

Journal of Chemical, Biological and Physical Sciences



An International Peer Review E-3 Journal of Sciences

Available online at www.jcbps.org

Section A: Chemical Sciences

CODEN (USA): JCBPAT

Research Article

Understanding of Reaction Mechanism: The Second Substitution of Chlorine on Chlorobenzene by ELF (Electron Localization Function) Method

Ibrahim Mboumbouo Ndassa ^{1*}, François Volatron ² and Bernard Silvi ²

^{1*} Department of Chemistry, High Teacher Training College, University of Yaounde 1, P. O. Box 47 Yaoundé, Cameroon.

² Laboratoire de Chimie Théorique (UMR-CNRS 7616), Université Pierre et Marie Curie, 4 place Jussieu, 75005 Paris, France.

Received: 19 October 2015; **Revised:** 27 October 2015; **Accepted:** 06 November 2015

Abstract: The potential energy surface of the chlorination reaction of chlorobenzene catalyzed by Aluminium Chloride has been investigated theoretically with hybrid Density Functional Theory (B3LYP) in order to determine the general reaction mechanism which is a model of aromatic substitution of benzene derivatives (contains a group with a double effect: donor and acceptor of electrons). By using the ELF (Electron Localization Function) method, we've also evaluated the electronic population of Wheland intermediates (σ complexes) to explain and understand the orientation of the second substitution of Chlorine on chlorobenzene. The results obtained showed that, the potential energy surface of this reaction has six stationary points. These results obtained from DFT calculations have been compared with CCSD (T) method which is the most powerful post-Hartree Fock method in terms of inclusion of dynamic correlation. The ELF analysis applied on the Wheland complexes explained the traditional orientation of this reaction which said that the orientation of the second substituent in ortho and para positions depend on the stability of the intermediates complexes σ_1 or σ_2 .

Keywords: ELF (Electron Localization Function), DFT (Density Functional Theory), Chlorobenzene, Chlorination, Electrophilic substitution, Wheland complex.

INTRODUCTION

Quantum chemistry has been well used and successful known in chemical reaction analysis and chemical reactivity¹⁻⁷. Theoretical Chemistry cannot be reduced only to obtain the geometry, the energies and the spectroscopy of proposed molecular structures. An important part of quantum chemical research is used to rationalize and to explain the results in terms of quantitative concepts obtained from calculations. The electrophilic substitution reaction is widely taught in most courses in organic chemistry⁸⁻¹⁰, but his mechanism has been very few studied and explained theoretically.

Olah and his collaborators have studied his mechanism and after an important experimental works, have showed the influence of the solvent in the electrophilic substitution reactions¹¹⁻¹⁴. Many theoretical works have been done to explain the mechanism of electrophilic substitution of non-substituted benzene¹⁵⁻²².

Recently, in our group we've studied in gas phase and in solution the general mechanism of chlorination reaction of nitrobenzene which is a model of an aromatic substitution of substituted benzene with a Π acceptor group²³. The ELF (Electron localization Function) analysis of different systems have shown the importance of this function to evaluate the electronic population of molecules^{24, 25}, to explain, understand and visualize the chemical bond²⁶.

On the substitution reactions of benzene derivatives, the orientation of the second substitute depends on the nature of the first and not of the electrophile. This point has been generally rationalized by analyzing with the aim of electronic structure of intermediates σ (so called Wheland complexes)²⁷. The experimental data proved that these σ complexes exist and are responsible for the orientation of the aromatic reactions²⁸⁻³⁸.

In this study, we've proposed to investigate the potential energy surface of the chlorination reaction of chlorobenzene (with Chlorine which have a double effect: donor and acceptor of electrons) in order to obtain his general mechanism, to evaluate the electronic population of intermediate complexes σ by using the ELF method with the aim to explain the orientation of the second substitution of chlorine on chlorobenzene.

THEORETICAL CALCULATIONS

For this chlorination reaction of chorobenzene in the presence of Aluminium Chloride as catalysts, the overall reaction is written as follows:



The calculations of the wave function have been carried out at the hybrid Hartree-Fock density functional method B3LYP level³⁹ and CCSD (T) level⁴⁰⁻⁴³ with the basis 6-31G** in Gaussian 03 software⁴⁴. The vibrational analysis has been carried out at each optimized geometry in order to confirm whether the obtained structure is located at an energy minimum or Transition State; all positive for a minimum and one imaginary for a Transition State (TS).

The topological analysis ELF has been done with TopMod package⁴⁵⁻⁴⁷ developed by Bernard Silvi and collaborators. All information is available on the site: <http://www.lct.jussieu.fr/silvi>. The three-dimensional representations (molecular structures and isosurface ELF) have been visualized with the software Amira 3.0⁴⁸ and MOLEKEL (available on the web site: <http://www.cscs.ch/molekel>).

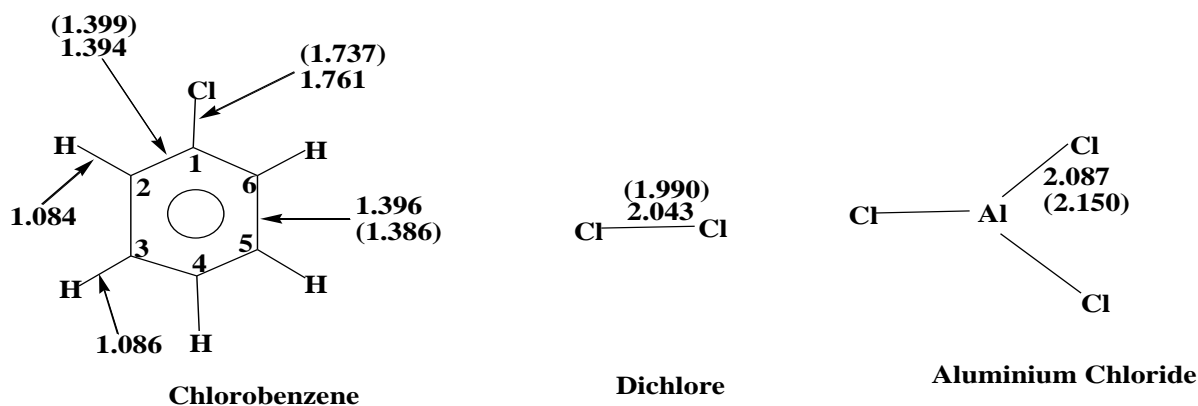
RESULTS AND DISCUSSIONS

The theoretical study of the second substitution of chlorine on chlorobenzene has given the relative energies illustrated in **Table-1** below:

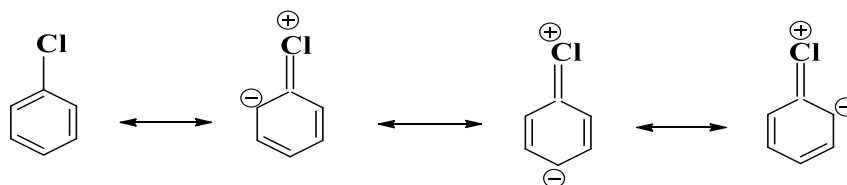
Table-1: Relative energies (ΔE) for the chlorination reaction of chlorobenzene in the gas phase; the reactants are taken as reference.

