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Theoretical investigation of the heterocyclic molecules type dioxolane obtained from the protection reactions between carbonyl compounds and diols

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Abstract

We reported in this work the addition reactions between a series of carbonyl compounds types 1a-d and 1a'-d' and (Z) and (E) diols 2 and 3 (Figure1, Figure2). The reactions between diols and series of carbonyl compound types 1a''-c'' protonated by Lewis acid are also studied (Figure3).This study of reactivity have explored by the theoretical study using the program Gaussian 09 using SCF calculations with 6-311G standard basis set. Then, we studied from thermodynamic and orbital point of view, the possibility and the stereoselectivity of reactions between substituted diols 3α-γ with carbonyl compound type 1a and 1d (Figure4).

1. Introduction

The protection [1,2] and deprotection of the functional group remain crucial challenges for organic chemists, while protection of the carbonyl group is done using different diols [3,4], as protective agents. Indeed, this reaction is catalyzed by different types of catalysts such as a protic acid or Lewis acid [5-11] to form cyclic dioxolane [12-14]. This cyclic compound can be hydrolyzed to reform both the diol and the starting carbonyl compound according to the deprotection process. Therefore, the protection of a carbonyl function becomes necessary when the reagent has several functional groups [15]. This carbonyl must be protected against nucleophilic attack until its electrophilic properties can be exploited [16]. Indeed, the protection plays an important role in organic, medicinal, drug design chemistry [17] and atmospheric photochemistry [18].

In this paper, we found interesting to carry out a theoretical study on the protection reactions of between carbonyl compounds and diols, which allow access to heterocyclic molecules such as dioxolane. To put this study in evidence, we studied in the first part of this work the addition reactions between (Z) and (E) diols and carbonyl compounds 1a-d and 1a'-d' (Figure1) and (Figure 2). Later, we determined the addition reactions between diols and carbonyl compounds 1a''-c'' protonated by Lewis acid H^+ (Figure3). In the second part of this work, we studied the influence of the substituted diols 3α-γ on the reactivity of compounds 1a and 1d (Figure 4).

2. Computational methods

This study was carried out using the Gaussian 09 program [19]. The calculations were performed using the ab-initio method of quantum chemistry with 6-311 G standard basis set.

Indeed, this method has been used to provide structural and energy properties for heterocyclic conjugated molecules [20, 21].

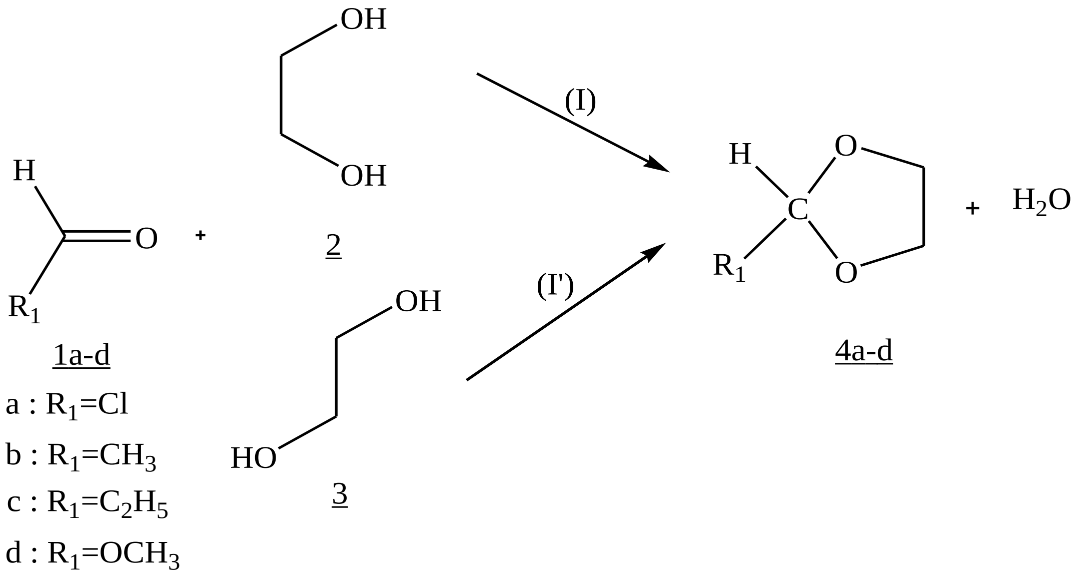

Figure 1: Addition Reaction between (Z) and (E) diols and carbonyl Compounds 1a-d

