(\mathbf{r})$, of this molecule in [7], also the molecular electrostatic potential of ethyne shows just that structure [11]. Therefore, Figure 4 shows the complete electron counting for the ethyne molecule.

3.3 Benzene, C_6H_6

Figure 5 shows the electron count for benzene. Since its C-C and C-H bonds have just two electrons each. The remaining six electrons will go to two fused toroids (three electrons each)

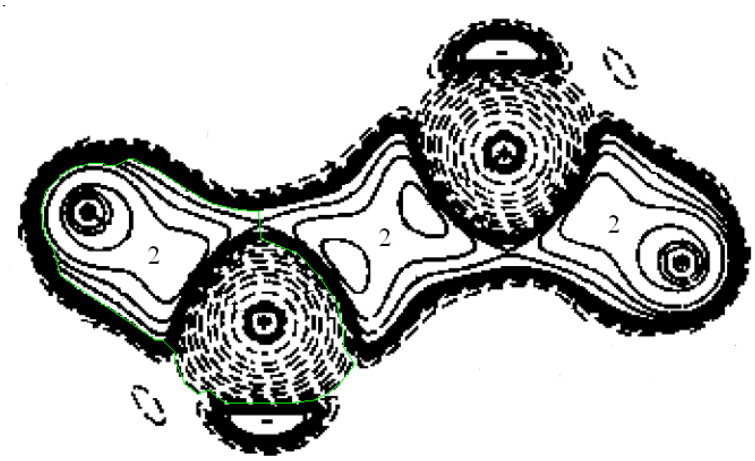

Figure 3: Contour map of the Ethane molecule and its electron count. The green line shows how the C-H bond was cut. The C-C bond was also cut accordingly.

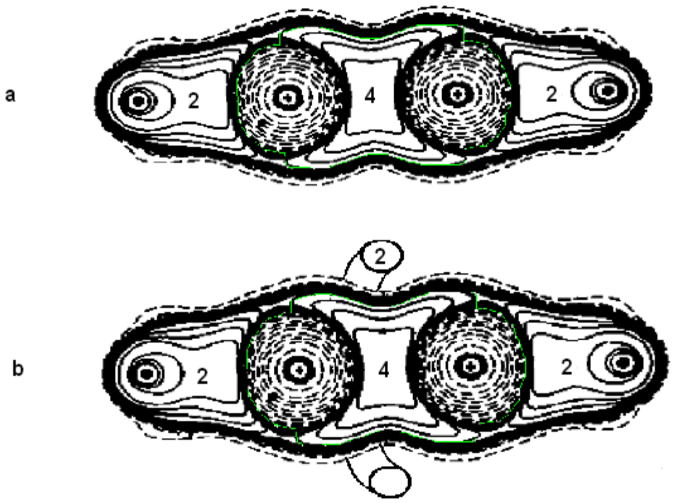

Figure 4: Contour map of the Ethyne molecule and its electron count. There is a lack of two electrons (a). This electrons are fused in a toroidal lone pair around the C-C bond (b). The green line shows how the C-C bond was cut.