	B3LYP/6-31G** ΔE (Kcal/mol)			CCSD (T) /6-31G** ΔE (Kcal/mol)		
	ortho	meta	para	ortho	meta	para
Reactants	0.0	0.0	0.0	0.0	0.0	0.0
Π_1	-10.5	-10.5	-10.5	-5.6	-5.6	-5.6
TS_1	-8.6	-5.2	-9.7	-6.1	-3.3	-6.3
σ_1	-19.0	-13.7	-17.5	-27.3	-18.3	-23.8
σ_2	-19.3	-18.4	-20.2	-24.3	-22.1	-23.6
TS_2	-17.7	-17.9	-16.0	-21.1	-19.1	-20.1
Π_2	-36.3	-38.3	-38.9	-43.6	-44.3	-44.9
Products	-25.2	-27.3	-27.6	-30.6	-32.4	-32.5

The Reactants and products



The geometric optimized parameters at the B3LYP level of reactants in Å are in good agreements with the experimental data in parentheses^{49, 50}. The mesomeric effects⁵¹ in the case of chlorobenzene are shown below:



The analysis of mesomeric effects on chlorobenzene confirms that the C_1-C_2 is more reinforced than C_2-C_3 bond. If we compare with the model system, the C_1-Cl bond in chlorobenzene is smaller (1.737 \AA) than CH_3-Cl (1.804 \AA). This analysis of the evolution of distance C-C and C-Cl in chlorobenzene is reinforced by ELF calculation on the different systems: the population of disynaptic basin V (C, Cl) increases from $1.27 e^-$ (CH_3-Cl) to $1.43 e^-$ in the chlorobenzene; in the same way, the electronic density of chlorine atoms decreases from $6.47 e^-$ (CH_3-Cl) to $6.32 e^-$ ($\phi-Cl$).

The ELF population of basins with correspondent bond lengths and ELF structure in the case of chlorobenzene are given respectively in **Figure 1** and **Figure 2** below:

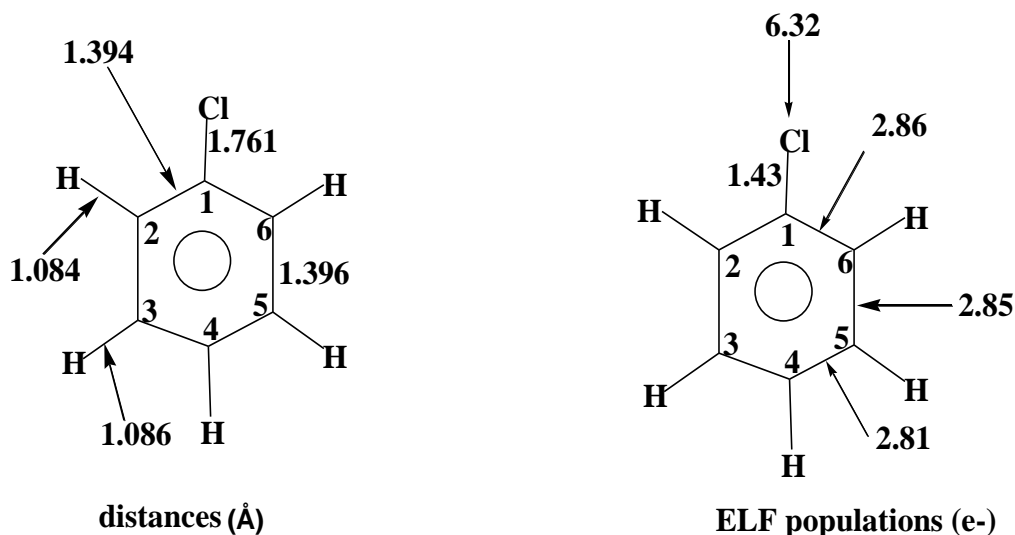


Figure 1: ELF population of basins with correspondent bond lengths in chlorobenzene.

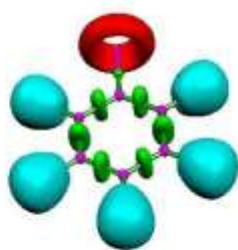


Figure 2: ELF structure of chlorobenzene.

The ELF function in the case of chlorobenzene permits us to analyse how the delocalization of Π system is done in this molecule. The population of disynaptic basin V (C_1, C_2) is the most important in the cycle ($2.86 e^-$) and correspond to the distance C_1-C_2 which is the smaller (1.394 \AA).

The population of the basin V (C_2, C_3) is a little fairly ($2.85 e^-$) and correspond to the distance a little extended (1.396 \AA). At the end, the most fairly population V (C_3, C_4) with $2.81 e^-$ correspond to the distance C_3-C_4 equal to C_2-C_3 (1.396 \AA). In the case of benzene, the synaptic basin V (C, C) has a population of $2.80 e^-$ with a distance of 1.396 \AA . The geometric structures obtained for products are elucidated in **Figure 3**.

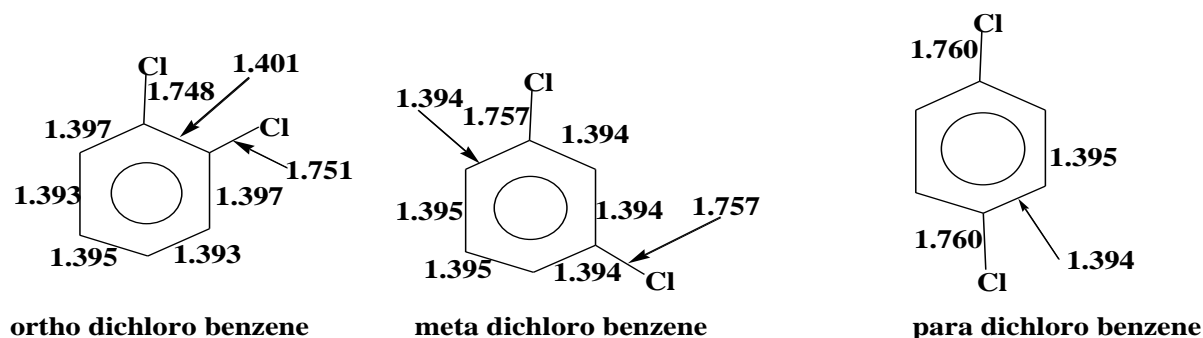


Figure 3: Geometric structures of products (the bond lengths are in Å).

