

Theoretical Study of the Reaction of (2, 2)-Dichloro (Ethyl) Arylphosphine with Bis (2, 2)-Dichloro (Ethyl) Arylphosphine by Hydrophosphination Regioselective by the DFT Method

Kouadio Valery Bohoussou¹, Anoubilé Benié², Mamadou Guy-Richard Koné¹, Affi Baudelaire Kakou², Kafoumba Bamba¹, Nahossé Ziao¹

¹Laboratoire de Thermodynamique et de Physico-Chimie du Milieu, UFR SFA, Université Nangui Abrogoua, Abidjan, République de Côte-d'Ivoire

²Laboratoire de Chimie Bio-Organique et de Substances Naturelles (LCBOSN), UFR SFA, Université Nangui Abrogoua, Abidjan, République de Côte-d'Ivoire

Email: anoubko@gmail.com

How to cite this paper: Bohoussou, K.V., Benié, A., Koné, M.G.-R., Kakou, A.B., Bamba, K. and Ziao, N. (2017) Theoretical Study of the Reaction of (2, 2)-Dichloro (Ethyl) Arylphosphine with Bis (2, 2)-Dichloro (Ethyl) Arylphosphine by Hydrophosphination Regioselective by the DFT Method. *Computational Chemistry*, 5, 113-128.

<https://doi.org/10.4236/cc.2017.53010>

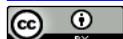
Received: April 10, 2017

Accepted: July 24, 2017

Published: July 27, 2017

Copyright © 2017 by authors and Scientific Research Publishing Inc. This work is licensed under the Creative Commons Attribution International License (CC BY 4.0).

<http://creativecommons.org/licenses/by/4.0/>



Open Access

Abstract

For this work, we have selected two reactions for the formation of (2,2)-dichloro (ethyl) Arylphosphine and bis (2,2)-dichloro(ethyl)arylphosphine compounds by hydrophosphination. Global and local reactivity parameters, thermodynamic parameters of reactions, Transition states, the Fukui function, the local softness, the local electrophilicity index, and nucleophilicity index, Natural population analyses (NPA) and Mulliken (MK) were calculated with DFT method at B3LYP/6-311+G(d, p) level. The analysis of potential energy surfaces and the nature of the reaction mechanism have been determined. The various results obtained revealed that the addition of Arylphosphine is regioselective. The phenylphosphine is more stable than the thiophenylphosphine. The theoretical results are consistent with experience.

Keywords

Hydrophosphination, Phosphine, HOMO, LUMO, Fukui Index, Transition State

1. Introduction

Organophosphorus compounds have enormous potentialities in various domains, including agriculture [1], medicine [2] [3], pharmacy, polymer sciences

[4], asymmetric catalysis [5] [6] [7] [8] [9], chemical and agro-food industries, but their strong odor, their toxicity, their great sensitivity to air and their great instability make these compounds difficult to manipulate. Predicting their stability is therefore a major challenge for the synthesis of new optically active compounds. It is to this concern that the theoretical study of the reaction of hydrophosphination of free phosphines comes to answer. The aim of this work is to determine by means of theoretical chemistry the transition states and the reaction mechanism of two free phosphines synthesized by Benié *et al.* [10]. Experimentally, these authors found that the addition of primary phosphine to 1, 1-dichloroethylene is regioselective [10] (Anti-Markovnikov).

2. Computational Details

2.1 Calculation Level

All the calculations, *i.e.* optimization of reactants and products, as well as calculations of vibration frequencies, were carried out with the Gaussian 03 software [11]. The calculations in blank and in the solvent were carried out with the basis set 6-31G(d, p) for the determination of the reaction pathway, and the basis set 6-311+G(d, p) for the determination of global and local reaction index. The calculations were performed using the gradient corrected functional of the Becke, Lee, Yang and Parr (B3LYP) [12] exchange and correlation derived from the functional density method [13]. The consideration of diffuse and polarization functions is important in the case of intermolecular interactions [14]. Polarization orbitals are very useful for locating transition states [14].

This is reflected in supprimer cette ligne de l'introduction below.

2.2. Thermodynamic Reaction Parameters

The knowledge of the variations of the energy contributions to the internal energy at 0 K and at 298 K between the products and the reactants contributes to the energy characterization of a chemical reaction (Figure 1). For a given energy parameter X , its variation is determined according to relation:

$$\Delta X = \sum X(\text{products}) - \sum X(\text{reactants}) \quad (1)$$

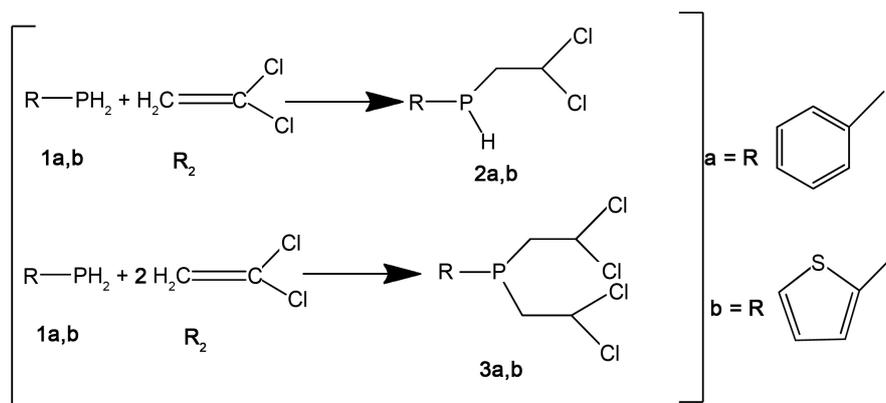


Figure 1. Addition reaction of free phosphine to dichloroethylene.