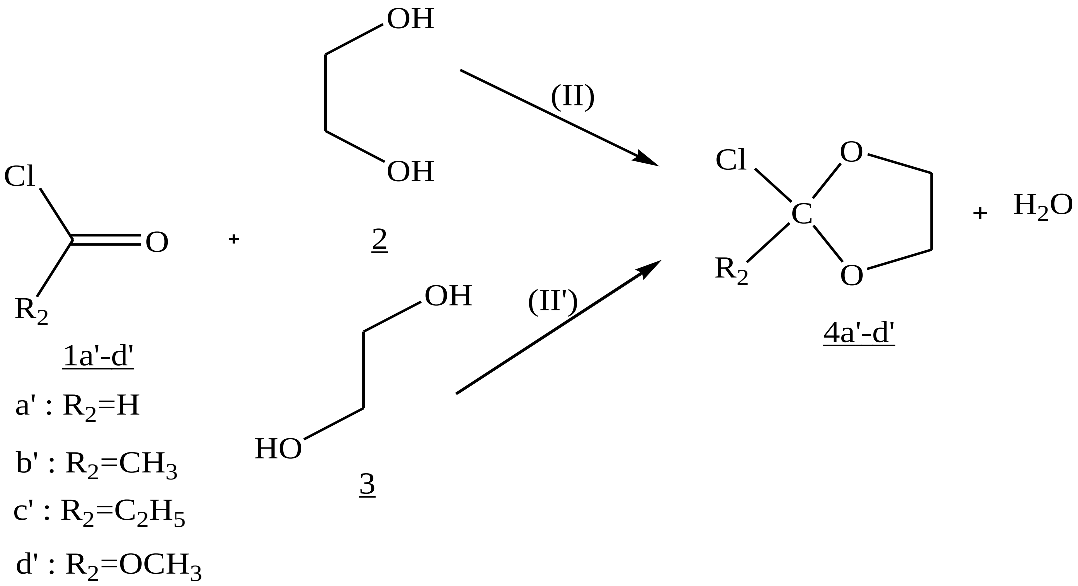

Figure 2: Addition Reaction between (Z) and (E) diols and carbonyl Compounds 1a’-d’

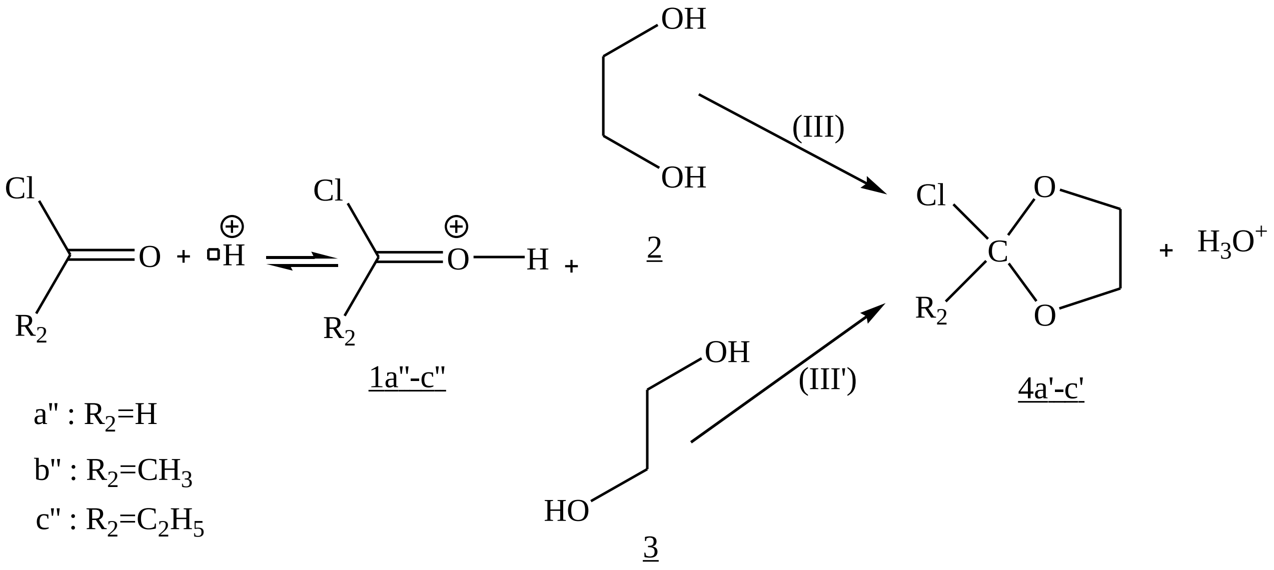

Figure 3: Addition Reaction between (Z) and (E) diols and carbonyl Compounds 1a’’-c’’