By comparing the three products of the reaction of chlorination of chlorobenzene, ortho product have the highest energy (-25.2 kcal/mol) than meta and para products which have the same energy (-27.5 and -27.6 kcal/mol). It is the same situation for CCSD (T) calculations where the relative energies of products follow the same order of stability than B3LYP calculations. The distance of C-Cl bond is smaller in ortho product (1.748 Å) than meta and para products where this bond have the same distance (1.757 and 1.760 Å). The repartition of the electronic population obtained with the ELF analysis for the three products of the reaction is in **Figure 4** below:

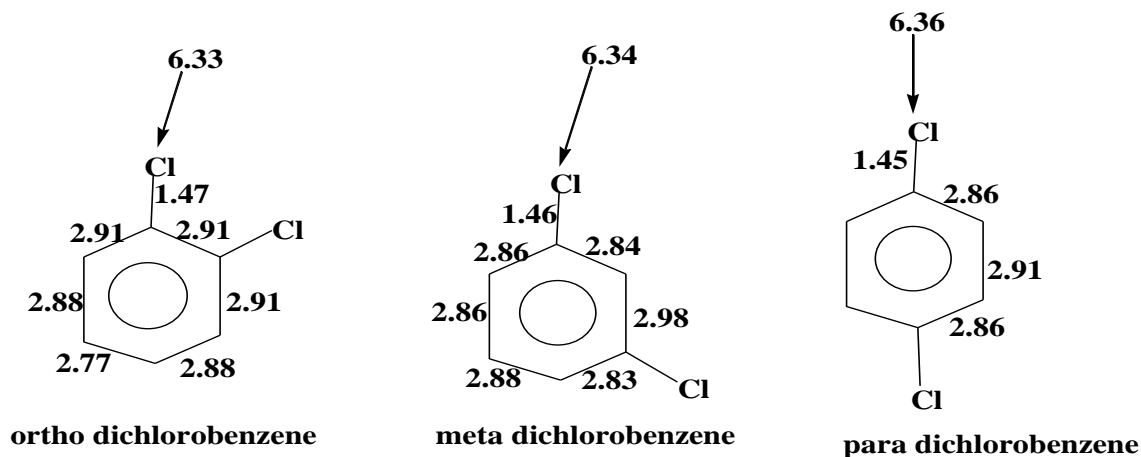


Figure 4: ELF population of basins in ortho, meta and para dichlorobenzene respectively. All electronic population of basins are in e-(electrons).

With the ELF analysis on the products, there is a small differentiation on the population of disynaptic basin $V(\text{C-Cl})$: 1.47 e- (for ortho product), 1.46 e- (meta) and 1.45 e- (para). By comparing this $V(\text{C,Cl})$ basin in the products of the reaction with the one in chlorobenzene (1.43 e-), we've realized that this population has a little increased. We have also observed the small difference on the population of monosynaptic basin $V(\text{Cl})$ in the products (6.33 e-, 6.34 e- and 6.36 e-) than the one of chlorobenzene (6.32 e-).

These differences of basins population explains the thermodynamic and geometric differences which have been observed between the different products. The ELF analysis on the products is directly linked to the geometric and thermodynamic analysis.

REACTIONAL INTERMEDIATES

Π_1 complex: This Π_1 complex is formed with the interaction between three reactants (chlorobenzene, chlorine and aluminium chlorine). In our study, one Π_1 complex has been localized for the three attack ways corresponding for a fixation on para position (**Figure 3**). The optimized geometry in **Figure 5** shows that C-Cl bond decreased from 1.761 Å in the reactant to 1.737 Å in the stabilized complex Π_1 . The situation is different for Cl-Cl and Al-Cl bonds which increases respectively from 2.087 Å to 2.278 Å and from 2.083 Å to 2.392 Å. The stabilization energy of this Π_1 complex is -10.5 kcal/mol compared to the isolated reactants. With CCSD (T) method, this stabilization energy becomes -5.6 kcal/mol.

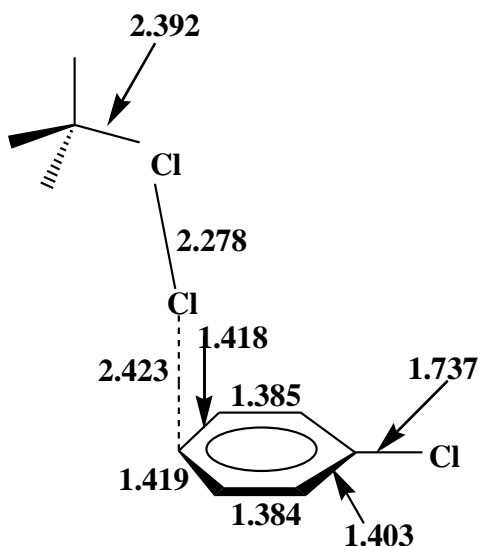


Figure 5: Π_1 complex para (Units of bond lengths of all parameters are Å).

Transition States TS1: Three Transition States TS₁ have been obtained respectively for ortho, meta and para position (**Figure 6**).

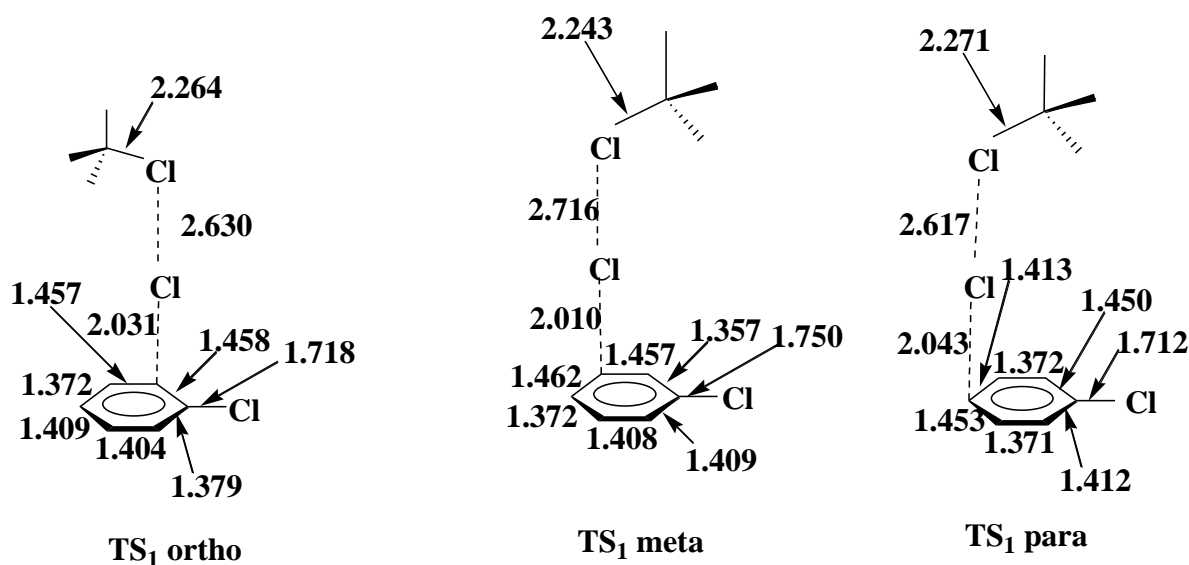


Figure 6. Transition States TS1 in the cases of ortho, meta and para position (Units of bond lengths of all parameters are Å). By comparing the energy of three TS₁, we have the small differentiation: the ortho (-8.6 kcal/mol) and para (-9.7 kcal/mol) positions are more stable than meta (-5.2 kcal/mol) position. With CCSD (T) calculations, the relative energies of TS₁ for ortho and para positions are more stable than the stabilized complex Π_1 (-6.2 kcal/mol), TS₁ meta remains less stable (-3.3 kcal/mol) than ortho and para.

