



Dynamic ^1H NMR Studies along with Theoretical Investigation around Carbon-Carbon Double Bond in Stable Phosphorus Ylide containing a 2-Thiazolin-2thiol

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ABSTRACT

In the present work, dynamic ^1H NMR effects were investigated within a particular stable phosphorous ylide involving 4, 5-dihydrothiazole-2-thiol around the carbon-carbon double bond ($\text{OCH}_3\text{-C=C-PPH}_3$) in the two *Z*- and *E*- rotational isomers. Activation parameters including ΔH^\ddagger , ΔG^\ddagger , ΔS^\ddagger were calculated in accord with dynamic ^1H NMR data for the rotational process. In addition, theoretical studies were investigated on the same bond using ab initio calculation at HF level and B3LYP method with 6-31G(d, p) basis set. In this case, the Gibbs free energy barrier ($\Delta G^\ddagger = 69.29$ and 67.42 $\text{kJ}\cdot\text{mol}^{-1}$) results were in a good agreement with the experimental data ($\Delta G^\ddagger = 68.71$ $\text{kJ}\cdot\text{mol}^{-1}$) for interchangeable process of rotational isomers between the two 4-*Ea* and 4-*Za*

Keywords: Dynamic ^1H NMR, Abinitio method, 4, 5-dihydrothiazole-2-thiol, Triphenylphosphine, Rotational energy barrier.

INTRODUCTION

The synthesis of phosphorus ylides is important in organic chemistry ¹⁻⁶ because they make stable carbanion. These reactions have gained more use in synthetic organic chemistry ⁷⁻¹¹ because of their application in the synthesis of organic products ¹²⁻¹⁴, especially in the synthesis of naturally occurring products with biological and pharmacological activities ^{15, 16}. These ylides are often prepared by treatment of a phosphonium salt with a base, and phosphonium salts are usually

obtained from the phosphine and an alkyl halide. Some ylides exhibited dynamic ^1H NMR effect that affords good information regarding the interchangeable process of rotational isomers that provide important kinetic data ¹⁷⁻²⁷. In previous works, dynamic ^1H NMR effects were reported for dimethyl-2-(4, 5 dihydrothiazolin-N-yl)-3-(triethoxyphosphorylidene)-butanedioate ²⁸. Now, we describe dynamic ^1H NMR effect for reaction between dimethyl acetylenedicarboxylate 2 and 2-thiazolin-2-thiol 3 in the presence of triphenylphosphine 1 for generation of phosphorous

ylide 4a involving the two *Z* - and *E*-rotational isomers. Synthesis of this reaction has been earlier reported²⁹ (Figure1-i)

MATERIAL AND METHODS

Triphenylphosphine, dialkyl acetylenedicarboxylates and 4, 5-dihydrothiazole-2-thiol were purchased from Fluka and without further purification. Quantum mechanical calculation has been performed using the Gaussian 03 package³⁰ at the HF^{31, 32} and B3LYP³³⁻³⁴ methods with 6-31G(d,p) basis set. The ¹H, ¹³C and ³¹P NMR spectra were recorded on a Bruker DRX-500 AVANCE instrument with CDCl₃ as solvent at 500.1, 125.8 and 202.4 MHz, respectively.

RESULTS AND DISCUSSION

The reaction between dimethyl acetylenedicarboxylate 2 and 4, 5-dihydrothiazole-2-thiol 3 in the presence of triphenylphosphine 1 was completed over a few hours (or after 8 hours) at ambient temperature in ethyl acetate as solvent. The ¹H and ¹³C NMR spectra of the product indicated formation of 4a. The structure of compound 4a was verified from elemental analyses data, mass, IR, ¹H, ¹³C and also ³¹P NMR spectra data. The mass spectra of 4a displayed molecular ion peak at *m/z*= 523. The ¹H and ³¹P spectra of stable ylide 4a are consistent with the presence of the two rotational isomer forms (*Z*-4a and *E*-4a, Figure 1-j), the C2-C₃ has a partial double bond character, due to the

Table 1: Selected ¹H chemical shifts (at 500.1 MHz, in ppm, Me4Si) for ylide 4a along with activation parameters in CDCl₃, for restricted rotational process around the carbon-carbon double bond P(Ph)₃ P-C C-OMe) in ylide 4a and speculative ylide 5a at 298 K (room temperature) and experimental temperature (313 K)