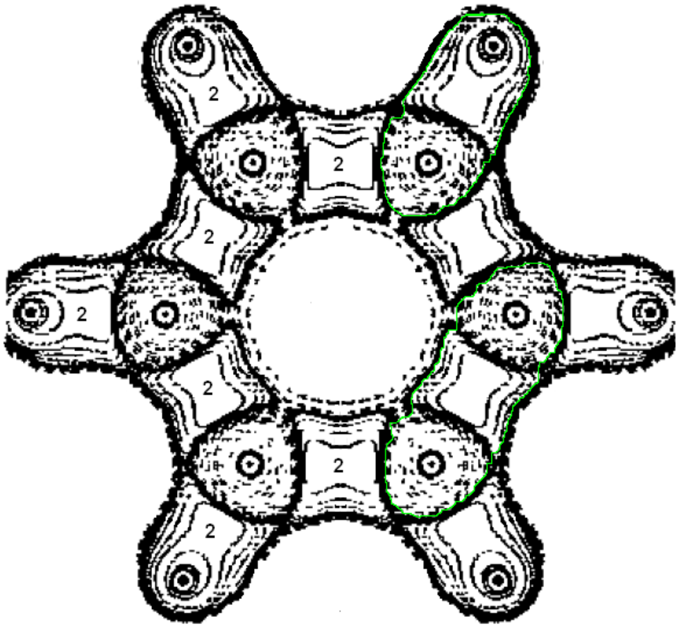

Figure 5: Contour map of the Benzene molecule and its electron count. There is a lack of six electrons. These electrons are fused in two lone pair at both sides of the C_6 ring. The green line shows how the bonds were cut.

at both sides of the C_6 molecular plane. The molecular electrostatic potential of benzene shows just that [11].

3.4 Ethene, C_2H_4

Figure 6 **a** shows so far, the electron counting extracted from the results in Figures 1 and 2. Since $4(1.824) + 2.6 \approx 10$, a deficit of two electrons remains unexplained. However, the C-C electron counting in the plane perpendicular to the molecular plane and at the C-C axis gives exactly 4 (see Figure 2 and 6 **b**). This probably means that the electron counting of the C-H bond is 2 in that plane. This revealed that one needs to check for the bond areas at different molecule's planes. Silvi et. al. reported two localization attractors at the plane perpendicular to the molecular plane for ethene: one over and another under the plane [5]. The results reported here counts 4 equally distributed in the whole area of such plane. Regardless the differences, this is an astonishing coincidence.

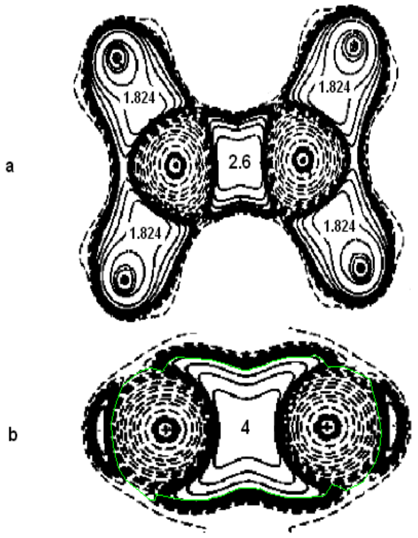

Figure 6: Contour map of the Ethene molecule and its electron count. The C-C bond electron count at the plane of the nuclei (a) is different from the count at the perpendicular plane (b). The green line shows how the C-C bond was cut.

4 Discussion

The case of the ethene molecule is teaching us, that the plane of the molecule does not necessarily have the "right" distribution of electrons to match the linear relationship found between the bond area and the bond energy. Therefore, the Laplacian of the electron density in the plane of the molecule and in the plane perpendicular to it are needed. This is important because most of the time just one plane is reported and because, in some cases, the bond energy does not correlate to the bond length [1].
Even though, after the topological analysis of the electron density of the chemical bond, Bader did not find any evidence of the Lewis electron pair [4], Silvi et.al. created a way to "localize" such electron pair. Where electrons are alone or forms 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 and an attractor can be located by using a "localization" function. For practical purposes, they required that the "localization" function to have their maxima corresponding to this "bosonic" regime. The actual values of localization functions are calculated from approximate wavefunctions provided by quantum chemistry. In turns, the integral of the charge density over the basin of an attractor provides the number of electrons that belong to that basin. An attractor for which the integral of the localization function is less than 2 will be called an unsaturated attractor [5]. Thus, Silvi came out with three different types of attractors: 1) Point attractor, normally found in the internuclear axis, 2) Ring attractors, centered on the axis and 3) spherical attractors, which are core attractors and they are centered on the bonding atom nucleus [5]. It is assumed that each attractor consists on a pair of electrons.