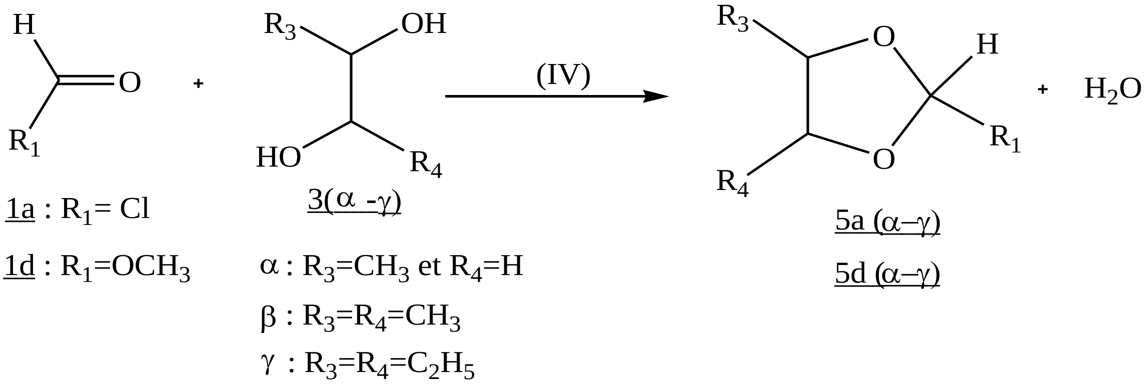

Figure 4: Addition reaction between substituted diols 3α-γ and carbonyl compounds 1a and 1d

3. Results and discussion

3.1. Thermodynamic study

3.1.1. Addition Reactions between Diols 2 and 3 with carbonyl Compounds 1a-d and 1a'-d'

We investigated from thermodynamic point of view, both the possibility and the stereoselectivity of the reactions (I), (I'), (II) and (II') (Figure 1 and Figure 2). In order to compare the reactivity of these carbonyl compounds with diols, we determined under standard conditions of temperature and pressure (T = 298.15 k; P = 1 atm (1 atm = 101.325 kPa)) variation of Gibbs free energy ΔrG, the variation of enthalpy ΔrH and the variation of internal energy ΔrU corresponding of these reactions. The results obtained are summarized in Table 1 and Table 2. In the case to react carbonyl compounds type 1a-d on the diols 2 and 3, we found negative values of Gibbs free energy variation (ΔrG) corresponding to the reactions (I) and (I'), so these reactions are possible from thermodynamic point of view, except in the case where ($R_1 = OCH_3$) 1d which is positive, that shows this reaction is impossible thermodynamically, this reaction become negative in the case of the reaction (II) and (II'). On the other hand, the addition reaction between carbonyl compounds type 1a'-d' with diols 2 and 3 are all negative. Therefore, these reactions are possible and favored thermodynamically.

Table 1: Thermodynamic parameters calculated in ($kcal.mol^{-1}$) of the reactions (I) and (I').

Product	ΔrG	ΔrH	ΔrU
6-311G			
Reaction I			
4a+H_2O	-4.309	-6.111	-6.111
4b+H_2O	-0.539	-2.855	-2.854
4c+H_2O	-0.800	-3.374	-3.374
4d+H_2O	3.057	0.284	0.285
Reaction I'			
4a+H_2O	-4.910	-7.476	-7.476
4b+H_2O	-1.140	-4.219	-4.218
4c+H_2O	-1.401	-4.738	-4.738
4d+H_2O	2.456	-1.079	-1.078

The values of enthalpy variation (ΔrH) are all negative, these reactions are consequently exothermic reactions except the reaction (I) or ($R_1 = OCH_3$) is positive which is already thermodynamically disadvantaged.

This finding is probably due to the presence of chlorine in compounds 1a'-d' which has an inductive effect (-I) introduced on the carbonyl function which makes the reaction more favored thermodynamically.

