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Dynamic ^{1}H NMR along with theoretical study around the carbon-carbon double bond in stable phosphorus ylide derived from triphenylphosphine

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Abstract: Theoretical studies on the basis of rotation around the carbon-carbon double bond in phosphorus ylide namely dimethyl-2-(indolin-2-one-1-yl)-3-(triphenylphosphanylidene) butanedioate was investigated using Ab initio method at HF/6-31G (d,p) and B3LYP/6-31G(d,p) levels of theory. Theoretical activation parameters at 345 K involving $\Delta S^{\neq}$, $\Delta H^{\neq}$ and $\Delta G^{\neq}$ along with kinetic parameters (E_a) were determined in comparison with the same parameters on the basis of calculated dynamic ^{1}H NMR data. There was a good agreement between theoretical (18±1kcal/mol) and experimental (17.5±1kcal/mol) activation energy.

Keywords: Dynamic ^{1}H NMR, 2-Indolinon, Triphenylphosphine, Rotational energy barrier.

Introduction

Recently, different reports have been published on the synthesis of stable phosphorous ylides [1-10] from the reaction between triphenylphosphine and reactive acetylenic esters in the presence of N-H, C-H, O-H or S-H heterocyclic compounds. These ylides usually exist as a mixture of the two geometrical isomers (**Z** and **E**). These compounds exhibit dynamic ^{1}H NMR [11-19] effect that affords good information regarding the interchangeable process of rotational isomers that provide important kinetic data. We now describe theoretical studies [12,13] as a complementary investigation on the basis of rotation around the carbon-carbon double bond in a phosphorus ylide namely dimethyl-2-(indolin-2-one-1-yl)-3-(triphenylphosphanylidene) butanedioate**.**

Results and discussion

The reaction between dimethylacetylendicarboxylate 2 and 2-indolinon 3 in the presence of triphenyl phosphine 1 has been reported earlier [20] for generation of phosphorous ylide 4 involving the two Z- and E-geometrical isomers (Figure **1**).

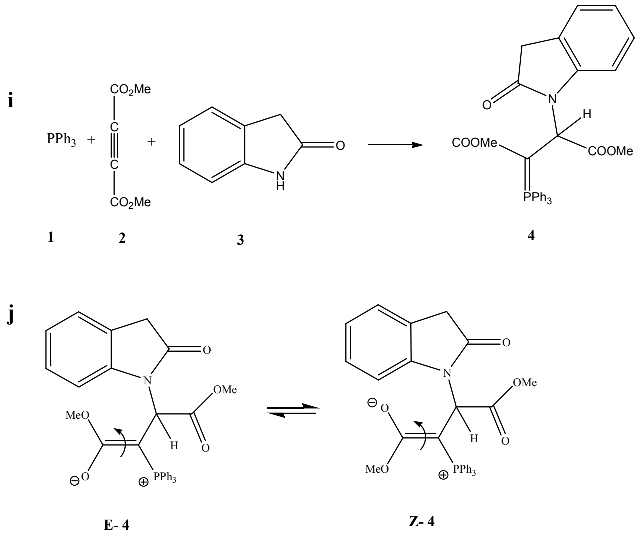

Fig. 1: i) Reaction between dimethyl acetylendicarboxylate **2** and 2- indolinon **3** in the presence of triphenylphosphine **1**

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for generation of phosphorousylide **4.** **j**) Interchangeable process between the two **E-4** and **Z-4** rotational isomers.

In order to determine theoretical rotational energy barrier in the interchangeable rotational processes of the two Z- and E-isomers in ylide 4, first their structures were optimized at HF/6-31G(d,p) level of theory by Gaussian 03 program package. Then, relative energy was plotted versus dihedral angle (O1C2C3P4, see Figure **2**) which is shown in Figure **3.** The energy profile was drawn in Figure **4**. The plot in Figure **3** was obtained by scanning method at HF/6-31G(d,p) level of theory by Gaussian 03 and each point was fully optimized in the relevant Figure. As can be seen, only one transition state (TS) has been appeared on a maximum point of this plot (Figure **3**).