Geometrically, the C-Cl bond is longer in TS₁ meta (1.750 Å) than ortho and para structures where this band has a little the same distance (\approx 1.717 Å). It is the same situation for Al-Cl bond where the distance is smaller in TS₁ meta (2.243 Å) than TS₁ ortho (2.264 Å) and TS₁ para (2.271 Å).

Intermediates complexes σ (sigma): After passing to the Transition States TS₁, the system arrives to Wheland complex which consist of two parts: cation being the traditional σ -complex $C_6H_5Cl_2^+$ and the counter anion $AlCl_4^-$ part. These two parts are mutually interacting with Coulombic forces. Since this species are purely ionic, the Coulombic interaction between $C_6H_5Cl_2^+$ and $AlCl_4^-$ causes the large stabilization of the σ -complexes intermediate whose energies are much more stable than the energy of the Π complex.

The intermediates σ_1 (sigma) obtained from the chlorination reaction of chlorobenzene are elucidated in **Figure 7** below (Units of bond lengths of all parameters are Å):

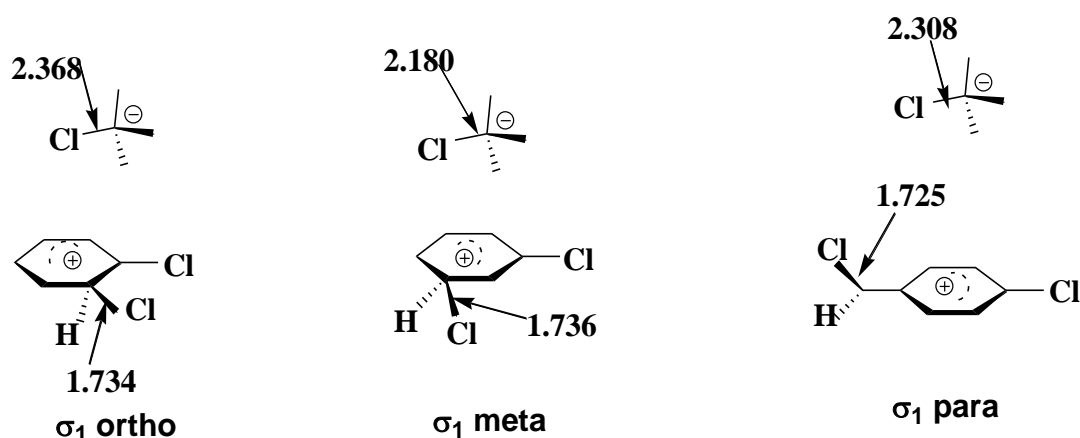


Figure 7: σ_1 (sigma) complexes in the cases of ortho, meta and para position respectively.

The results shows that σ_1 meta complex is less stable (-13.7 kcal/mol) than σ_1 ortho complex (-19.0 kcal/mol) and para (-17.5 kcal/mol). With B3LYP method, this energetically differentiation is not important as in the case of chlorination of aniline⁵².

With CCSD (T) calculations, the difference of energy is important: the energy of Wheland complexes are -27.3 kcal/mol for ortho, -18.3 kcal/mol for meta and -23.3 kcal/mol for para; the meta complex remains the less stable of them. Geometrically, the distance Al-Cl is small in σ_1 meta complex (2.180 Å) than σ_1 ortho complex (2.368 Å) and para (2.308 Å).

The C-Cl bond is longer in the meta (1.736 Å) than the ortho (1.734 Å) and para complex (1.725 Å). The distance and ELF analysis round the aromatic cycle of σ_1 complexes gives the results below in **Figure 8** and **Figure 9** respectively:

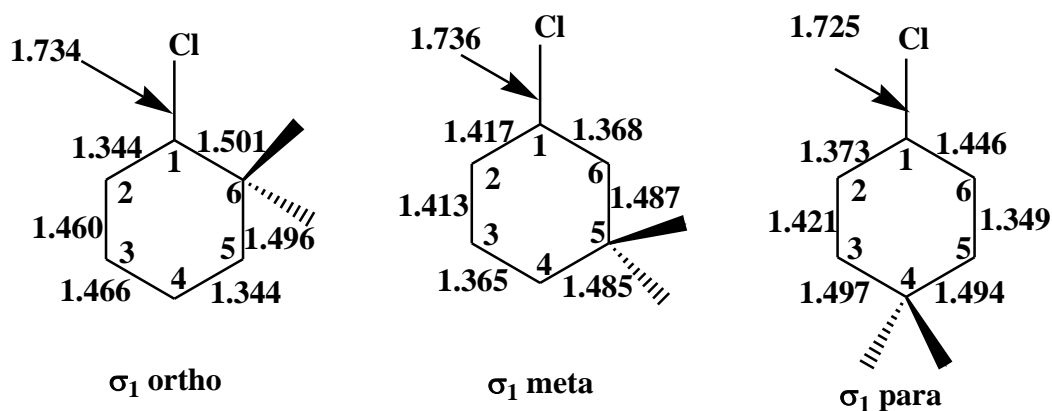


Figure 8: Distance analysis round the aromatic cycle of σ_1 complexes (Units of bond lengths of all parameters are Å).

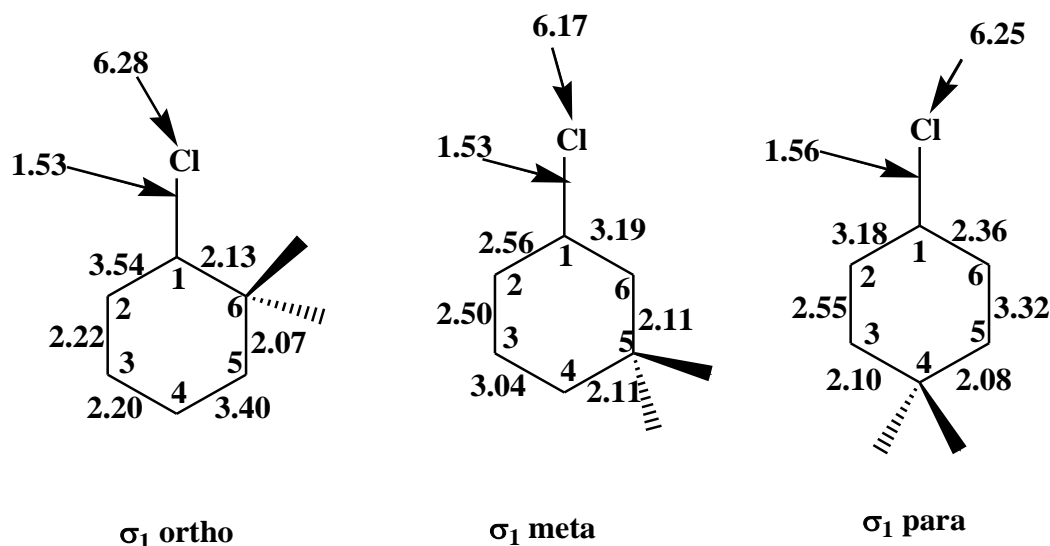


Figure 9: ELF analysis round the aromatic cycle of σ_1 complexes. All electronic population of basins are in e-(electrons).

