

## Theoretical study around the C=C bond in a stable phosphorus ylide derived from hexamethylphosphorous triamide

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**Abstract:** A theoretical study has been performed within the phosphorus ylide derived from hexamethylphosphorous triamide around the carbon-carbon double bond ( $\text{OCH}_3\text{-C}=\text{C-P}(\text{NMe}_2)_3$ ) using *ab initio* and DFT methods at the HF/6-31G\*\* and B3LYP/6-31G\*\* levels of theory in gas phase. Also, effects of temperature and solvent media were investigated. The results showed that the B3LYP/6-31G\*\* level at solvent media and experimental temperatures provides better data in relation to experimental dynamic  $^1\text{H}$  NMR data.

**Keywords:** Ylide, Isomer, DFT, *Ab initio*, Energy Barrier.

### Introduction

Phosphorus-carbon bond formation [1-9], is an active and important research area, as new reactions are continuously being developed for the preparation of organophosphorus compounds such as phosphinates and phosphonates [10-13]. The synthesis of phosphorus ylides is important in organic chemistry because of their application in the synthesis of organic products [14-21]. They are of interest as building blocks for the preparation of alkenes, heterocyclic compounds [22-23], and natural products [24]. Phosphorus ylides are reactive systems which take part in many valuable reactions of organic synthesis [24-26]. These are most often prepared by the treatment of a phosphonium salt with a base. Most of the phosphonium salts are usually made from the phosphine and an alkyl halide [14-19], and also they are obtained by a Michael addition of phosphorus nucleophiles to activated olefins [19-20].

Rotational barriers are significant in determining the inherent "stiffness" of macromolecular chains and

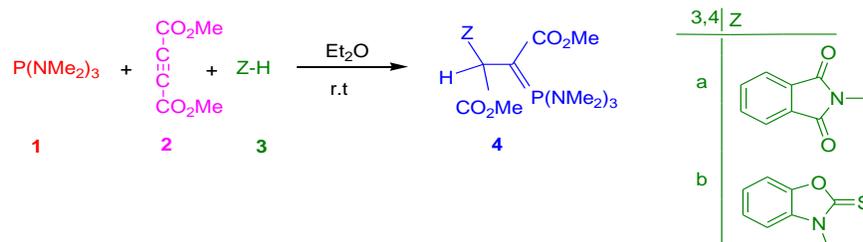
hence are used to assess isomerism. Intra and intermolecular hydrogen bonding, and steric interactions serve to change the rotational barriers sufficiently [27]. These ylides usually exist as a mixture of the two geometrical isomers (*Z* and *E*) that exhibit dynamic  $^1\text{H}$  NMR effects. Rotational about the bond has been generally studied by dynamic  $^1\text{H}$  NMR spectroscopy and theoretical methods. These studies afforded good information regarding the interchangeable process of rotational isomers and provide important kinetic data. In this article, towards of our dynamic studies [11, 28, 29], the energy barrier in carbon-carbon partial double bond rotation were theoretically examined in detail [29, 30-32]. As a model, theoretical studies on the two geometrical isomers involving 2-chloroaniline are carried out using DFT and *ab initio* methods.

### Results and discussion

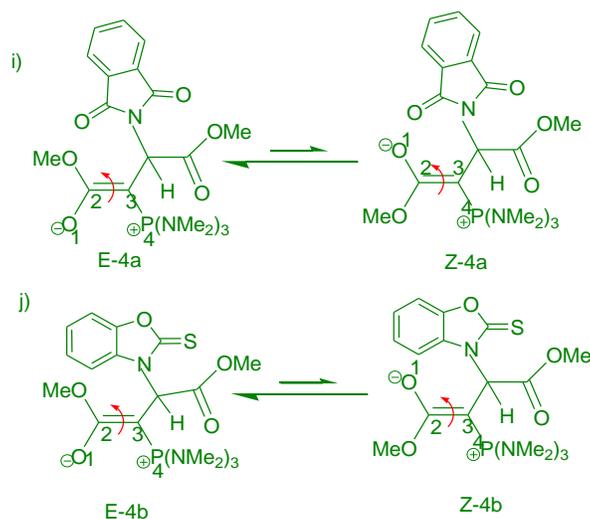
Synthesis of reaction between Hexamethylphosphorous triamide **1**, dimethyl acetylenedicarboxylate **2** and N-H acids **3a, b** for the preparation of stable phosphorus ylides **4a, b** involving

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the two *Z*- and *E*-geometrical isomers (Figures 1 and 2) along with the Dynamic  $^1\text{H}$  NMR has been earlier published [33].