The variation of the internal energy at 298 K, constitutes a sum of the different contributions Electronic, translation, rotation, vibration and internal energy at 0K according to the relation:

$$\Delta E = \Delta E_{\text{electronic}}^0 + \Delta E_{\text{rotation}}^0 + \Delta E_{\text{translation}}^0 + \Delta E_{\text{vibration}}^0 + \Delta E_{0\text{K}} \quad (2)$$

$E_{0\text{K}}$ commonly referred to as Zero Point Vibrational Energy (*ZPVE*) translates the vibrational energy at the zero point induced by the $3N - 6$ (respectively $3N - 5$) normal vibration modes of frequency ν_i of the N cores of a non-Linear (or of a linear molecule) to 0 K. It is defined by the following relation:

$$ZPVE = \frac{1}{2} R \sum_{i=1}^{3N-6} \frac{h\nu_i}{k} \quad (3)$$

k the Boltzmann constant; h the Planck constant; R the perfect gas constant). As for the contributions of rotation and translation, they are derived from the approximation of perfect gases by the relation:

$$\Delta E_{\text{translation}}^0 = \Delta E_{\text{rotation}}^0 = -\frac{3}{2} RT \quad (4)$$

To obtain the corresponding energy at 298 K, it is necessary to take into account the additional energy due to the population of the vibration levels during the temperature rise from 0 to 298 K, defined by the relation:

$$E_{\text{vib,thermal}}^0 = R \sum_i^{3N-6} \frac{h\nu_i/k}{e^{(h\nu_i/298\text{K})} - 1} \quad (5)$$

It follows that the internal energy variation at 298 K can be written as:

$$\Delta E_{298\text{K}}^0 = \Delta E_{\text{elec}}^0 + \Delta ZPVE + \Delta E_{\text{vib,thermal}}^0 - 3RT$$

From this relationship, the enthalpy of reaction at 298 K is deduced. It corresponds to the variation of the corrected internal energy of the term $\Delta(PV)$, either ΔnRT (Δn being the change in the number of gaseous moles during the reaction):

$$\Delta H_{298\text{K}}^0 = \Delta E_{298\text{K}}^0 + \Delta nRT \quad (7)$$

The entropy contributions of translation, rotation and vibration of a given species to 298 K are grouped in the total entropy term S . The entropy of the reaction is determined according to the relation:

$$\Delta S = \sum S(\text{products}) - \sum S(\text{reactants}) \quad (8)$$

The Gibbs energy at 298 K, related to the reaction, is simply obtained by the relation:

$$\Delta G_{298\text{K}}^0 = \Delta H_{298\text{K}}^0 - T\Delta S_{298\text{K}}^0 \quad (9)$$

2.3. Conceptual DFT Reactivity Parameters

2.3.1. Global Reactivity Descriptors

According to Parr, the electronic chemical potential (μ) can be defined from the Lagrange multiplier [13]. This definition is exactly the same deduced by Pearson.

$$\mu = \left(\frac{\partial E}{\partial N} \right)_{v(r)} = -\chi \quad (10)$$

The electronic chemical potential μ can be calculated from the energies of the frontier molecular orbitals E_{HOMO} and E_{LUMO} as follows

$$\mu = \frac{1}{2}(E_{\text{LUMO}} + E_{\text{HOMO}}) \quad (11)$$

Other parameters of global reactivity called global hardness (η) and overall softness (S) were introduced from the variation of energy from one stationary state to another. These parameters are given by:

$$dE = \mu dN + \int \rho(r) \delta v(r) dr \quad (12)$$

With μ : chemical potential, $\rho(r)$: electron density, $v(r)$: external potential of the system.

The first partial derivative of μ with respect to N (the total number of electrons) is defined as the overall hardness η of the system [15] [16]. It is related to the quantity S which is the global softness of the system.

$$2\eta = \left(\frac{\partial \mu}{\partial N} \right)_{v(r)} = \left(\frac{\partial^2 E}{\partial^2 N} \right) = \frac{1}{S} \quad (13)$$

The global hardness η can also be calculated from the energies of the frontier molecular orbitals E_{HOMO} and E_{LUMO} as follows

$$\eta = (E_{\text{LUMO}} - E_{\text{HOMO}}) \quad (14)$$

From the chemical hardness, a further parameter of reactivity is determined in order to define the energy stability due to the charge transfer. Global electrophilicity index (ω) [17] which is linked to the chemical potential by the following relation

$$\omega = \frac{\mu^2}{2\eta} \quad (15)$$

It should be noted that the nucleophilic index cannot be defined by a variational procedure, because there is no molecular electronic stabilization along the subtraction of the electron density of a molecule. In lack of a nucleophilic descriptor, Domingo *et al.* [18] proposed that the hypothesis that a weakly electrophilic molecule is systematically highly nucleophilic is true only for simple molecules. High values of nucleophilic correspond to low values of ionization potential and vice versa. Domingo *et al.* used the energy of the Highest Occupied Molecular Orbital (E_{HOMO}) obtained by the Kohn-Sham method [18]. The empirical (relative) nucleophilic index (N) [19] is defined as follows:

$$N = \left(\varepsilon_{\text{HOMO}(\text{Nucleophile})} - \varepsilon_{\text{HOMO}(\text{TCE})} \right) \quad (16)$$

$\varepsilon_{\text{HOMO}(\text{TCE})}$: Energy of tetracyanoethylene (TCE)

Here, tetracyanoethylene is taken as the reference in the nucleophilicity scale, because it presents lowest HOMO energy.

The maximum charge transfer (ΔN_{max}) represents the maximum load pro-

portion a system can acquire from its environment [20]. It is defined as follows:

$$\Delta N_{\max} = -\mu/\eta \quad (17)$$

Electrophilicity gap ($\Delta\omega$) between the reactants makes it possible to predict the polarity of the reaction [21]. This descriptor is defined by:

$$\Delta_{\omega}^* = (\omega)_{\text{phosphine}} - (\omega)_{\text{dichloroethene}} \quad (18)$$

The last descriptor of the reactivity studied, the HOMO-LUMO energy gap which is a parameter which makes it possible to predict the global reactivity of an electron acceptor.

2.3.2. Local Reactivity Descriptors

Fukui functions (f_k) corresponding to the site k of a molecule is defined as the first derivative of the electronic density $\rho(r)$ of a system with respect to the number of electrons N to a constant external potential $v(r)$ [22].

$$f_k = \left[\frac{\partial \rho(r)}{\partial N} \right]_{v(r)} = \left[\frac{\delta \mu}{\delta v(r)} \right]_N \quad (19)$$

The condensed form of Fukui functions in a molecule with N electrons has been proposed by Yang *et al.* [23] by:

$$f_k^+ = q_k(N+1) - q_k(N) \quad \text{for nucleophilic attack} \quad (20)$$

$$f_k^- = q_k(N) - q_k(N-1) \quad \text{for electrophilic attack} \quad (21)$$

$$f_k^0 = 1/2 [q_k(N+1) + q_k(N-1)] \quad \text{for radical attack} \quad (22)$$

with

$q_k(N)$: Electronic population of the atom k in the neutral molecule

$q_k(N+1)$: Electronic population of the k atom in the anionic molecule

$q_k(N-1)$: Electron population of the k atom in the cationic molecule

The product of the global electrophilic index ω and the electrophilic Fukui index f_k^+ make it possible to identify the most electrophilic site. This site is identified by the determination of the local electrophilic index (ω_k) [24], defined as:

$$\omega_k = \omega f_k^+ \quad (23)$$

Similarly, the most nucleophilic site can be identified by the local nucleophilic index, N_k [25]; Defined as the product of the global nucleophilic index N and the nucleophilic Fukui index f_k^- .

$$N_k = N f_k^- \quad (24)$$

According to Domingo *et al.*, The local electrophile ω_k and local nucleophilic index N_k are reliable descriptors for the prediction of the most favorable nucleophilic-electrophilic interaction for the formation of a chemical bond between two atoms [26]. This chemical bond takes place between the nucleophilic site (characterized by the highest N_k value) of the nucleophilic molecule and the electrophilic site (characterized by the greater ω_k value) of the electrophilic molecule.