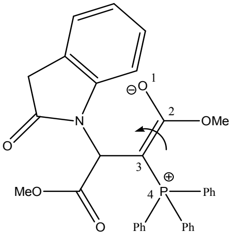

Fig. 2: The performance of $O_1C_2C_3P_4$ dihedral angel in a synthesized phosphorus ylide **4**.

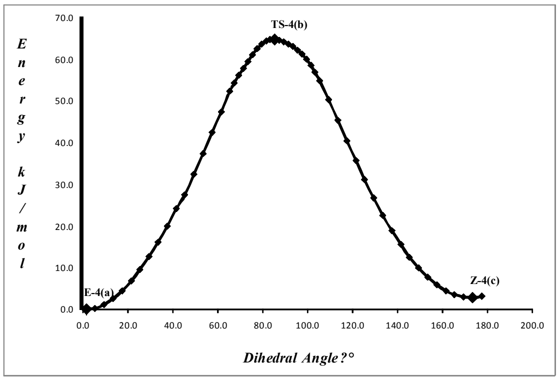

Fig. 3: Relative energy in phosphorus ylide **4** versus dihedral angels O1C2C3P4.

The corresponding structures, with respect to all points (a, b and c) in Figure **3** were shown in Figure **5.** On the basis of theoretical calculations, for synthesized ylide 4, and data obtained from the Figures **2** and **3**, the free Gibbs rotational energy barrier ($\Delta G^{\neq}$), $\Delta H^{\neq}$ and $\Delta S^{\neq}$ calculated around carbon-carbon double bond at all temperatures investigated. These results have been compared with the experimental data that was obtained by dynamic ^{1}H NMR data [18] (Table **1**). In addition, other parameters such as activation energy and rate constant are reported in Table **1** for the ylide 4. As can be seen, the difference between the experimental and theoretical data at the same temperature (345k) in both methods at HF/6-31G (d,p) and B3LYP/6-31G(d,p) levels of theory is relevant to the different media. Experimental data (on the basis of ^{1}H NMR study) at 345k is related to solution medium ($CDCl_3$ solvent), whereas theoretical data were calculated using ab initio method at HF/6-31G(d,p) and B3LYP/6-31G(d,p) levels of theory in gas phase. Nevertheless, there is a good agreement between the activation energy in both theoretical and experimental data. In spite of different media, molecular structure of relevant ylide 4 could be accounted as an effective factor for the difference between the theoretical and experimental data. In the present work, molecular structures of ylide 4 involving large atoms such as six oxygen atoms, one phosphorus and one nitrogen atom are huge along with the large numbers of other atoms, for this reason, employment of higher level of theory with basis set higher than HF/6-31G(d,p) and B3LYP/6-31G(d,p) levels of theory is impossible for a higher performance to gain more accurate calculations, this limitations causes a small difference between both the experimental and theoretical data.

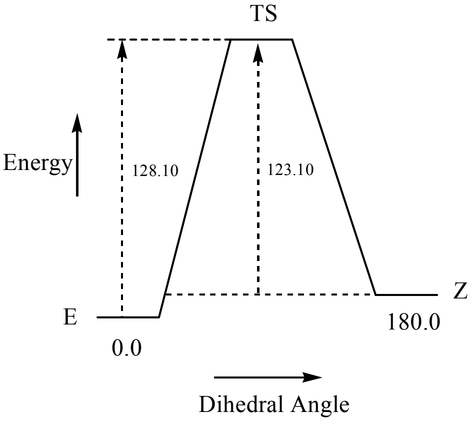

Fig. 4: The profile energy for the synthesized ylide 4.