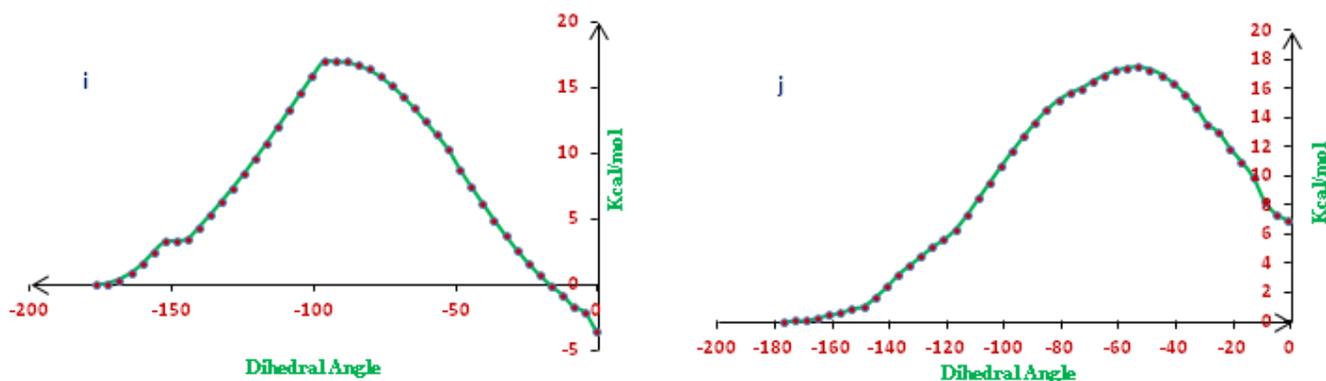
**Figure 1:** Reaction between hexamethylphosphorous triamide **1** and dimethyl acetylenedicarboxylate **2** and N-H acids **3** for generation of phosphorus ylide **4a** and **4b**.



**Figure 2:** Interchangeable processes between the two i) *E*-4a, *Z*-4a and j) *E*-4b, *Z*-4b rotational isomers.

In order to determine theoretical rotational energy barrier ( $\Delta G^\ddagger$ ) in the rotational interchangeable processes of the two *Z*- and *E*-isomers in ylide **4a-b**, first their structures were optimized at HF/6-31G\*\* level of theory by Gaussian 03 program package [34]. Then, relative energy was plotted versus dihedral angle ( $\text{O}_1\text{C}_2\text{C}_3\text{P}_4$ , see Figure 2) which is shown in Figure 3.

The plot in Figure 3 was obtained by scanning method at HF/6-31G\*\* and B3LYP/6-31G (d,p) levels 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 point of these plots (Figure 3).



**Figure 3:** i) Relative energy in phosphorus ylide **4a** versus dihedral angles  $\text{O}_1\text{C}_2\text{C}_3\text{P}_4$ , j) Relative energy in phosphorus ylide **4b** versus dihedral angles  $\text{O}_1\text{C}_2\text{C}_3\text{P}_4$ .

The corresponding structures with respect to all points (*Z*, *Ts* and *E*) in Figure 3 are shown in Figures 4 and 5. The free Gibbs rotational energy barrier ( $\Delta G^{\ddagger}_{\text{calcd}}$ ), activation enthalpy ( $\Delta H^{\ddagger}$ ) and activation entropy ( $\Delta S^{\ddagger}$ ) are calculated using the relevant plots around carbon-carbon double bond in gaseous phase. These results have been compared with the

experimental data that was obtained by dynamic  $^1\text{H}$  NMR data (Tables 1 and 2) [33]. For better comparison of theoretical and experimental data, calculations are also performed in solution medium ( $\text{CDCl}_3$ ) for the two ylides **4a** and **4b**. The results are accumulated in Tables 1 and 2.