These results of distance and ELF population round the aromatic cycle of σ_1 complexes are summarized in **Table-2**. The distance C₁-Cl is smaller in σ_1 para complex (1.725 Å) than the other two complexes where they have a little the same distance (1.734 and 1.736 Å respectively for ortho and para complex). These distances are smaller than the same distance in chlorobenzene (1.761 Å).

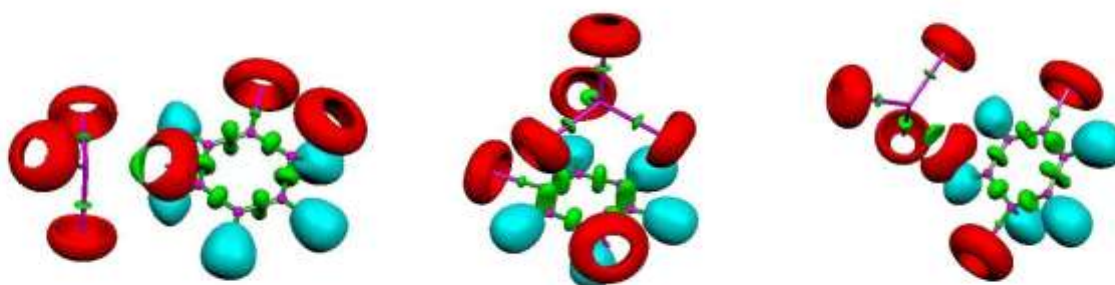
The ELF analysis on these C₁-Cl bond shows that this bond has the high electronic population (1.56 e-) in para complex and this population is the same (1.53 e-) in ortho and meta complexes. These populations of disynaptic basin are higher than V (C, Cl) in chlorobenzene (1.43 e-).

The electronic density on chlorine in meta complex (6.17 e-) is smaller than the ones in ortho complex (6.28 e-) and para (6.25 e-). This electronic density of chlorine in chlorobenzene is 6.32 e-. This situation shows that there is a transfer of electrons from chlorine to aromatic cycle.

Table-2: Distance analysis at B3LYP level and ELF analysis of chemical bonds round the aromatic cycle of σ_1 complexes.

	Distance analysis at B3LYP level (Å)			ELF analysis (electrons)		
	σ_1 ortho	σ_1 meta	σ_1 para	σ_1 ortho	σ_1 meta	σ_1 para
Cl	-	-	-	6.28	6.17	6.25
C ₁ -Cl	1.734	1.736	1.725	1.53	1.53	1.56
C ₁ -C ₂	1.344	1.417	1.373	3.54	2.56	3.18
C ₂ -C ₃	1.460	1.413	1.421	2.22	2.50	2.55
C ₃ -C ₄	1.466	1.365	1.497	2.20	3.04	2.10
C ₄ -C ₅	1.344	1.485	1.494	3.40	2.11	2.08
C ₅ -C ₆	1.496	1.487	1.349	2.07	2.11	3.32
C ₆ -C ₁	1.501	1.368	1.446	2.13	3.19	2.36

The sum of ELF population on double bonds in ortho complex (6.94 e-) and para complex (6.50 e-) are more important than meta complex (6.23 e-). This differentiation explains the high stability of σ_1 ortho and para compared to σ_1 meta. This conjugation round the aromatic cycle is responsible of the stability of Wheland complexes: The delocalization is very important in aromatic cycle of ortho and para complex; this delocalization is less important in meta complex. The ELF structures of σ_1 ortho, meta and para respectively, are illustrated in **Figure 10** below:

**Figure 10:** ELF structures of σ_1 ortho, meta and para respectively.

The geometric structures of σ_2 complexes which are not so different to σ_1 are illustrated in **Figure 11** (Units of bond lengths of all parameters are Å): In these structures of σ_2 , the substituted chlorine atom of the cation is situated in opposite side with the counter anion AlCl_4^- .

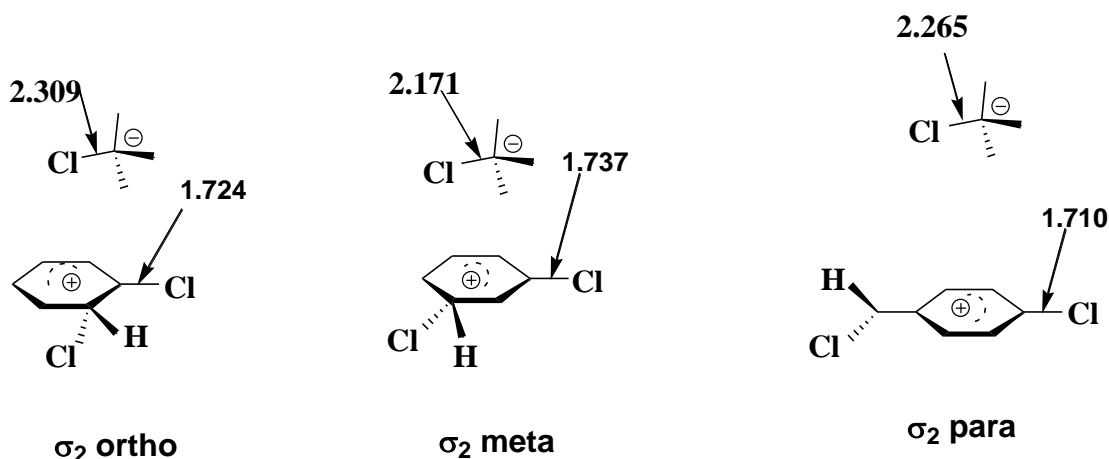


Figure 1: Geometric Structures of σ_2 ortho, meta and para respectively.

σ_2 complexes are a little more stable than σ_1 complexes but are fit the same order of stability : σ_2 ortho (-19.3 kcal/mol) and para (-20.0 kcal/mol) are more stable than meta complex (-18.4 kcal/mol). The CCSD (T) calculation gives the energies with the different order of stability. Geometrically, the distance Al-Cl is longer in σ_2 complexes ortho (2.309 Å) and para (2.265 Å) than meta complex (2.171 Å). The C-Cl bond is longer in meta complex (1.737 Å) compared to ortho (1.724 Å) and para (1.710 Å).