Conclusion

The theoretical results, obtained from Ab initio method at HF/6-31G(d,p) and B3LYP/6-31G(d,p) levels of theory in comparison with data emerge from the experimental dynamic ^{1}H NMR indicated that activation energy for interchangeable process between the two rotational isomers (4-E and 4-Z) were consistent with the experimental dynamic ^{1}H NMR data. Although, there is a difference between theoretical thermodynamic values and those obtained experimentally by ^{1}H NMR, it is not unexpected, because of the different media. In experimental methods (^1H NMR) all thermodynamic data were obtained in solvent media ($CDCl_3$), but in theoretical method all parameters emerge from theoretical calculations in gas phase. In addition, for huge molecular structure of ylide 4 employment of higher level of theory with basis set higher than HF/6-31G (d,p) and B3LYP/6-31G(d,p) levels is impossible. This limitation causes a small difference between both the experimental and theoretical data.

Table 1. Selected ^1H chemical shifts (at 500.1 MHz, in ppm, Me_4Si) along with activation parameters in $CDCl_3$, for restricted rotational process around the carbon-carbon double bond ($(OEt)_3P–C\neq C–OMe$).

	E_a(kcal/mol)	$\Delta S^\#$ (cal/mol K)	$\Delta H^\#$ (kcal/mol)	$\Delta G^\#$ (kcal/mol)	$\Delta\upsilon$ (Hz)	δ (ppm)	T_c (K)
Experimental[a]	18.0±1	-24.9	17.2	26.0±1	15.00	3.75, 3.78	345
Theoretical[b]	28.8±1	-8.4	28.2	30.6±1	–	–	298
Theoretical[c]	28.7±1	-8.6	28.1	31.1±1	-	-	345
Theoretical[d]	17.5±1	-5.5	14.0	15.9±1	-	-	345

a On the basis of reports on literature[18]

b Data obtained using *ab initio* method at HF/6-31G(d,p) level of theory at 298 K for synthesized ylide 4.

c Data obtained using *ab initio* method at HF/6-31G(d,p) level of theory at 345 K for synthesized ylide 4.

d Data obtained using *ab initio* method at B3LYP/6-31G(d,p) level of theory at 345 K for synthesized ylide 4.

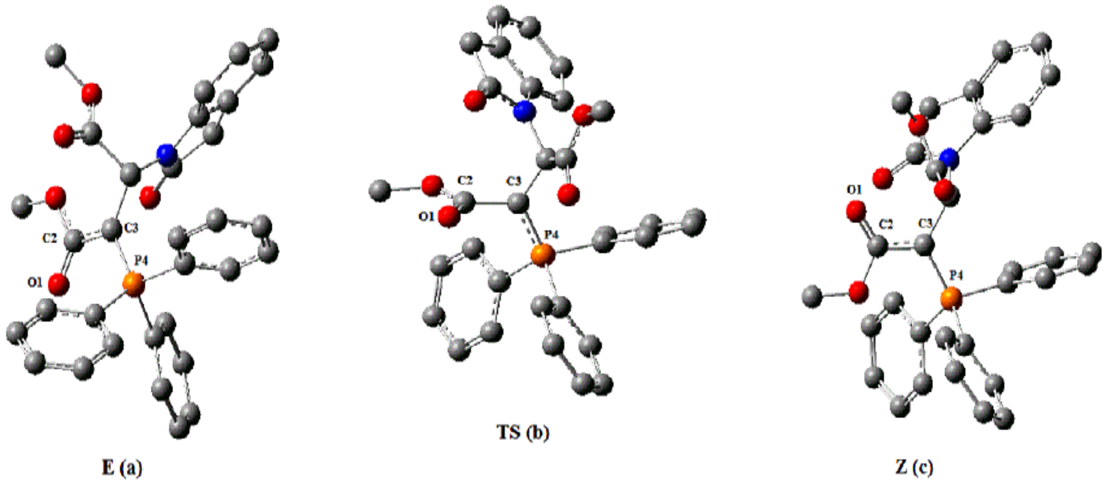

Figure 5. Structures corresponding to a, b and c points with respect to Figure **3**.

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