	S [#] (J/mol)	H [#] (kJ/mol)	ΔG [#] (kJ/mol)	ν(HZ)	δ (ppm)	Tc (K)
Experimental ^a	28.66	74.67	68.71	9.41	5.55, 5.5	313
Theoretical ^b	-11.04	65.88	69.16	-	-	298
Theoretical ^c	-11.31	65.75	69.29	-	-	313
Theoretical ^d	-23.32	60.12	67.42	-	-	313
Theoretical ^e	-15.97	68.39	73.15	-	-	298

^a Experimental Data obtained from the ¹H NMR study²⁸

$$(k_c = \frac{\pi \Delta \square}{\sqrt{2}}, \Delta G^\ddagger = 4.57 T_c (9.97 + \log \frac{T_c}{\Delta}), \Delta H^\ddagger = -R \times 2.303 \times \frac{\Delta \log k_c / T_c}{\Delta 1/T_c}, \Delta S^\ddagger = \frac{\Delta H^\ddagger - \Delta G^\ddagger}{T})$$

^b Theoretic data obtained using *ab initio* calculation at HF/6-31G(d,p) level of theory for a synthesiZed ylide **4a** at **298K**. ($\Delta H^\ddagger = H_{TS} - H_Z$, $\Delta G^\ddagger = G_{TS} - G_Z$, $\Delta S^\ddagger = \frac{\Delta H^\ddagger - \Delta G^\ddagger}{T}$)

^cTheoretical data obtained using *ab initio* calculation at HF/6-31G(d,p) level of theory at experimental temperature (313K) for synthesiZed ylide 4a.

^dTheoretical data obtained using *ab initio* calculation at B3LYP method with 6-31G(d,p) basis set at experimental temperature (313K)for a synthesiZed ylide 4a.

^eTheoretical data obtained using *ab initio* calculation at HF/6-31G(d,p) level of theory for a speculative ylide 5a at 298K.

Table 2: The relative energy (kJ/mol) between the two isomers of ylid 4a, obtained at HF/6-31G(d,p) and B3LYP method with 6-311++G(d,p) basis set

isomer	HF	B3LYP
E	48.93	40.41
Z	0	0

Table 3: Frequency data obtained for all TS, E-4a and Z-4a structures in the ylide 4a

Isomer	First Frequency
E-4a	20.68
TS	- 66.16
Z-4a	13.74

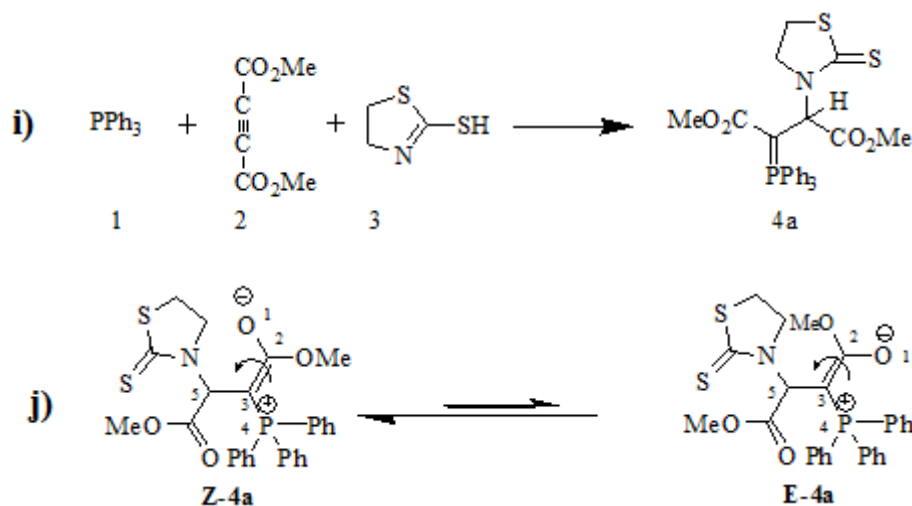


Fig. 1(i). Reaction between dimethyl acetylenedicarboxylate 2 and 4, 5-dihydrothiazole-2-thiol 3 in the presence of triphenylphosphine 1 for preparation of phosphorus ylide 4a. j) Interchangeable process of rotational isomers in the two 4-Ea and 4-Za isomers