Therefore, in the case of ethane, Silvi found a point attractors at the internuclear axis between the carbons. This is consistent with the number of electrons found in Figure 3. Nevertheless, contrarily to what is shown in Figure 3 for the C-H bond, Silvi find that the point attractor for the C-H bond not at the internuclear axis but very near the hydrogen atom. The problem with a point attractor very near to the hydrogen is that this bond would not be covalent but ionic. This feature occurs all along the structures provided by Silvi [5]. Probably this is due to the fact that the electron localization function is being performed between different kind of atoms in the bond C-H. This is because it is observed that the point attractor occurs at the mid point of the internuclear axis in the C-C bond. Whereas, Figure 1 presents evidence that the C-H Lewis pair is related to the area of the whole structure found, keeping the covalent character of this bond.

In the case of ethyne, Silvi found a ring attractor centered on the C-C axis. This is observed as the ring structure in Figure 4. The structure found by Silvi, however, does not count the other 4 electrons forming part of the C-C bond in this molecule. Given that the localization is found where the electrons behave like bonsons, Silvi's structure should have shown two more point attractors at the mid point of the C-C axis in this molecule.

In the case of benzene, Silvi found point attractors, claiming two electrons each, in all benzene's C-C bonds. This is also observed in Figure 5. Again, the distribution attained in the present paper counts and distributes the total number of valence electrons. In he case of benzene, six extra electrons are outside of the plane of the molecule forming two rings (three electrons each). That structure has been found by using molecular electrostatic potentials [11].

In the case of ethene, Silvi found two point attractors above and under the molecular plane. Figure 6 showed that this is true and that the electron distribution not necessarily reside on the molecular plane. Shall this be support to the "banana" representation of the double bond? Figure 6 explicitly depicts that such representation is inaccurate. This is because more than 2 electrons (in this case 4) can be fused in the same region of space. Therefore, the overlap of π orbitals is superfluous and the Laplacian of the electron density does not show any evidence of it.

Albeit the total number of valence electrons is not assigned, the electron distribution found in all the molecules presented in this paper complements Silvi's [5]. Given that the method used here is completely different and it is not influenced by a model,[1] these previous electron distributions are validated.

The same three shapes described in [6], are observed again in Figures 3 to 6. These shapes are the "attractors" identified by Bader et.al. after the topological analysis of a large number of molecules [10]. Specifically, the core attractor can be identified as the sphere in a sphere, *ss* shape; the bonding attractor as the two separated spheres, *tss* shape and the non-bonding attractor as the toroidal shape. Given that the same shapes has been observed for the deuteron [3], it is believed that these attractors are actually different shapes of the bonding electron. Contrarily to Bader conclusion, the evidence of the existence of the Lewis pair reported here is overwhelming.

It is inferred that bonding electrons will naturally repel each other, not because electrostatic

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[1] the shape of the structures observed in molecular bonds has been seen experimentally in the nucleus of the atom [3].

repulsion[2] but because of mass repulsion. An activation energy would be needed to overcome this mass repulsion. After that, the bond occurs as a consequence of bonding electrons mass fusion. Consequently, the mass defect or gain produced will translate to an energy release (larger bond area) or gain (shorter bond area) respectively. In the case of chemical bonding, however, the mass defect is way smaller than in nuclear fusion and hence, way lower energy is released [12]. This is the origin of the chemical energy and it is consistent with special relativity, through $\triangle m = \frac{\triangle E}{c^2}$. Once the chemical bond is understood as the mass fusion of bonding electrons, it is easy to understand that **"the same number of electrons (two) can present different bond energies"**.