On the other hand, we reported that the absolute values of Gibbs free energy variation (ΔrG) corresponding to reaction (I') are respectively larger than those corresponding to reaction (I), the same case for reactions (II) and (II'). This allowed us to say that the carbonyl compounds react preferentially with Z configuration diol 3 than E configuration diol 2. These results are also confirmed by the measured of the internal energy variation

(ΔrU), we notice that the absolute values of ΔrU corresponding to these reactions (I, I', II and II') follows the same order of evolution of Gibbs free energy variations. Respectively, this confirms again that the favorable products of the reaction are obtained by reaction between carbonyl compounds type 1a'-d' with Z configuration diol 3.
From the values of Gibbs free energy (ΔrG), we concluded that the reaction (II') corresponding to the carbonyl compounds type 1a'-d' is more favored thermodynamically than the other reactions (I), (I') and (II).Moreover, this reaction give the favored product 4a'.

Table 2: Thermodynamic parameters calculated in (kcal.mol^{-1}) of the reactions (II) and (II').

Product	ΔrG	ΔrH	ΔrU
6-311G			
Reaction II			
4a'+H_2O	-4.309	-6.111	-6.111
4b'+H_2O	-1.620	-4.369	-4.369
4c'+H_2O	-1.580	-4.531	-4.531
4d'+H_2O	-0.448	-2.614	-2.613
Reaction II'			
4a'+H_2O	-4.910	-7.476	-7.476
4b'+H_2O	-2.222	-5.734	-5.734
4c'+H_2O	-2.181	-5.895	-5.895
4d'+H_2O	-1.049	-3.978	-3.977

3.1.2. Addition Reactions between Diols 2 and 3 and carbonyl Compounds 1a''-c'' in the Presence of Lewis acid H^+

Like the Table 3 shows, we studied the variation of Gibbs free energy (ΔrG) corresponding to reaction (III) and (III') are more important in absolute value, than the variation of Gibbs free energy (ΔrG) relative to reaction (II) and (II') . which explains the importance of the presence of acid. The association between the oxygen atom of the carbonyl compounds 4a''-c'' and H+, drains the electrons to H+. The whole (-C=O$^+$-H) behaves as a more electronegative group than the oxygen alone, this group has a lower energy level. In the presence of electrophilic activation by the Lewis acid H $^+$,the coefficient on the carbon atom increases which leads to the increase of the intensity of the main stabilizing interaction and the decrease of the destabilizing secondary interaction.

Table 3: Thermodynamic parameters calculated in (kcal.mol^{-1}) of the reactions (III) and (III').

Product	ΔrG	ΔrH	ΔrU
6-311G			
Reaction III			
4a''+H_3O^+	-22.737	-23.987	-23.988
4b''+ H_3O^+	-5.804	-8.436	-8.436
4c''+ H_3O^+	-2.964	-6.909	-6.909
Reaction III'			
4a''+ H_3O^+	-23.338	-25.351	-25.352
4b''+ H_3O^+	-6.405	-9.800	-9.801
4c''+ H_3O^+	-3.566	-5.545	-5.545

3.1.3. Addition Reactions between Diols 3α, 3β and 3γ and carbonyl Compounds 1a and 1d

As shown in (Table 4, Reaction IV), we noticed that the values of Gibbs free energy (ΔrG) of the carbonyl compound 1a with the diol substituted on the both sides by two (C_2H_5) 3γ is greater than the diol substituted on the both sides by two (CH_3) 3β, which is larger than the diol substituted on only one side (CH_3) 3α.

We also found that the values of Gibbs free energy (ΔrG) corresponding to the carbonyl compound 1d with diols 3α and 3β which are positive become negative in the case where the diol is 3γ. What demonstrates that the reaction between the carbonyl compound and both diols 3β and 3γ are more favored than the reaction between the carbonyl compounds and diol 3α from thermodynamic perspective.

These results show that the substituent on diols increase the reactivity of the carbonyl function and this increasing of substituent makes the reaction more stable and more favored from thermodynamic point of view.