Transition States TS₂: The second phase of the reaction of chlorination of chlorobenzene consists to the transformation of σ_2 complexes to Π_2 complexes via the second Transition States (TS₂). The geometric structures of TS₂ are elucidated in **Figure 12**.

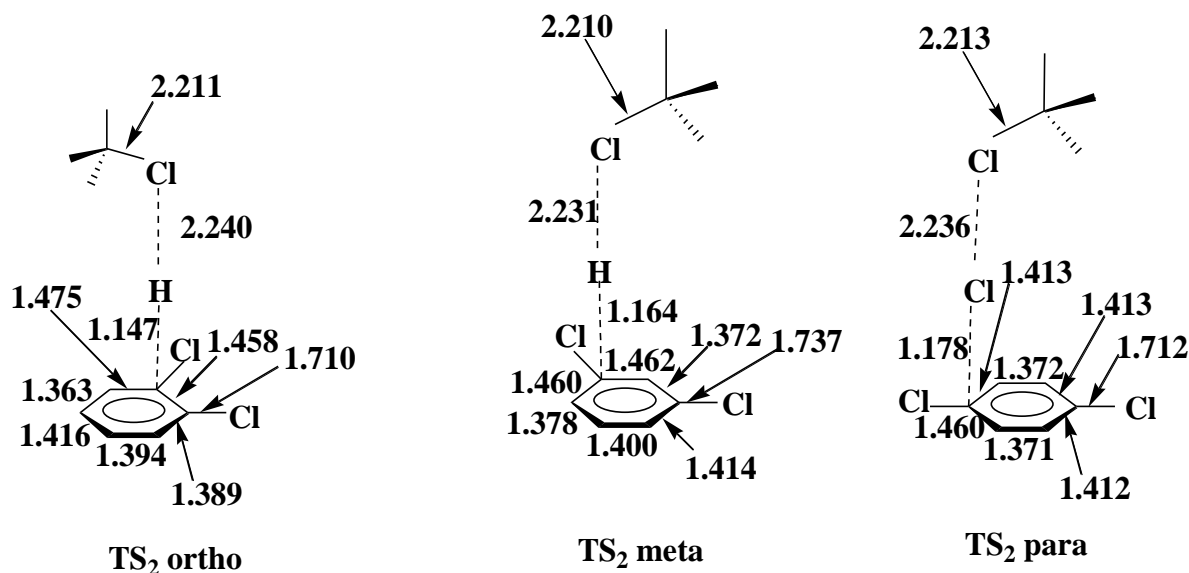


Figure 12: Transition States TS₂ in the cases of ortho, meta and para position (Units of bond lengths of all parameters are Å).

The relative energies obtained shows that the Transition States TS₂ ortho and para with the respective energy of -16.0 and -17.7 kcal/mol are more stable than TS₂ meta (-14.7 kcal/mol). The activation barriers calculated from σ_2 complexes are 3.3 kcal/mol for ortho, 3.7 kcal/mol for meta and 2.5 kcal/mol for para. The CCSD (T) calculation gives the results with the different order of stability for ortho and para positions: TS₂ ortho (-21.1 kcal/mol) and para (-20.1 kcal/mol) are more stable than TS₂ meta (-19.1 kcal/mol). The distance of C-Cl bond is longer in TS₂ meta (1.737 Å) compared to TS₂ ortho (1.710 Å) and para (1.714 Å)

Π_2 complex

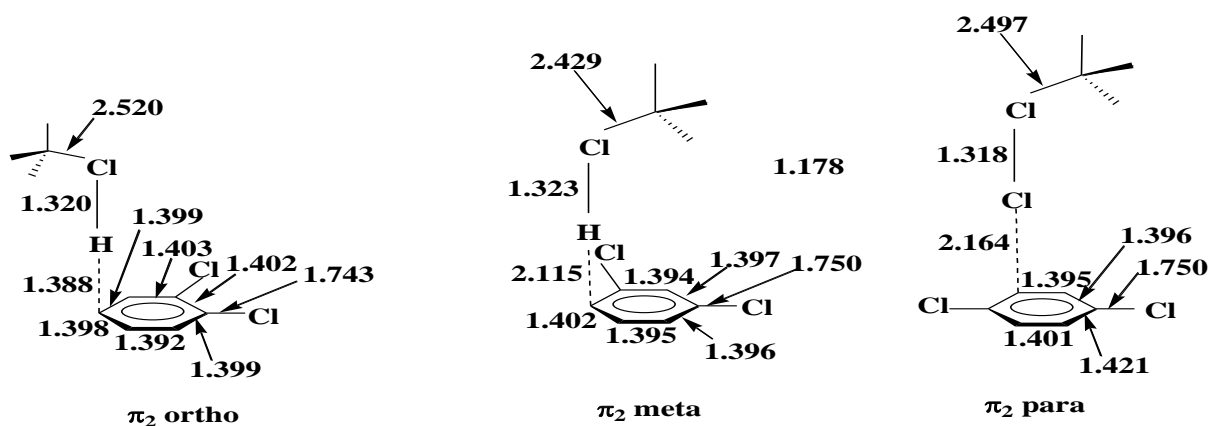


Figure 13: Π_2 for ortho, meta and para position (Units of bond lengths of all parameters are Å).