An straightforward consequence of these findings is its connection with thermodynamics. The reaction enthalpy will be related to variations in bond area between products and reactants. This is because in comparison with the reactant's, a minimum mass energy state will correspond to a larger area in the products' chemical bonds. This is clearly observed in Figure 2, where ethyne may be hydrogenated to ethene and to ethane. This process will increase the bond area and release the chemical energy. Consequently, hydrogenation of ethyne all the way to ethane is an exothermic reaction [13]. Given that one property of mass is to tense the space around it [14], this "bond area increase" occurs because the bond is trying to reduce its tension on its surrounding space. An alternative way to lower such tension is by spreading the molecule's bonds. This is because the spreader the molecule, the less tension. For example, this will set a difference between structural isomers. The standard entropy of formation S^{θ}_{298} for neo-pentane is 217, iso-pentane 260 and n-pentane 263 J $K^{-1}mol^{-1}$. Neo-pentane is the most symmetric isomer and the one with less entropic contribution for its formation. This is followed by iso-pentane, which is less symmetric than neo-pentane. Finally, n-pentane gives the largest entropic contribution to its formation, i.e. it is the spreadest isomer. This is the origin of entropy.

Therefore, the geometric equivalent of the Gibbs free energy will have an area related term: enthalpy and shape related term: entropy. Both controlled by the product's final geometry. This final geometry intends to reduce the tension exerted on the space around the molecule by the two means at disposal and this is why the Gibbs free energy determine the chemical reaction spontaneity. Molecules will react spontaneously to produce larger areas bonds (lower enthalpy) and less symmetric molecules (higher entropy). The energies of this functions set the degree at which the space is curved around them.

5 Conclusions

A new experimental method to calculate the localization and number of electrons shared in a chemical bond has been developed and validated. The electron localization function is contained in the relationship between the bond area and the bond energy. The mass fusion of bonding electrons with its mass loss or gain, is the probable origin of the chemical energy. These mass energy changes inversely relates to their bond areas. This indicates that the mass

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[2] every bonding electron charge is neutralized by the counter charge of the bonding atom nucleus.

defect and gains are related to the tension that the mass exerts on its surrounding space. Thermodynamics functions are related to the geometry of the chemical transformation. This is because such geometry set the two ways the tension of the product's surrounding space is reduced.

References

[1] M. Kaupp, D. Danovich and S. Shaik, "Chemistry is about energy and its changes: A critique of bond-length/bond-strength correlations" Coor. Chem. Rev. 344 (2017) 355.

[2] R.F.W. Bader, "Atoms in Molecules, a Quantum Theory", Clarendon Press, Oxford, 1990, pp. 175.

[3] J.L. Forest, V. R. Pandharipande, Steven C. Pieper, R. B. Wiringa, R. Schiavilla and A. Arriaga, Phys. Rev. C, 54(1996)646-667.

[4] R.F.W. Bader, "Atoms in Molecules, a Quantum Theory", Clarendon Press, Oxford, 1990, pp.163.

[5] B. Silvi and A. Savin, Nature 371 (1994) 683.

[6] Yepez, Omar. New Lewis Structures through the application of the Hypertorus Electron Model. Available from Nature Precedings, http://dx.doi.org/10.1038/npre.2010.5336.1, (2010).

[7] R. F.W. Bader, S. Johnson, T. H. Tang and P.L.A. Popelier, J. Phys. Chem., 100 (1996) 15398.

[8] Bader R.F.W. and Keith T.A., J. Chem. Phys. 99 (1993) 3683.

[9] Wai-To Chan and I. P. Hamilton, J. Chem. Phys. 108 (1998) 2473.

[10] R.F.W. Bader, "Atoms in Molecules, a Quantum Theory", Clarendon Press, Oxford, 1990, pp. 294.

[11] Gadre S.R., Bhadane, P. K., Resonance, "Electrostatic in Chemistry: 3. Molecular Electrostatic Potentials: Visualization and Topography", July (1999) 14.

[12] Treptow R. S., J. Chem. Educ., 82 (2005) 1636.

[13] Scott D. Barnicki "Synthetic Organic Chemicals" in Handbook of Industrial Chemistry and Biotechnology edited by James A. Kent, New York : Springer, 2012. 12th ed.

[14] Einstein, Albert (1916). "The Foundation of the General Theory of Relativity". Annalen der Physik. 354 (7): 769.