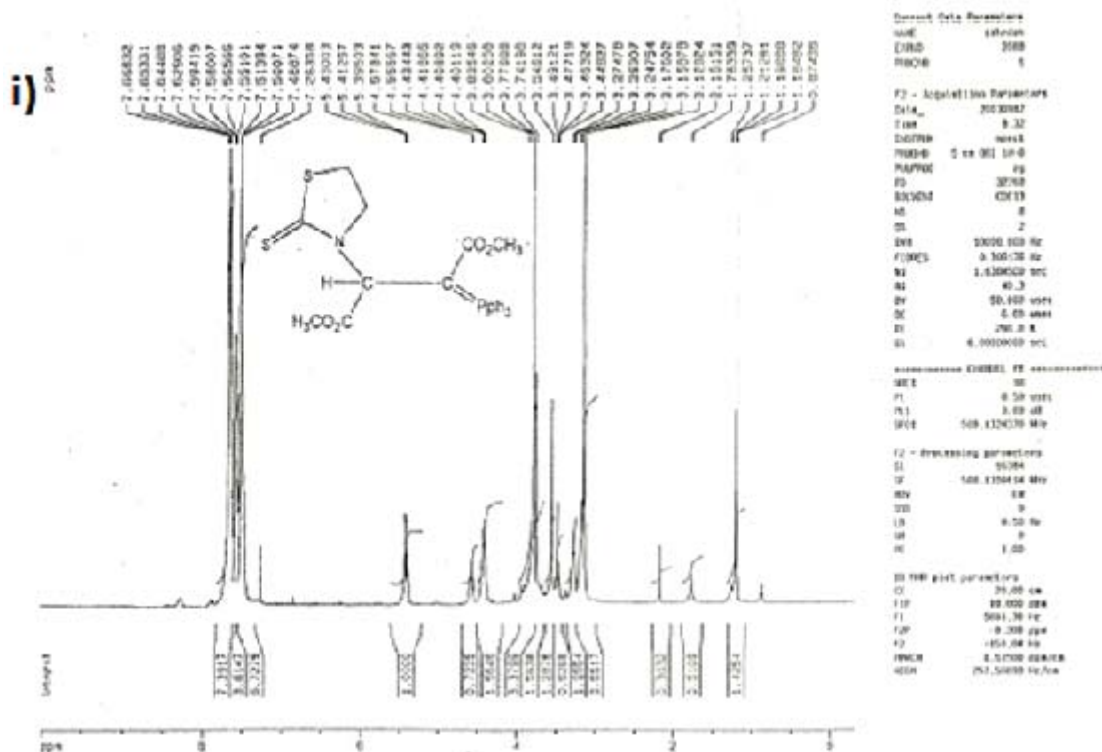


Fig. 2: ^1H NMR spectra of compound 4a

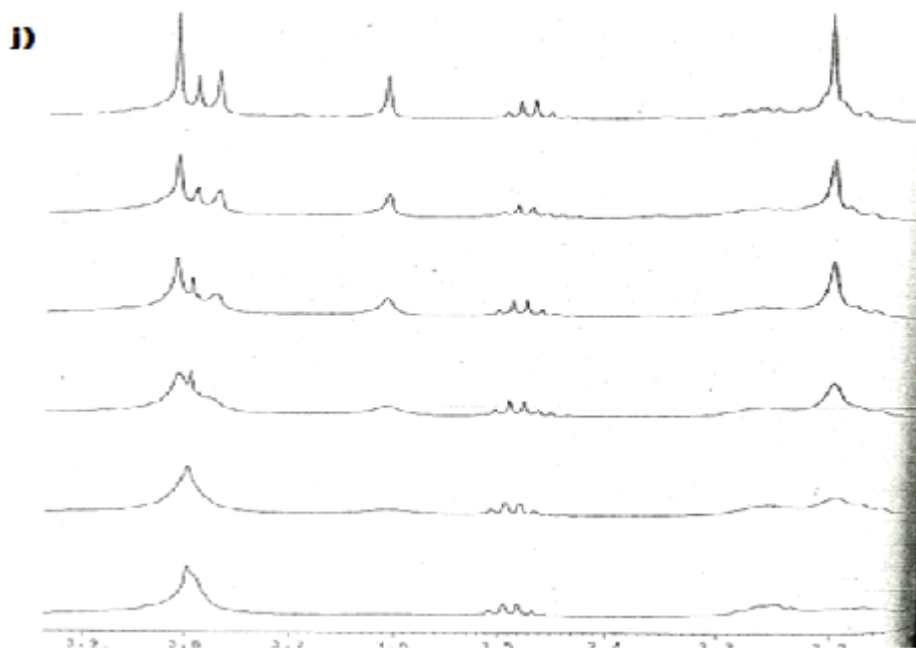


Fig. 3: Dynamic ^1H NMR effects at variant for methoxy groups in compound 4a

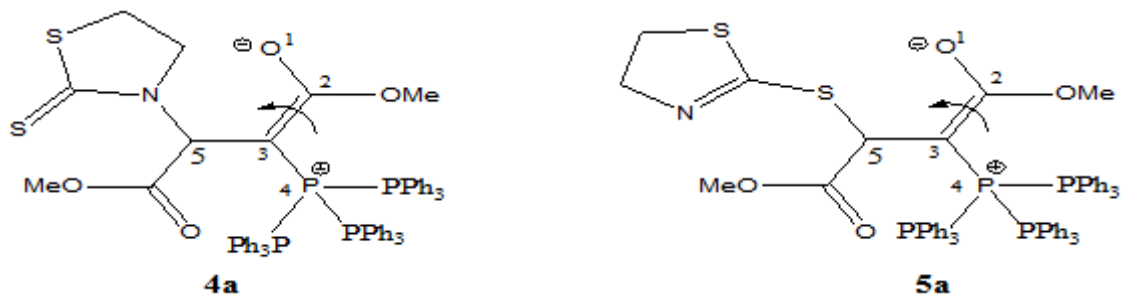


Fig. 4: The performance of O1C2C3P4 dihedral angle in a synthesized phosphorus ylide 4a and in a speculative ylide 5a

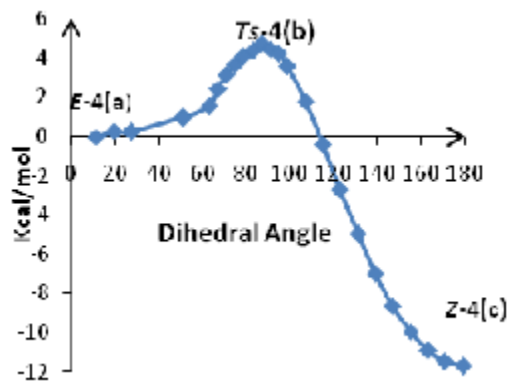


Fig. 5: Relative energy versus dihedral angle O1C2C3P4 in phosphorus ylide 4a

conjugation with adjacent carbonyl group of CO₂Me and C=P⁺(PPh)₃, as shown in Figure 1-j.

The rotation around the carbon-carbon double bond (H₃COO-C=C-PPh₃) in the *Z*-4a and the *E*-4a geometrical isomers is slow on the NMR time scale at ambient temperature. Thus, this provides a mixture of the two *Z*-4a and *E*-4a geometrical isomers. The ¹H NMR spectra of the phosphorous ylide 4a exhibit two doublets for the methine proton (H-C-C-P, ³J_{PH} = 17.5 Hz) at δ = 5.5 and 5.55 ppm (Figure 2) and two singlets