The condensed Fukui Functions f_k^\mp and the global softness S also make it

possible to determine the local softness S_k [27], defined by:

$$S_k = \left[\frac{\partial \rho(r)}{\partial \mu} \right]_{v(r)} = \left[\frac{\partial \rho(r)}{\partial N} \right] \left[\frac{\partial N}{\partial \mu} \right]_{v(r)} = S f_k \quad (25)$$

The condensed local softnesses S_k^\mp can be calculated from the following expressions:

$$S_k^+ = S f_k^+; S_k^- = S f_k^-; S_k^0 = S f_k^0 \quad (26)$$

where +, -, and 0 signs show nucleophilic, electrophilic, and radical attack, respectively.

According to the rule of Gazquez-Mendez [28], Two chemical species interact through the atoms having equal or neighboring softnesses.

3. Results and Discussion

3.1. Thermodynamic Parameters

The standard internal energy ($\Delta_r E_{298}^0$), the standard entropy ($\Delta_r S_{298}^0$), the standard enthalpy ($\Delta_r H_{298}^0$) and the standard free enthalpy ($\Delta_r G_{298}^0$) characterizing the hydrophosphination reaction of the primary phosphines (1a, 1b) on dichloroethylene (R_2) are summarized in **Table 1**.

Table 1. Thermodynamic parameters characterizing the hydrophosphination reaction of compounds 1a and 1b on R_2 calculated at B3LYP 6-311+G(d, p).

REACTANTS	PRODUCTS	$\Delta_r E_{298}^0$ (kcal)	$\Delta_r H_{298}^0$ (kcal/mol)	$\Delta_r S_{298}^0$ (cal/K-mol.)	$\Delta_r G_{298}^0$ (kcal/mol)
1a + R_2	2a	-19.135	-19.709	-39.870	-7.822
2a + R_2	3a	-36.688	-37.838	-80.466	-13.847
1b + R_2	2b	-19.356	-19.925	-40.022	-7.992
2b + R_2	3b	-36.986	-38.135	-80.370	-14.173

All the values of the standard thermodynamic reaction parameters of the molecules are negative. These negative values of enthalpy and free enthalpy, respectively, translate an exothermic and spontaneous reaction under the conditions of the study. Negative values of internal energy reflect the formation and existence of products 2a, 2b, 3a and 3b. As far as entropy is concerned, all negative values reflect a decrease in disorder. Considering the free enthalpies of reaction, the order of decreasing stability of the products is deduced as follows: the tertiary phosphines 3a and 3b formed are more stable than the secondary phosphines 2a and 2b either (3a) more stable than (2a) and (3b) more stable than (2b).

3.2. Prediction of Electrophilic and Nucleophilic Character of Reactant

The values of the global descriptors of reactivity of reactants 1a, 1b and R_2 are given in **Table 2** below.

Table 2. Global descriptors of chemical reactivity of reactants 1a, 1b and R₂ at B3LYP/6-311 +G(d, p).

	E_{HOMO} (eV)	E_{LUMO} (eV)	μ (eV)	χ (eV)	η (eV)	S (eV ⁻¹)	ω (eV)	N	ΔN_{max}	Δ_{ω}^*
1a	-6.963	-0.964	-3.964	3.964	6.000	0.166	1.309	2.525	0.661	0.075
R ₂	-7.497	-0.990	-4.244	4.244	6.507	0.154	1.384	1.992	0.652	
1b	-6.745	-1.100	-3.923	3.923	5.645	0.177	1.363	2.744	0.695	0.021
R ₂	-7.497	-0.990	-4.244	4.244	6.507	0.154	1.384	1.992	0.652	

$E_{\text{HOMO}}(\text{TCE}) = -9489$ eV at Level B3LYP/6-311+ G(d, p).

The analysis of the chemical reactivity parameters **Table 2** shows that, the chemical potential μ of the compound 1a ($\mu = -3.964$ eV) is found on an energy level higher than that of the compound R₂ ($\mu = -4.244$). This observation shows that the transfer of electrons will take place from compound 1a to compound R₂. Regarding the nucleophilic index, compounds 1a ($N = 2.525$) and 1b ($N = 2.744$) have values significantly greater than compound R₂ ($N = 1.992$). This means that the compounds 1a and 1b are nucleophiles while the compound R₂ is an electrophile. This trend is confirmed by the analysis of the electrophilic index values (ω) with the larger values for the compound R₂. The hardness η shows that the free phosphines 1a and 1b having 6.000 eV and 5.645 eV values respectively are lower than that of dichloroethylene R₂ (6.507 eV). This means that the free phosphines 1a and 1b maintains their electrons weak in their environment, unlike the dichloroethylene R₂ which maintains them in its environment. Therefore electron transfer takes place from the phosphine to the dichloroethylene.

Global electrophilicity gap parameter of the two reactants (1a/R₂ and 1b/R₂) is less than 1. This indicates a weak polar character for this addition. The last parameter studied is the HOMO-LUMO energy gap of the reactants 1a/R₂ and 1b/R₂ (**Figure 2**).

On the HOMO-LUMO energy analysis (**Figure 2**), the energy gap HOMO (1a)-LUMO (R₂) which is 5.973 eV is less than that in the HOMO (R₂)-LUMO (1a) gap which is 6.533 eV. Similarly, the energy gap HOMO (1b)-LUMO (R₂) is less than that corresponding to the gap HOMO (R₂)/LUMO (1b), which shows that the phosphines behave here as electron donors and Dichloroethylene as an electron acceptor. These results confirm the nucleophilic character of the free phosphines studied and the electrophilic character of dichloroethylene. Moreover, the energy gap HOMO (1b)-LUMO (R₂) which is 5.755 eV is less than the energy gap HOMO (1a)-LUMO (R₂) which is 5.973 eV. This shows that thiophenylphosphine is more reactive than phenylphosphine and therefore less stable than phenylphosphine. Moreover, the isodensity map of the energy of the Highest Occupied Molecular Orbital of the phosphines 1a and 1b (**Figure 2**) shows that the molecular orbital HOMO is very condensed at the level of the phosphorus atom, so that the electron transfer takes place at level of that atom.