Table 4: Thermodynamic parameters calculated in (kcal.mol^{-1}) of the reactions (IV)

Product	ΔrG	ΔrH	ΔrU
6-311G			
Reaction IV			
5aα+H_2O	-5.603	-8.133	-8.133
5aβ+H_2O	-7.545	-10.155	-10.155
5aγ+H_2O	-15.205	-17.646	-17.646
5dα+H_2O	2.227	-1.216	-1.216
5dβ+H_2O	0.065	-2.991	-2.990
5dγ+H_2O	-7.533	-10.518	-10.518

3.2. Frontiers orbitals study

Frontier molecular orbital (FMO) [22], simplifies reactivity to interaction between the lowest unoccupied molecular orbital (LUMO) of one reactant and the highest occupied molecular orbital (HOMO) of the other, providing that the ΔE energy gap that separates them has to be the lowest possible [23].

Based on the calculation method SCF with 6-311G standard basis set, we determined the energies of the LUMO and the HOMO for the Z configuration diol 3 as well as the carbonyl compounds 1a', 1b', 1c' and 1d'. We determined the values of the global electrophilicity $\omega = \mu^2 / (2\eta)$ [24] of these molecules 1a'-d' and the diol 3 .To determined this electrophilicity, we calculated the chemical potential ($\mu \approx (E_{HOMO} + E_{LUMO})/2$) [25-27] which is a negative value and chemical hardness $\eta \approx (E_{LUMO} - E_{HOMO})$ for these molecules. As shown in (Table 5), we noticed that the diol 3 and the compound 1a' are more electrophilic than the molecules 1b', 1c' and 1d'. According to the theory of frontier orbital, we noted that the preferential interaction is between the HOMO of the diol 3 and the LUMO of the formyl chloride 1a', since we observed a favorable overlap between the HOMO of the diol 3 and the LUMO of the formyl chloride 1a'. But the overlap between the HOMO of the diol 3 and the LUMO of the other carbonyl compounds is not very favorable.

These observations allowed us to confirm that the reaction between the diol 3 and formyl chloride 1a' is more favored than the reactions between the diol 3 and other carbonyl compounds 1b', 1c' and 1d', which affirm the results found by the thermodynamic study.

It turns out from the results in table 6, that the gap ΔE_1 of the reaction between the diol 3 and the carbonyl compound protonated by Lewis Acid 1a'' is less in energy than the gap ΔE_2 in the case of the reaction between the diol 3 and the carbonyl compound 1a'. Therefore the reaction should be easier in the case of the carbonyl compound protonated by Lewis acid 1a'' addition on the diol 3. The Lewis acid (Which mean's the entities has an electronic gap) catalyze the reaction by decreasing the energy of the LUMO of carbonyl compound 1a'' which leads to decreases the energy gap between Frontier orbital of both partners.