arising from methoxy groups at 3.53 and 3.75 ppm and also at 3.13 and 3.78 ppm for the two minor (*E*-4a) and major (*Z*-4a) geometrical isomers, respectively

(Figure 3). Effects of dynamic ¹H NMR around the partial carbon-carbon double bond will be argued next. On the basis of ¹H NMR spectra at high temperature, two sharp signals were observed for the methoxy groups at 40°C (313 K), due to a fast rotation around the carbon-carbon double bond (Figure 3). Investigation of such behavior in the phosphorous ylide 4a at variable temperatures allowed us to calculate the Gibbs free energy barrier (ΔG[‡]) for the restricted rotation around the carbon-carbon double bond in 4a (Table 1).

Using the expression $k_c = \pi\Delta\nu/\sqrt{2}$, the first-order rate constant was calculated for this rotation at 40°C. Application of the absolute rate theory with

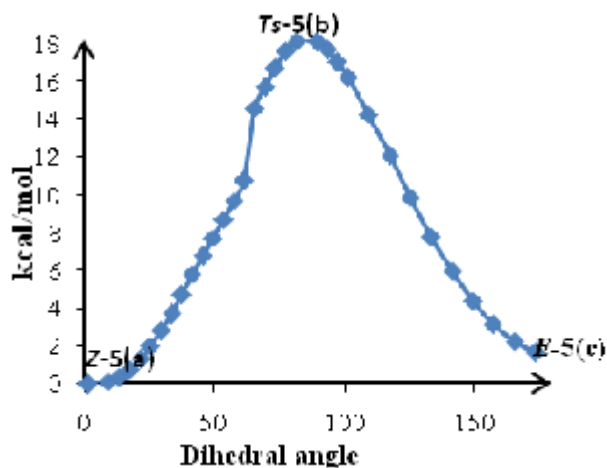


Fig. 6: Relative energy versus dihedral angle O1C2C3P4 in a speculative phosphorous ylide 5a