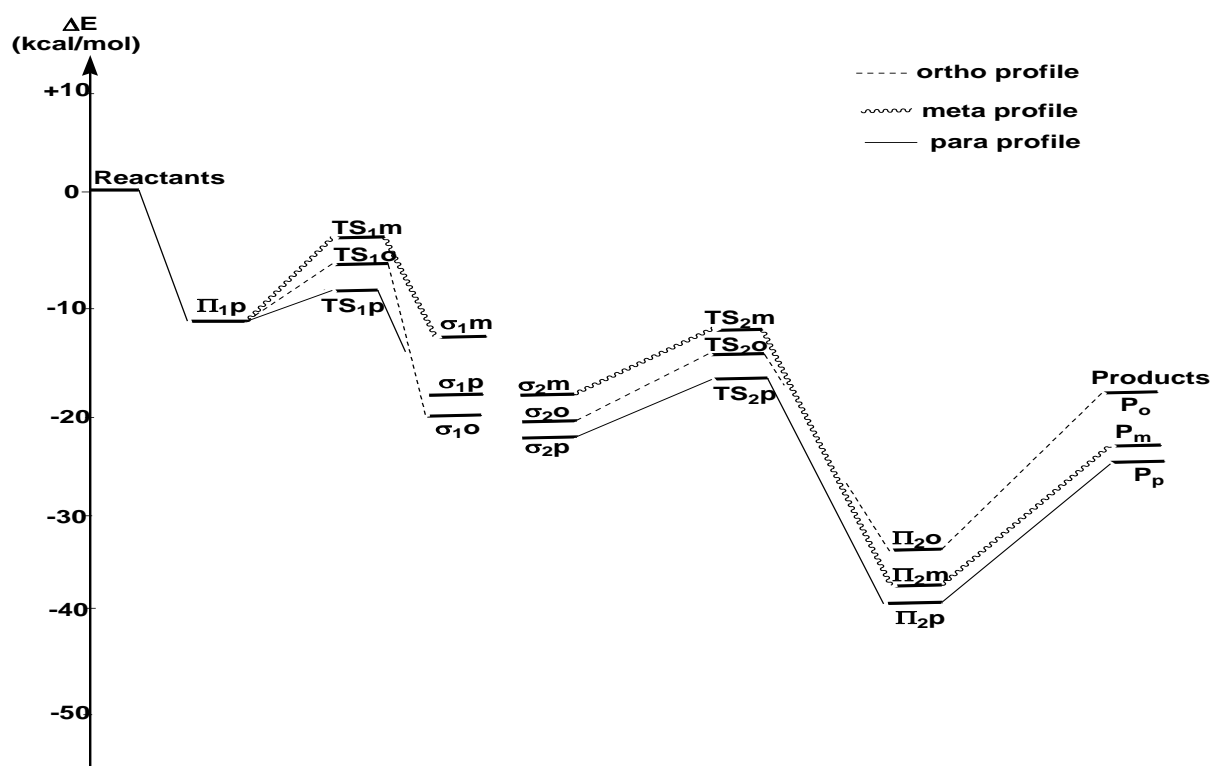


Figure 14: Overall mechanism at B3LYP level of chlorination reaction of chlorobenzene in gas phase for ortho, meta and para position.

As in the case of nitrobenzene ²³, Π_2 meta and para with the relative energies (-38.6 kcal/mol) are more stable than Π_2 ortho (-36.3 kcal/mol). The CCSD (T) calculations are given the results in conformity with B3LYP. This thermodynamic differentiation is found on geometrical analysis: The distance of C-Cl bond are equal in Π_2 meta and para complexes (1.750 Å) and longer than the one in Π_2 ortho complex (1.743 Å).

Table-1 gives the relative energies calculated for all the potential energy surface of chlorination of chlorobenzene for ortho, meta and para positions. All the relative energies are negative as in the cases of chlorination of aniline ⁵² and chlorination of non-substituted benzene ²². At the end of this study, the profiles of three potential energy surfaces obtained for this second substitution of chlorine on chlorobenzene are represented in **Figure 14**.

CONCLUSION

In this work we've studied at B3LYP level the second substitution of chlorine on chlorobenzene in order to obtain his overall mechanism. Six stationary points have been localized on this potential energy surface for ortho, meta and para position. For the three cases, the limiting step of the reaction is the transformation of π_1 to σ_1 via Transition State TS_1 and the reaction is on kinetic control. The ortho and para ways have the priority compared to meta way. This situation permit us to validate the classic interpretation given to this reaction: the orientation of this reaction in ortho and para positions is governed by the relative stability of Wheland complexes (σ_1 or σ_2). This stability has been proved by the important delocalization in ortho and para complexes compared to meta complex. This preference of the reaction has also been explained by the geometric analysis with DFT calculations and ELF analysis applied to Wheland intermediates.

REFERENCES

1. K. J. Fukui, T. Yonezawa, H. Shingu. *J. Chem. Phys.* 1952, **20**, 722.
2. R.B. Woodward, R. Hoffmann, *Angew. Chem. Int. Ed. Engl.* 1969, **8**, 781.
3. R.G. Parr, R.A. Donnelly, M. Levy, W.E. Palke. *Nanoscience and Advancing Computational Methods in Chemistry. J. Chem. Phys.* 1978, **68**, 3801.
4. R.G. Parr, R.G. Pearson. Absolute hardness: companion parameter to absolute electronegativity. *J. Am. Chem. Soc.* 1983, **105**, 7512.
5. P. Geerlings, F. De Proft, W. Langenaeker. Conceptual density functional theory. *Chem. Rev.* 2003, **103**, 1793.
6. S.S. Shaik. Ideas of Quantum Chemistry. *J. Am. Chem. Soc.* 1981, **103**, 3692.
7. S. Shaik, A. Shurki. An accurate barrier for the hydrogen exchange reaction from valence bond theory, *Angew. Chem. Int. Ed. Engl.* 1999, **38**, 586.
8. R.O.C. Norman, R. Taylor. *Electrophilic Substitution in Benzenoid Compounds*, Elsevier, Amsterdam, 1965.
9. L.M. Stock. *Aromatic Substitution Reaction*, Prentice-Hall, New Jersey, 1968.
10. R. Taylor. *Electrophilic Aromatic Substitution*. John-Wiley, New York, 1990.
11. G.A. OLAH. Aromatic substitution, Mechanism of electrophilic aromatic substitutions. *Acc. Chem. Res.* 1971, **4**, 240.

12. G.A. OLAH. Organic reaction mechanism. *Chem. Soc.* 1964, **19**, 62.
13. G.A. OLAH, S.J. Kuhn, S.H. Flood, B.A. Hardie. Nitration and Aromatic Reactivity. *J. Am. Chem. Soc.* 1964, **86**, 1039.
14. G.A. OLAH, S.J. Kuhn, B.A. Hardie. Friedel-Crafts and Related Reactions: Miscellaneous reactions. 1964, **86**, 1060.
15. G. Raos, L. Astorri, M. Raimondi, D. Cooper, J. Gerratt, P. Karadakov. Spin-coupled Valence Bond theory. *J. Phys. Chem.* 1997, **101**, 2886-2892.
16. L. Chen L, H. Xiao, J. Xiao, X. Gong. Quantum Mechanical Theory of Reactivity and Selectivity in Organic and Organometallic Reactions. *J. Phys. Chem.* 2003, **107**, 11440-11444.
17. H. Xiao, L. Chen, X. Ju, G. Ji. A theoretical study on nitration mechanism of benzene and solvent effects. *Sci. in China Series B-Chem.* 2003, **46**, 453-464.
18. A. Corma, G. Sastre, P.M. Viruela. A quantum-chemical study of para/ortho-toluene alkylation by adsorbed methoxy species on zeolites. *J. Mol. Catalysis A-Chemical.* 1995, **100**, 75-85.
19. K. Szabo, A. Hornfeldt, S. Gronowitz. Theoretical Study on Mechanism and Selectivity of Electrophilic Aromatic Nitration. *J. Am. Chem. Soc.* 1992, **114**, 6827-6834.
20. P. Esteves, B. Louis. Experimental and DFT Study of the Partial Oxidation of Benzene by N₂O over H-ZSM-5: Acid Catalyzed Mechanism. *J. Phys. Chem.* 2006, **B 110**, 16793-16800.
21. M. Altarawneh, S. Rawadieh. Theoretical study on thermochemical parameters and IR spectra of chlorinated isomers of nitrobenzene. *Can. J. Chem.* 2013, **91**, 999–1008.
22. Y. Osamura, K. Terada, Y. Kobayashi, R. Okazaki, Y. Ishiyama. A molecular orbital study of the mechanism of chlorination reaction of benzene catalyzed by Lewis acid. *J. Mol. Struct.* 1999, **461**, 399-416.
23. I.M. Ndassa, G. Bebga, M. Signé, F. Volatron, B. Silvi. Theoretical study of Chlorination Reaction of nitrobenzene. *J. Adv. Chem.* 2015, **11**, 3784-3793.
24. S. Noury, F. Colonna, A. Savin, B. silvi. Analysis of the delocalization in the topological theory of chemical Bond. *J. Mol. Struct.* 1998, **59**, 450.
25. I.M. Ndassa, B. Silvi, F. Volatron. Understanding Reaction Mechanisms in Organic Chemistry from Catastrophe Theory: Ozone Addition on Benzene. *J. Phys. Chem.* 2010, **A 114**, 12900–12906.
26. J.P. Piquemal, J. Pilmé, O. Parisel, H. Gerard, I. Fourré, J. Berges, C. Goulaouen, A. De Lalande, M.C. Van severin, B. Silvi. What can be learnt on biological or biomimetic systems with the topological analysis of the electron localization function. *Int. J. Quant. Chem.* 2008, **108**, 1951.