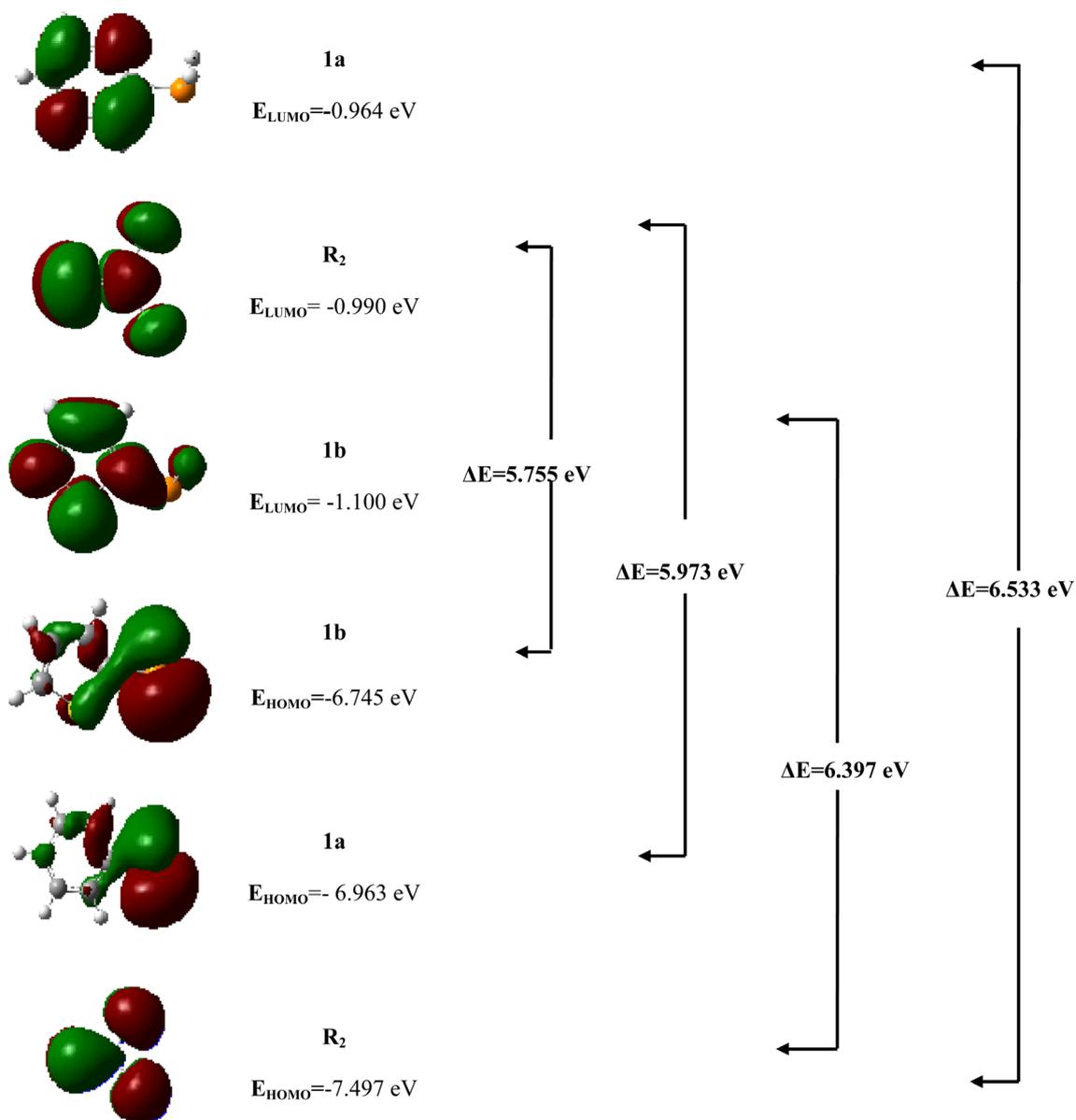


Figure 2. Highest occupied molecular orbital, lowest unoccupied molecular orbital and energy gap HOMO-LUMO for the two possible combinations.

3.3. Prediction of Local Descriptors of Reactant

3.3.1. Prediction Using the Domingo Model

The values of the local reactivity descriptors, in this case the Fukui function (f_k^+ , f_k^-), the local softness (S_k^- , S_k^+), the local electrophile power (ω_k), and the dual descriptors (N_k) of the reactivity have been determined. These values of the local descriptors on the atoms P₁, P₂, C₁ and C₂ of the reactants 1a, 1b and R₂ calculated according to the model of Domingo *et al.* With the Natural Population Atomic (NPA) [29] [30] [31] and Mulliken (MK) [31] approaches at B3LYP/6-311+G(d, p) are reported in **Table 3**.

On analysis of the values in **Table 3**, phosphines 1a and 1b have the highest values of the local nucleophilic indices N_k . Similarly, the carbon C₁ of the

compound R₂ has the highest value of the local electrophilic index (ω_k). This shows that the most favored interaction takes place between the P₁ atom of the compound 1a and the C₁ atom of the compound R₂ for the first reaction, and between the P₂ and C₁ atoms for the second reaction. Therefore, the formation of experimentally observed P₁-C₁ and P₂-C₁ bonds are correctly predicted by the Domingo model with the Mulliken and NPA approaches.

Table 3. Local reactivity descriptors on the P₁, P₂, C₁ and C₂ atoms of reactants 1a, 1b and R₂ using NPA and Mulliken population analyzes at B3LYP/6-311 + G(d, p).

Reactants		1a	1b	R ₂	
Atoms		P ₁	P ₂	C ₁	C ₂
Mulliken	f_k^+			0.621	0.316
	f_k^-	0.325	0.245		
	ω_k			0.859	0.543
	N_k	0.821	0.672		
NPA	f_k^+			0.474	0.189
	f_k^-	0.423	0.301		
	ω_k			0.656	0.262
	N_k	1.068	0.823		

3.3.2. Prediction Using the Gazquez-Mendez Model

The prediction according to the Gazquez-Mendez model presents values of the Fukui function (f_k^+ , f_k^-), local softness S_k^+ for reactants R₂ and local softness S_k^- for reactants 1a or 1b. These values of the local descriptors on the atoms P₁, P₂, C₁ and C₂ of the reactants 1a, 1b and R₂ were calculated according to the Gazquez-Mendez model with the NPA population analyzes and MK at the B3LYP 6-311+G level (d, p) are given in **Table 4**.