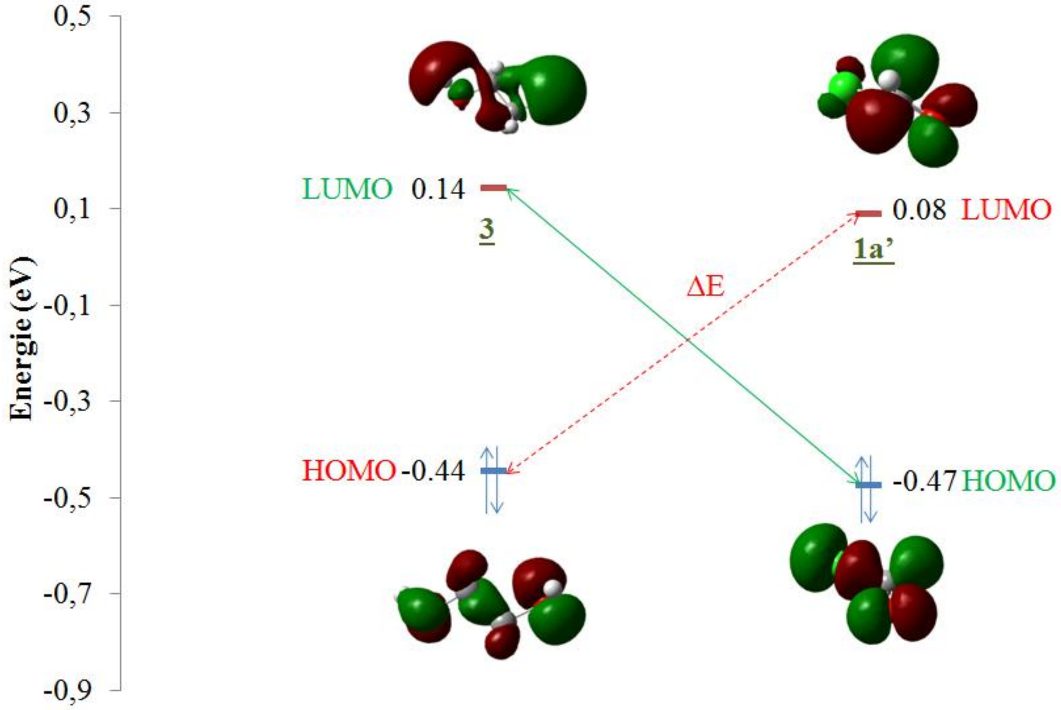

Figure 5: orbital diagram of the reaction between diol 3 and formyl chloride 1a'. Energies in (eV), the value of isocontour = (0.04 u.a)

Table 5: Global indices of reactants carbonyl compounds 1a', 1b', 1c' and 1d' and diol 3

Product	HOMO	LUMO	μ	η	ω
			6-311G		
3	-0.4457	0.1425	-0.1516	0.5882	0.0195
1a'	-0.4754	0.0892	-0.1930	0.5646	0.0330
1b'	-0.4579	0.1083	-0.1748	0.5663	0.0269
1c'	-0.4506	0.1044	-0.1731	0.5551	0.0269
1d'	-0.4786	0.1089	-0.1848	0.5876	0.0290

Table 6: Global indices of reactants carbonyl compounds 1a', 1d' and diol 3

Product	HOMO	LUMO	μ	η	ω
			6-311G		
3	-0.4457	0.1425	-0.1516	0.5882	0.0195
1a'	-0.4754	0.0892	-0.1930	0.5646	0.0330
1a''	-0.7286	-0.2031	-0.4658	0.5254	0.2065

On the other hand, we determined the energies of the LUMO and the HOMO of the formyl chloride 1a', diol 3α and diol 3β. It can be seen that the difference of energy HOMO-LUMO ΔE_1 is smaller in the case of the formyl chloride 1a' reaction with the diol 3β that in the case of the reaction between formyl chloride 1a' with the diol 3α. Therefore the reaction should be easier in the case of the addition formyl chloride 1a' on the diol 3β.

This explains reasonably that the reaction between the carbonyl compound 1a' and the diol 3β is more favored than the reaction between the carbonyl compound 1a' and the diol 3α. These results confirm the results previously found by the thermodynamic study.