**Table 1:** Selected  $^1\text{H}$  chemical shifts (at 500.1 MHz, in ppm,  $\text{Me}_4\text{Si}$ ) along with activation parameters in  $\text{CDCl}_3$ , for restricted rotational process around the carbon-carbon double bond ( $(\text{NMe}_2)_3\text{P}-\text{C}=\text{C}-\text{OMe}$ ) in ylide **4a**.

	$\Delta S^{\ddagger}$ (kJ/mol)	$\Delta H^{\ddagger}$ (kJ/mol)	$\Delta G^{\ddagger}$ (kJ/mol)	$\Delta\nu$ (Hz)	$\delta$ (ppm)	$T_c$ (K)
Experimental <sup>a</sup>	0.042	78.00	<b>65.4±1</b>	10.0	5.16, 5.17	300
Theoretical <sup>b</sup>	-0.014	77.47	81.80	-	-	298
Theoretical <sup>c</sup>	-0.020	67.75	73.78	-	-	300
Theoretical <sup>d</sup>	-0.019	65.84	<b>71.52</b>	-	-	300
Theoretical <sup>e</sup>	-0.015	77.47	82.04	-	-	300
Theoretical <sup>f</sup>	-0.020	75.10	81.13	-	-	300

<sup>a</sup> On the basis of literature [33]

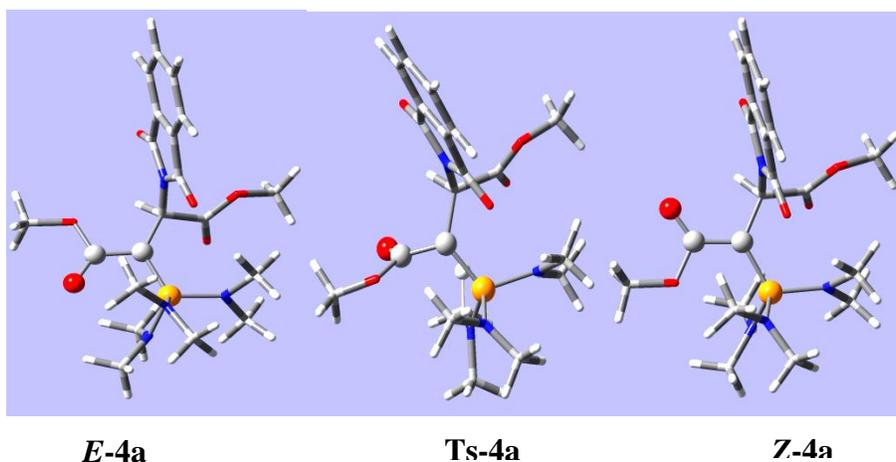
<sup>b</sup> Data obtained using DFT method at B3LYP/6-31G\*\* level of theory in gaseous phase

<sup>c</sup> Data obtained using DFT method at B3LYP/6-31G\*\* level of theory in gaseous phase

<sup>d</sup> Data obtained using DFT method at B3LYP/6-31G\*\* level of theory in solvent ( $\text{CDCl}_3$ )

<sup>e</sup> Data obtained using *ab initio* method at HF/6-31G\*\* level of theory in gaseous phase

<sup>f</sup> Data obtained using *ab initio* method at HF/6-31G\*\* level of theory in solvent ( $\text{CDCl}_3$ )



**Figure 4:** Structures corresponding to *E*, *Ts* and *Z* points with respect to Figure 3i.

**Table 2:** Selected  $^1\text{H}$  chemical shifts (at 500.1 MHz, in ppm,  $\text{Me}_4\text{Si}$ ) along with activation parameters in  $\text{CDCl}_3$ , for restricted rotational process around the carbon-carbon double bond ( $(\text{NMe}_2)_3\text{P}-\text{C}=\text{C}-\text{OMe}$ ) in ylide **4b**.