Examination of the values in **Table 4** indicates that the phosphines 1a, 1b and dichloroethylene R₂ have similar values of local softnesses (S_k^- , S_k^+) respectively on P₁, P₂ and C₁ atoms by the approach of Mulliken. This observation shows

Table 4. Values of Fukui Functions (f_k^+ , f_k^-), local softnesses S_k^+ for reactants R₂ and local softness S_k^- for reactants 1a and 1b calculated by NPA, MK.

Reactants		1a	1b	R ₂	
Atomes		P ₁	P ₂	C ₁	C ₂
Mulliken	f_k^+			0.621	0.316
	f_k^-	0.325	0.245		
	S_k^+			0.092	0.047
	S_k^-	0.093	0.094		
NPA	f_k^+			0.474	0.189
	f_k^-	0.423	0.301		
	S_k^+			0.069	0.028
	S_k^-	0.068	0.053		

that the most favored interaction takes place between the P₁ atom of the compound 1a and the C₁ atom of the dichloroethylene for the first reaction and the P₂ atom of the compound 1b and the C₁ atom of the dichloroethylene for the second reaction. Also in **Table 4**, with the NPA approach, the values of the local softnesses S_k^- of the phosphines 1a and 1b on the atoms P₁ and P₂ are closer to the values of the local softnesses S_k^+ . The C₁ atom of the compound R₂ compared to the C₂ atom, which also confirms the interaction between the phosphors of the various phosphines and the least substituted carbon.

3.4. Potential Energy Surfaces and Prediction of the Reaction Mechanism

3.4.1. In the Gas

In order to elucidate the reaction mechanism and compare the stability of the formed phosphines, the values of the reactant energies, the energies of the products, the energies of the transition states and the activating energies are presented in **Table 5** below.

Table 5. The energies of the transition states (E_{TS}), activation (E_a) and reactants corresponding to the formation of products 2a and 2b calculated at the B3LYP/6-31G(d, p).

	E_{products} (Hartree)	$E_{\text{reactants}}$ (Hartree)	E_{TS} (Hartree)	E_a (Kcal/mol)
T _{S1} (Pathway 2a)	-1572.02164	-1572.02164	-1572.02158	0.03765
T _{S2} (Pathway 2b)	-1892.770	-1892.772	-1892.725	29.4925

From **Table 5**, it can be seen that the activation energy found by the reaction pathway give a value of 0.03765 kcal/mol. This value is inferior to what has been found by the reaction pathway through 2b (29.4925 kcal/mol). The phosphine 2a is more stable than that of 2b.

In order to show that the transition states (TS) are well connected to minima (reactants and products), the calculation of the Intrinsic Reactions Coordinates (IRC) and the curves of the reaction pathway, $E = f(RC)$ are shown in **Figures 3-5**.

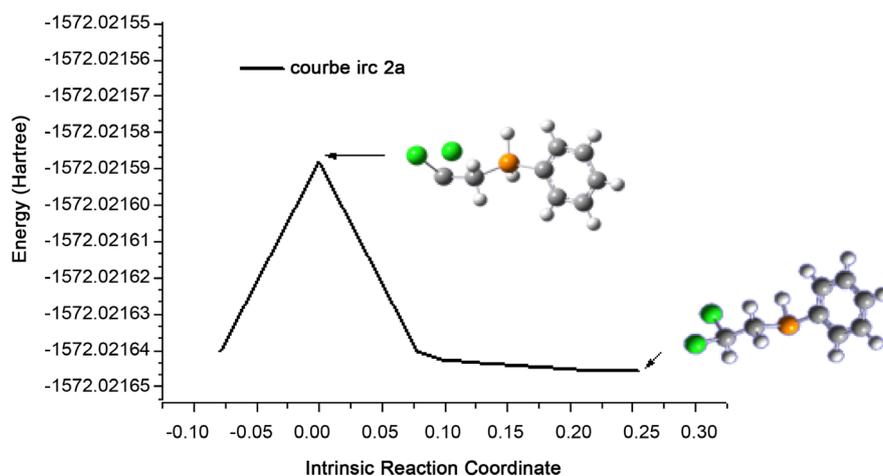


Figure 3. IRC curve of reaction pathway 2a.

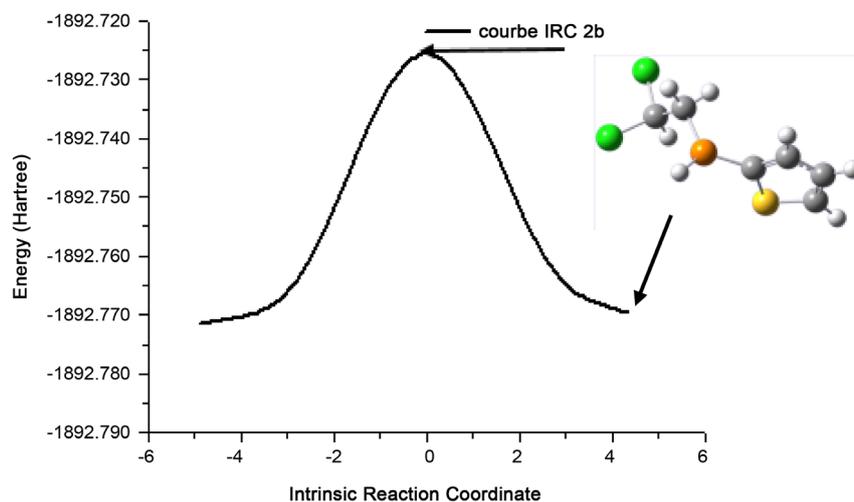


Figure 4. IRC curve of reaction pathway **2b**.

The evolution of the IRC curve (**Figure 4**), Indicates that the energy of the product obtained (-1892.770 Hartree) is greater than that of the reactant (-1892.772 Hartree) with thiophenyl as radical. This means that the compound (**2b**) obtained is kinetically unstable. The product **2a** is therefore more stable than the product **2b**, under the same conditions.