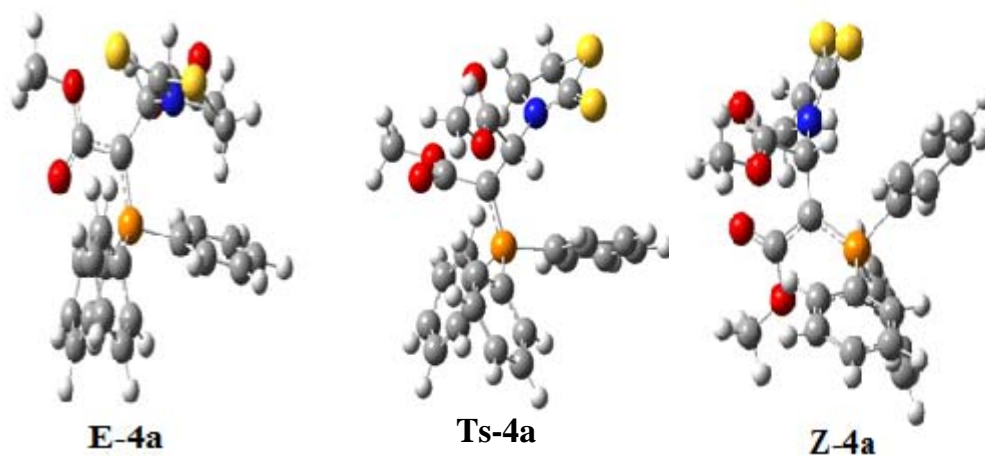


Fig. 7: Structures corresponding to a, b and c points with respect to Figure 1-j

a transmission coefficient (k) of one, gave a Gibbs free energy barrier. These values are reported in Table 1. Effect of temperature on the rate constant was investigated on the basis of measurement of different chemical shifts in a series of other separate experiments. The results were too small so that the changes in first-order rate constant and Gibbs free energy barrier were negligible in comparison with the results obtained at 40°C (313K).

In order to determine theoretical rotational energy barrier around the C=C bond in ylide 4a (Figure 1-j), first their structures were optimized at HF/6-31G level^{30, 30} of theory by Gaussian 03 program package²⁹ and relative energy between the two isomers calculated at HF/6-31G(d, p) level and B3LYP method with 6-311++G(d, p) basis set. The results are given in Table 2.

Then, relative energy was plotted versus dihedral angle O1C2C3P4 (Figure 4) as shown in Figure 5. The plots in Figure 5 and 6 were obtained by scanning method at HF/6-31G(d, p) level of theory by Gaussian 03 and each point in both figures were fully optimized. A repetition of this behavior was carried out for a speculative ylide 5a (Figure 4) in comparison with the synthesized ylide 4a. In a speculative ylide 5a, sulfur atom in conjugate base of N-H acid has been joined to C5 in phosphorus ylide, while in ylide 4a nitrogen atom of conjugate base has been joined to C5 atom. The results shown in Figure 6 and Table 1.

The corresponding structures, with respect to all points (a, b and c) in Figure 5 were drawn in Figure 7. Frequency calculations were employed for all transition and stationary points (TS, E-4a and Z-4a) and the results are reported in Table 3. First negative frequency value could be considered as a strong proof for confirming of TS structure

On the basis of theoretical calculations, for synthesized ylide 4a, and data obtained from the Figures 5 and 6, the Gibbs free energy barrier (ΔG^\ddagger , ΔH^\ddagger and ΔS^\ddagger calculated around the carbon-carbon double bond for both the speculative and synthesized ylide. As can be seen from Table 3; A) there is, relatively, a good agreement between the experimental data (a) and theoretical data (b, c) at 298K and experimental temperature (313). B) there is also a good consistent at both HF level and B3LYP method with 6-31G(d, p) basis set (c, d) with experimental data (a). In addition, theoretical Gibbs free energy barrier for a speculative ylide 5a (Table 1, e) is higher than both Gibbs free energy obtained from experimental data (Table 1, a) and theoretical data (Table 1, b, c and d) in a synthesized ylide 4a. These results indicate that why the ylide 4a is practically generated easier than the speculative ylide 5a.

CONCLUSION

The theoretical results on the basis of mechanical calculations, obtained from ab initio calculation at HF level and B3LYP method with 6-31G (d, p) basis set indicated that activation parameters ($\Delta G^\ddagger = 69.29$ and 67.42 $\text{kJ}\cdot\text{mol}^{-1}$, respectively) for interchangeable process between the two rotational isomers (4-E and 4-Z) were relatively consistent with the experimental dynamic ^1H NMR data ($\Delta G^\ddagger = 68.71$ $\text{kJ}\cdot\text{mol}^{-1}$). In addition, the results show that generation of the synthesized ylide, 4a is more possible than the speculative ylide, 5a because, of the less free Gibbs energy barrier.

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