	$\Delta S^{\ddagger}$ (kJ/mol)	$\Delta H^{\ddagger}$ (kJ/mol)	$\Delta G^{\ddagger}$ (kJ/mol)	$\Delta\nu$ (Hz)	$\delta$ (ppm)	$T_c$ (K)
Experimental <sup>a</sup>	0.166	116.5	<b>64.3±1</b>	10.0	6.01, 6.11	313
Theoretical <sup>b</sup>	-0.012	65.02	68.77	-	-	298
Theoretical <sup>c</sup>	-0.011	69.02	72.58	-	-	313
Theoretical <sup>d</sup>	0.016	72.13	<b>67.10</b>	-	-	313
Theoretical <sup>e</sup>	-0.011	70.72	74.07	-	-	313
Theoretical <sup>f</sup>	-0.041	69.24	82.23	-	-	313

<sup>a</sup> On the basis of literature [33]

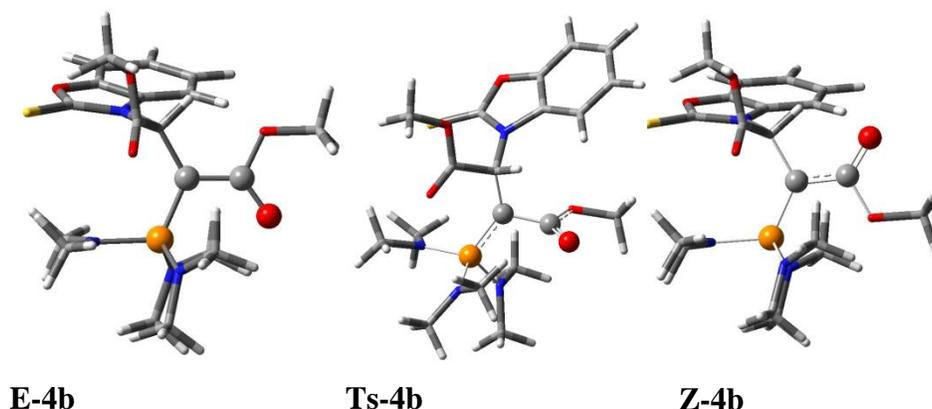
<sup>b</sup> Data obtained using DFT method at B3LYP/6-31G\*\* level of theory in gaseous phase

<sup>c</sup> Data obtained using DFT method at B3LYP/6-31G\*\* level of theory in gaseous phase

<sup>d</sup> Data obtained using DFT method at B3LYP/6-31G\*\* level of theory in solvent ( $\text{CDCl}_3$ )

<sup>e</sup> Data obtained using *ab initio* method at HF/6-31G\*\* level of theory in gaseous phase

<sup>f</sup> Data obtained using *ab initio* method at HF/6-31G\*\* level of theory in solvent (CDCl<sub>3</sub>)



**Figure 5:** Structures corresponding to *E*, *Ts* and *Z* points with respect to Figure 3j.

The results indicated that there is a good agreement between the experimental rotational energy barrier ( $\Delta G_{\text{exp}}^{\ddagger}$ ) and those obtained at the B3LYP/6-31G (d,p) level ( $\Delta G_{\text{calcd}}^{\ddagger}$ ) in solvent (CDCl<sub>3</sub>). It seems that the B3LYP/6-31G (d,p) is a suitable level for the calculation of restricted rotational process around the C=C double bond in a huge molecule like the ylides **4a** and **4b** with the large atoms such as 6 oxygen, 4 nitrogen and 1 phosphorus atoms.

### Conclusion

Four rotational processes around the OCH<sub>3</sub>-C=C-P(NMe<sub>2</sub>)<sub>3</sub> bonds were investigated using theoretical calculations at the HF/6-31G\*\* and B3LYP/6-31G\*\* levels of theory.

Theoretical data in accordance with the dynamic <sup>1</sup>H NMR indicated that the rotational energy barrier around the C=C bond is considerably high, and observation of the two rotational isomers, *E-4* and *Z-4*, is possible (seen as a single isomer) at high temperature. Herein, the B3LYP/6-31G\*\* level was recognized as a suitable level. It seems that employment of the DFT method is more preferable than the *ab initio* method for a huge molecule like the ylides **4** that suffers from crowds of atoms during the interchangeable rotational processes.

### Acknowledgement

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