Figure 3 shows that the phosphorus carbon (P-C) bond is established in the transition state on the most hydrogenated C_1 carbon and the hydrogen of the phosphorus then on the C_2 carbon bonded to the chlorine. Similarly, the phosphorus carbon bond is established first on the most hydrogenated carbon during the formation of the product **3a**. In the transition state, the hydrogen carbon bond is not yet established (**Figure 5**).

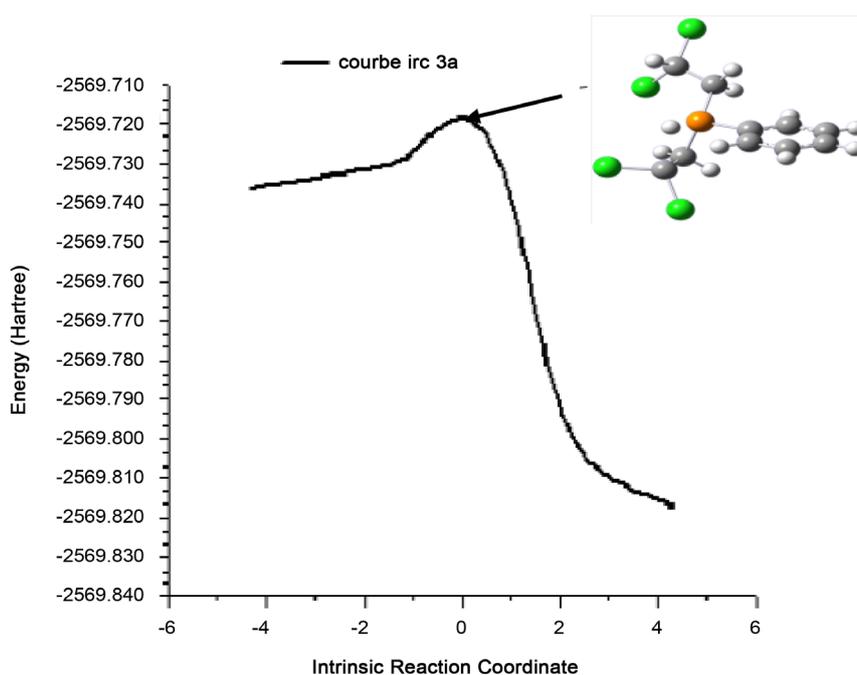


Figure 5. IRC curve of reaction pathway **3a**.

Reaction pathway therefore makes it possible to propose the following reaction mechanism **Figure 6**.

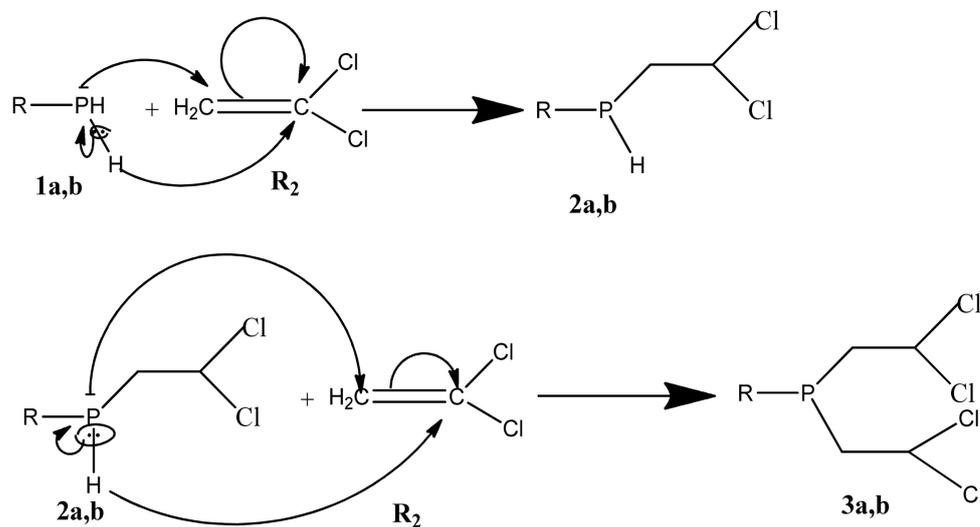
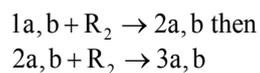


Figure 6. Proposed Mechanism for the Hydrophosphination of free phosphine with dichloroethylene.

The products 3a and 3b have been obtained after the formation of the products 2a and 2b.

Thus, during the addition of 1a to R_2 , respectively 1b to R_2 , two reactions occur in succession:



This explains the stability of the products 3a and 3b obtained experimentally and the fact that they are major products [10].

Products 3a and 3b are obtained in an excess of reactant (R_2), unlike product 2a and 2b which require less reactant.

3.4.2. In the Solvent

The influence of the solvent on the getting of the product 2a was envisaged at B3LYP/6-31G (d, p). The results are shown in **Table 6** below.

Table 6. Energies of the transition states (E_{TS}), activation (E_a) and reactants corresponding to the formation of product 2a in some solvents calculated at B3LYP/6-31G(d, p).

Solvents	$E_{Products}$ (Hartree)	$E_{Reactants}$ (Hartree)	E_{TS} (Hartree)	E_a (kcal/mol)
Acetonitrile	-1572.081	-1572.080	-1572.076	2.636
DMSO	-1572.081	-1572.081	-1572.076	2.636
Méthanol	-1572.081	-1572.080	-1572.076	2.573
Nitro-methane	-1572.081	-1572.081	-1572.076	2.636
Diéthyléthere	-1572.073	-1572.073	-1572.069	2.510
THF	-1572.077	-1572.077	-1572.072	2.573

The study of the addition reaction envisaged in the solvents gives satisfactory results at the level of theory used. The activation barrier ($E_a = 2.51$ kcal / mol) is the lowest when the diethylene is used as a solvent. The diethylene favors the obtaining of a product kinetically more stable product. Consequently, the product 2a can be obtained optimally in diethylene. These theoretical predictions are in agreement with the experimental studies carried out (Figure 7).