27. G.G. Wheland. A Quantum Mechanical Investigation of the Orientation of Substituents in Aromatic Molecules. *J. Am. Chem. Soc.* 1942, **64**, 900.
28. G. Koleva, B. Galabov, J.I. Wu, H.F. Schaefer III, P.V.R. Schleyer. Electrophile affinity: A Reactivity Measure for Aromatic Substitution. *J. Am. Chem. Soc.* 2009, **131**, 14722-14727.
29. F.A. Carey, R. Sundberg. *J. Advanced Organic chemistry Part A, Structure and Mechanisms*. 4th ed., Springer, New York, Chapter. 2000, **10**.
30. N. Isaacs. *Physical Organic Chemistry*. 2nd ed., Longman, Singapore. 1995, Chapter 10.
31. M.B. Smith, J. March. *March's advanced organic Chemistry Reactions. Mechanisms and Structure*, 6th ed., Wiley, New York. 2006, Chapter 11.
32. S.M. Hubig, J.K. Kochi. Direct Observation of the Wheland Intermediate in Electrophilic Aromatic Substitution. Reversible Formation of Nitrosoarenium Cations. *J. Am. Chem. Soc.* 2000, **122**, 8279-8288.
33. J. Rosenthal, D.I. Schutser. Challenges at the Molecular frontier. *J. Chem. Educ.* 2003, **80**, 6.
34. P.J. Silva, M.J. Ramos. Computational Studies on the Reactivity of Substituted 1, 2-Dihydro-1, 2-azaborines. *J. Org. Chem.* 2009, **74**, 6120-6129.
35. C. Boga, E.D. Vecchio, I. Forlani, A. Mazzanti, C.M. Lario, P.E. Todeso and S. Tozzi, Meisenheimer–Wheland Complexes between 1, 3, 5-Tris (N, N-dialkylamino) benzenes and 4, 6-Dinitrotetrazolo [1, 5-*a*] pyridine. Evidence of Reversible C–C Coupling in the S_EAr/S_NAr Reaction. *J. Org. Chem.* 2009, **74**, 5568-5575.
36. R. Corriu, C. Coste. *Tetradron*. 1969, **25**, 4949-4965.
37. H.C. Brown, J.D. Brady, Solubility of Hydrogen Chloride at Low Temperatures. A Measure of the Basic Properties of Aromatic Nuclei; π - and σ -Complexes and Their Role in Aromatic Substitution. *J. Am. Chem. Soc.* 1952, **74**, 3570.
38. J.M. Gnaïm, R.A. Sheldon. Regioselective bromination of aromatic compounds with Br₂/SO₂Cl₂ over microporous catalysts. *Tetradron Lett.* 2005, **46**, 4465-4468.
39. A.D. Becke. Density Functional Thermochemistry. *J. Chem. Phys.* 1993, **98**, 5648–5652.
40. A.D. Becke. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev.* 1988, **A 38**, 3098–3100.
41. C. Lee, Y. Yang, R.G. Parr. Density-functional exchange-energy approximation with correct asymptotic behaviour. *Phys. Rev.* 1988, **B 37**, 785.
42. B. Miehlich, A. Savin, H. Stoll, H. Preuss. Ab initio counterpart of infrared atomic charges. *Chem. Phys. Lett.* 1989, **157**, 200.

43. N. Szabo, S. Ostlund. Modern Quantum Chemistry. McGraw-Hill, Nova New York, 1989.
44. R.J. Bartlett, G.D. Purvis. Quadratic configuration interaction. A general technique for determining electron correlation energies. *Int. J. Quant. Chem.* 1978, **14**, 516.
45. G.D. Purvis, R.J. Bartlett. A full coupled-cluster singles and doubles model: The inclusion of disconnected triples. *J. Chem. Phys.* 1982, **76**, 1910.
46. G.E. Scuseria, C.L. Janssen, H.F. Schaefer III. The open-shell restricted Hartree—Fock singles and doubles coupled-cluster method including triple excitations CCSD (T). *J. Chem. Phys.* 1988, **88**, 7382.
47. M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, Robb M.A., J.R. Cheeseman, Montgomery J.A. Jr, T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople. Gaussian 03. Revision A.1, Gaussian, Inc., Wallingford CT. 2003.
48. S. Noury, X. Krokidis, F. Fuster, B. Silvi. Topmod package. Université Pierre et Marie Curie. 1997.
49. S. Noury, X. Krokidis, F. Fuster, B. Silvi. Computational tools for the electron localization function topological analysis. *Comput. & Chem.* 1999, **23**, 597.
50. E. Matito, B. Silvi, M. Duran, M. Solà. Electron localization function at the correlated level. *J. Chem. Phys.* 2006, **125**, 024301.
51. Amira 3.0, TGS, Template Graphics Software, Inc., San Diego, USA, 2002.
52. S. Cradock, J.M. Muir and D.W. H. Rankin. The molecular structure of chlorobenzene, determined by the combined analysis of electron diffraction, rotation constant and liquid crystal nuclear magnetic resonance data. *J. Mol. Struct.* 1990, **220**, 205-215.
53. N.P. Penionzhkevich, N.I. Sadova, L.V. Vilkov. An electron diffraction study of the structure of the molecules of chlorobenzene in the gaseous phase. *J. struct. Chem.* 1979, **20**, 446-448.

54. A. Francis Carey, J. Richard Sundberg. *Advanced Organic Chemistry*, Part A: Structure and Mechanisms, Springer fifth Edition, USA, 2008.
55. I.M. Ndassa, F. Volatron, B. Silvi. Modelization of Chlorination of aniline: A DFT study. *Acta Chim. Pharm. Ind.* 2015, **5**, 73-79.

***Corresponding author: Ibrahim Mbouombouo Ndassa;** Department of Chemistry, High Teacher Training College, University of Yaounde 1, P. O. Box 47 Yaoundé, Cameroon. Email: indassa@yahoo.fr