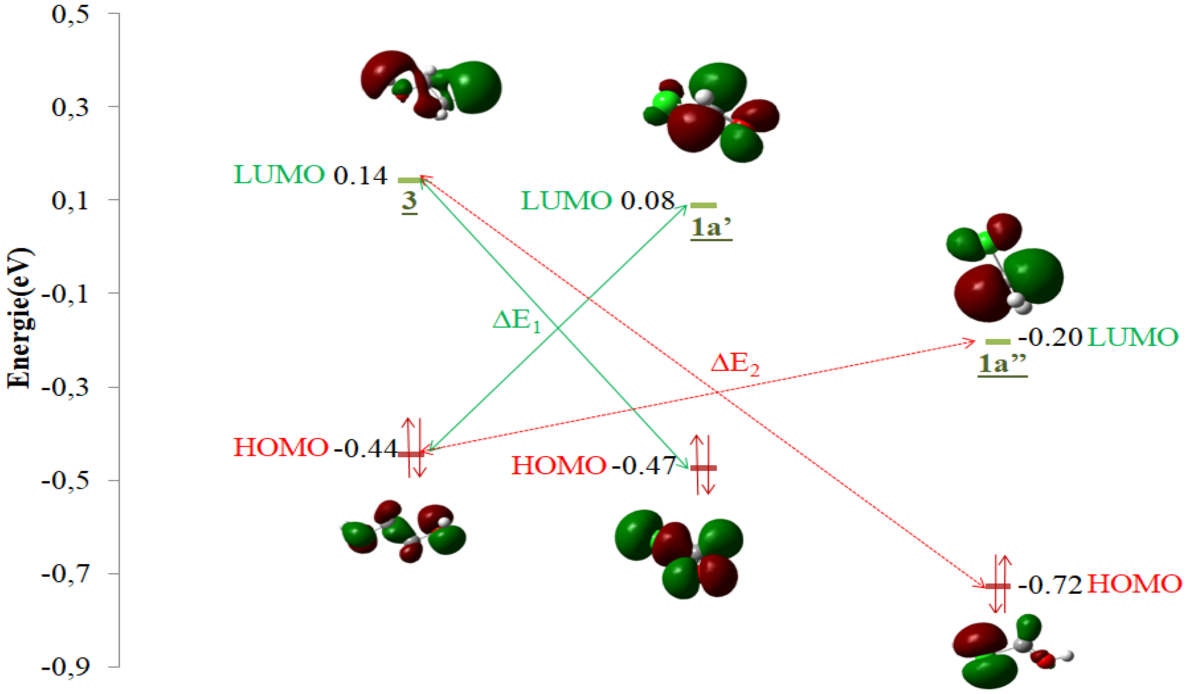

Figure 6: orbital diagram of the reaction between the diol 3 and the carbonyl compound 1a' and 1a''. Energies in (eV), the value of isocontour = (0.04 u.a).

Table 7: Global indices of the formyl chloride 1a' and diols 3α and 3β.

Product	HOMO	LUMO	μ	η	ω
		6-311G			
1a'	-0.4754	0.0892	-0.1930	0.5646	0.0330
3α	-0.4395	0.1435	-0.1479	0.5831	0.0187
3β	-0.4324	0.1391	-0.1466	0.5716	0.0188

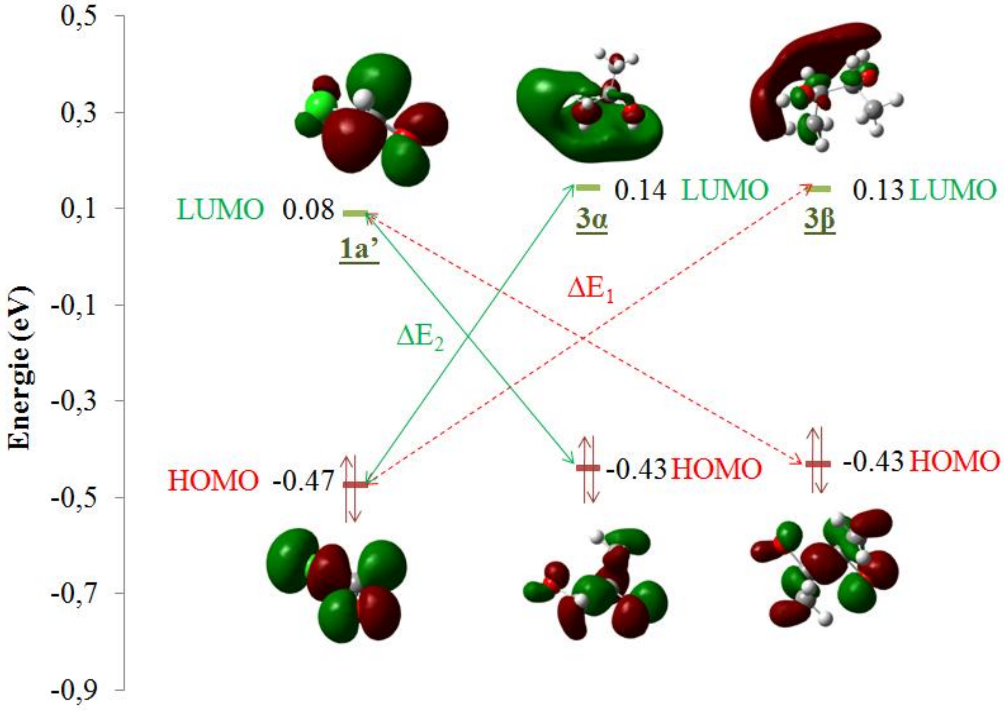

Figure 7: orbital diagram of the reaction between the formyl chloride 1a' and diols 3α and 3β. Energies in (eV), the value of isocontour = (0.04 u.a).

Conclusion

The present theoretical study shows the protection reactions of carbonyl compounds by diols. We found that the carbonyl compounds react preferentially with the Z-configuration diol than that with the E-configuration diol.

The calculations confirm that the reactions between the diol and the carbonyl compounds type 1a'-d' are possible and favorable thermodynamically. We also found that the reactions between the diol and the carbonyl compounds type 1a''-c'' protonated by Lewis acid are more stable from thermodynamic point of view.

We concluded that the reactivity of the carbonyl function and the stability of these reactions were proposed to be enhanced by the presence of chlorine which has an inductive effect (-I), also it was increasing by the diols substituent's and the Presence of Lewis acid H^+ on the other hand.

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