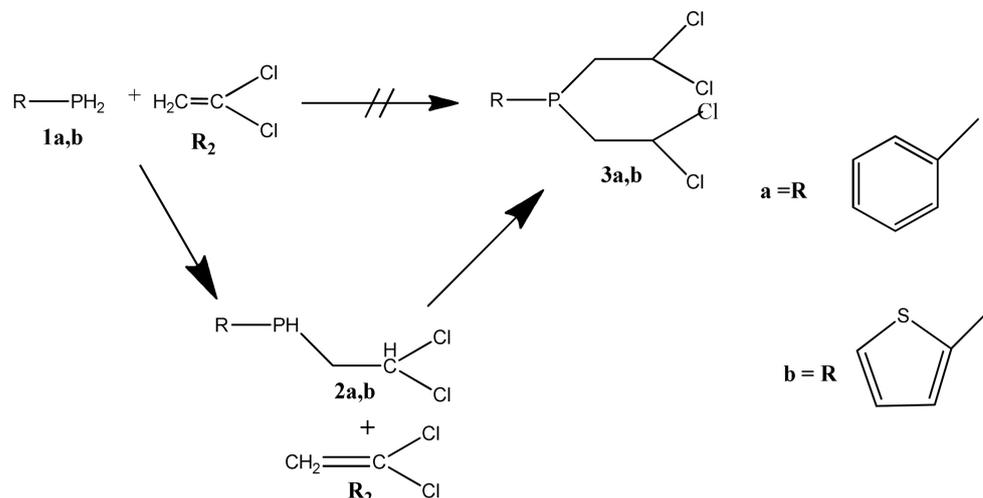


Figure 7. Double addition of free phosphine with dichloroethylene to obtain (2, 2)-Dichloro (Ethyl) Arylphosphine.

4. Conclusion

The reaction mechanism and the transition states of the two free phosphines were studied by the DFT method. Electrophilic and nucleophilic character, electrophilic and nucleophilic local indices, Fukui Functions, condensed local softness, thermodynamic quantities of the addition reaction of two arylphosphines on dichloroethylene, localization of transition states, atomic electronic populations and reactivity indices calculated by means of natural population analyses (NPA) and Mulliken (MK), and analysis of the potential energy surface have allowed us to conclude that: the most favored interaction takes place between the phosphorus atom (P_1) of the arylphosphine and the most hydrogenated carbon (C_1) of the dichloroethylene.

The majority product is obtained after a successive addition of the Arylphosphine to the dichloroethylene and then an addition of the product obtained (2, 2) dichloro (ethyl) Arylphosphine to the dichloroethylene. 2, 2-dichloro (ethyl) Arylphosphine can be obtained after a single step in the solvent (diethylene). The addition reaction of Arylphosphine on dichloroethylene is regioselective “anti-Markovnikov”. Phenylphosphine is more stable than thiophenylphosphine. The total energy values of the reaction are negative, which implies that the reaction is exothermic.

References

- [1] Sharma, S.B., Sayyed, R.Z., Trivedi, M.H. and Gobi, T.A. (2013) Phosphate Solubi-

- lizing Microbes: Sustainable Approach for Managing Phosphorus Deficiency in Agricultural Soils. *Springerplus*, **2**, 587. <https://doi.org/10.1186/2193-1801-2-587>
- [2] Nigam, S., Burke, B.P., Davies, L.H., Domarkas, J., Wallis, J., Waddell, F.P.G., Waby, J.S., Benoit, D.M., Seymour, A., Cawthorne, C., Higham, L.J. and Archibald, S.J. (2016) Structurally Optimised BODIPY Derivatives for Imaging of Mitochondrial Dysfunction in Cancer and Heart Cells. *Chemical Communications (Cambridge)*, **52**, 7114-7117. <https://doi.org/10.1039/C5CC08325G>
- [3] Katti, K.V., Pillarsetty, N. and Raghuraman, K (2003) New Vistas in Chemistry and Applications of Primary Phosphines. *Topics in Current Chemistry*, **229**, 121-141. <https://doi.org/10.1007/b11153>
- [4] Clark, T.J., Rodezno, J.M., Clendenning, S.B., Aouba, S., Brodersen, P.M., Lough, A.J., Ruda, H.E. and Manners, I. (2005) Rhodium Dehydrocoupling of Fluorinated Phosphine-Borane Adducts: Synthesis, Characterization, and Properties of Cyclic and Polymeric Phosphinoboranes with Electron-Withdrawing Substituents at Phosphorus. *Chemistry: A European Journal*, **11**, 4526-4534. <https://doi.org/10.1002/chem.200401296>
- [5] Xiao, Y., Sun, Z., Guo, H. and Kwon, O. (2014) Chiral Phosphines in Nucleophilic Organocatalysis. *Beilstein Journal of Organic Chemistry*, **10**, 2089-2121.
- [6] Clarke, T.P. and Landis, C.R. (2004) Recent Developments in Chiral Phospholane Chemistry. *Tetrahedron Asymmetry*, **15**, 2123-2137. <https://doi.org/10.1016/j.tetasy.2004.06.025>
- [7] Hoge, G. and Samas, B. (2004) Application of *P*-Chirogenic Bisphospholane Ligands to Rhodium Catalyzed Asymmetric Hydrogenation of α - and β -Acetamido Dehydroamino Acid Derivatives. *Tetrahedron: Asymmetry*, **15**, 2155-2157. <https://doi.org/10.1016/j.tetasy.2004.04.041>
- [8] Brauer, D.J., Kottsieper, K.W., Roßenbach, S. and Stelzer, O. (2003) Novel P,N Ligands Derived from (*R*)- and (*S*)-1-Phenylethylamine with (2*R*,5*R*)-2,5-Dimethylphospholanyl Groups (DuPHAMIN) for Asymmetric Catalysis. *European Journal of Inorganic Chemistry*, **2003**, 1748-1755. <https://doi.org/10.1002/ejic.200200388>
- [9] Herrbach, A., Marinetti, A., Baudoin, O., Guénard, D. and Gueritte, F.J. (2003) Asymmetric Synthesis of an Axially Chiral Antimitotic Biaryl via an Atropo-Enantioselective Suzuki Cross-Coupling. *Journal of Organic Chemistry*, **68**, 4897-4905.
- [10] Benié, A., Dénis, J.M. and Békro, Y.A. (2010) Synthesis of Free and Complexes 2,2-Dichloro(ethyl)Arylphosphine and bis(2,2)Dichloro(ethyl)Arylphosphine by Regioselective Hydrophosphination. *European Journal of Scientific Research*, **47**, 164-168. http://www.lablcbosn.com/wp-content/uploads/2015/09/ejsr_47_2_01.pdf
- [11] Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Montgomery, Jr., J.A., Vreven, T., Kudin, K.N., Burant, J.C., Millam, J.M., Iyengar, S.S., Tomasi, J., Barone, V., Mennucci, B., Cossi, M., Scalmani, G., Rega, N., Petersson, G.A., Nakatsuji, H., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Klene, M., Li, X., Knox, J.E., Hratchian, H.P., Cross, J.B., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R.E., Yazyev, O., Austin, A.J., Cammi, R., Pomelli, C., Ochterski, J.W., Ayala, P.Y., Morokuma, K., Voth, G.A., Salvador, P., Dannenberg, J.J., Zakrzewski, V.G., Dapprich, S., Daniels, A.D., Strain, M.C., Farkas, O., Malick, D.K., Rabuck, A.D., Raghavachari, K., Foresman, J.B., Ortiz, J.V., Cui, Q., Baboul, A.G., Clifford, S., Cioslowski, J., Stefanov, B.B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Martin, R.L., Fox, D.J., Keith, T., Al-Laham, M.A., Peng, C.Y., Nanayakkara, A., Challacombe, M., Gill, P.M.W., Johnson, B., Chen, W., Wong, M.W., Gonza-

- lez, C. and Pople, J.A. (2004) Gaussian 03, Revision C. 01. Gaussian Inc., Wallingford.
- [12] Becke, A.D. (1993) A New Mixing of Hartree-Fock and Local Density-Functional Theories. *Journal of Chemical Physics*, **98**, 1372-1377. <https://doi.org/10.1063/1.464304>
- [13] Parr, R.G. and Yang, W. (1989) Density-Functional Theory of Atoms and Molecules. Oxford University Press, New York, Oxford.
- [14] De Castro, E.V.R. and Jorge, F.E. (1998) Accurate Universal Gaussian Basis Set for All Atoms of the Periodic Table. *Journal of Chemical Physics*, **108**, 5225-5229. <https://doi.org/10.1063/1.475959>
- [15] Parr, R.G. and Pearson, R.G. (1983) Absolute Hardness: Companion Parameter to Absolute Electronegativity. *Journal of the American Chemical Society*, **105**, 7512-7516. <https://doi.org/10.1021/ja00364a005>
- [16] Yang, W. and Parr, R.G. (1985) Hardness, Softness, and the Fukui Function in the Electronic Theory of Metals and Catalysis. *Proceedings of the National Academy of Sciences*, **82**, 6723-6726. <https://doi.org/10.1073/pnas.82.20.6723>
- [17] Chattaraj, P.K., Sarka, U.R. and Roy, D.R. (2006) Electrophilicity Index. *Chemical Reviews*, **106**, 2065-2091. <https://doi.org/10.1021/cr040109f>
- [18] Domingo, L.R., Aurell, M.J., Perez, P. and Contreras, R. (2002) Quantitative Characterization of the Global Electrophilicity Power of Common Diene/Dienophile Pairs in Diels-Ald Reactions. *Tetrahedron*, **58**, 4417-4423.
- [19] Domingo, L.R., Chamorro, E. and Pérez, P. (2008) Understanding the Reactivity of Captodative Ethylenes in Polar Cycloaddition Reactions. A Theoretical Study. *The Journal of Organic Chemistry*, **73**, 4615-4624. <https://doi.org/10.1021/jo800572a>
- [20] Parr, R.G., von Szentpaly, L. and Liu, S. (1999) Electrophilicity Index. *Journal of the American Chemical Society*, **121**, 1922-1924. <https://doi.org/10.1021/ja983494x>
- [21] Delgado, J.S., Aizman, A., Domingo, L.R. and Contreras, R. (2010) Understanding the Influence of Lewis Acids in the Regioselectivity of the Diels-Alder Reactions of 2-Methoxy-5 Methyl 1,4 Benzoquinone: A DFT Study. *Chemical Physics Letters*, **449**, 272.
- [22] Parr, R.G. and Yang, W. (1984) Perspective on Density Functional Approach to the Frontier-Electron Theory of Chemical Reactivity. *Journal of the American Chemical Society*, **106**, 4049-4050.
- [23] Domingo, L.R. and Saez, J.A. (2009) Understanding the Mechanism of Polar Diels-Alder Reactions. *Organic and Biomolecular Chemistry*, **7**, 3576-3583. <https://doi.org/10.1039/b909611f>
- [24] Toledo, O.R. and Contreras, R. (2014) Philicity and Fugality Scales for Organic Reactions. *Advances in Chemistry*, **2014**, 1-13.
- [25] Reed, A.E. and Weinhold, F. (1983) Natural Atomic Orbitals and Natural Population Analysis. *Journal of Chemical Physics*, **78**, 4066-4073. <https://doi.org/10.1063/1.445134>
- [26] Domingo, L.R., Aurell, M.J., Perez, P. and Contreras, R. (2000) Quantitative Characterization of the Local Electrophilicity of Organic Molecules. Understanding the Regioselectivity on Diels-Alder Reactions. *Journal of Chemical Physics*, **106**, 6871-6875. <https://doi.org/10.1021/jp020715j>
- [27] Yan, W.G. and Parr, R.G. (2000) Hardness, Softness, and the Fukui Function in the Electronic Theory of Metals and Catalysis. *Proceedings of the National Academy of Sciences*, **82**, 6723-6726.

- [28] Mendez, F. and Gazquez, J.L. (1994) Chemical Reactivity of Enolate Ions: The Local Hard and Soft Acids and Bases Principle Viewpoint. *Journal of the American Chemical Society*, **116**, 9298-9301. <https://doi.org/10.1021/ja00099a055>
- [29] Reed, A. and Weinhold, E.F. (1983) Natural Atomic Orbitals and Natural Population Analysis. *Journal of Chemical Physics*, **78**, 4066-4073.
- [30] Reed, A.E., Weinstock, R.B. and Weinhold, F. (1985) Natural Atomic Orbitals and Natural Population Analysis. *Journal of Chemical Physics*, **83**, 735-746. <https://doi.org/10.1063/1.449486>
- [31] Besler, B.H., Merz, K.M.J. and Kollman, P.A. (1990) Atomic Charges Derived from Semi Empirical Methods. *Journal of Computational Chemistry*, **11**, 431-439. <https://doi.org/10.1002/jcc.540110404>



Scientific Research Publishing

Submit or recommend next manuscript to SCIRP and we will provide best service for you:

Accepting pre-submission inquiries through Email, Facebook, LinkedIn, Twitter, etc.

A wide selection of journals (inclusive of 9 subjects, more than 200 journals)

Providing 24-hour high-quality service

User-friendly online submission system

Fair and swift peer-review system

Efficient typesetting and proofreading procedure

Display of the result of downloads and visits, as well as the number of cited articles

Maximum dissemination of your research work

Submit your manuscript at: <http://papersubmission.scirp.org/>

Or contact cc@scirp.org

