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Dynamic ¹H NMR studies of hindered internal rotations in the synthesized particular phosphorus ylide: Experimental and theoretical approaches





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HIGHLIGHTS

- Two rotational isomers of the synthesized ylide indicated experimentally.
- The barriers around the selected bonds are obtained by the dynamic ¹H NMR.
- DFT and ab initio methods are performed.
- The calculated barriers confirmed the experimental data.

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Keywords: D ¹H NMR Rotational barrier DFT Ab initio Ylide ABSTRACT

Dynamic ¹H NMR measurements were performed within the synthesized particular phosphorus ylide involving 4-formylphenyl phenylcarbamate. Four rotational process and thereby parameters were targeted for rotation around the C=C, C-C, HC–NC and OC–NC bonds. The Gibbs free activation energy in CDCl₃, ΔG_{exp}^{+} , was found to be 64 ± 2, 50 ± 2, 41 ± 2 and 63 ± 2, respectively. These findings were compared with related ab initio and DFT results on simulated situation. Theoretical methods tested, were comparable to the present D ¹H NMR data.

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Introduction

Multicomponent reactions (MCRs) by virtue of their convergence, productivity, facile execution and generally high yields of products have received great attention from combinatorial chemistry [1-5]. These reactions have gained more use in synthetic organic chemistry [6-13]. The fascinating chemistry that stems from the addition of nucleophiles to activated acetylenic

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compounds has evoked considerable interest. Usually, the addition of nucleophiles devoid of an acidic hydrogen atom leads to a 1:1 zwitterionic intermediate that can undergo further transformations culminating in a stabilized product [14]. It is known that groups such as triphenylphosphine, [15–17] pyridine, [18–20] amines [21,22] and isocyanides [23] can invoke a zwitterions formation. Moreover, MCRs are important systems in organic chemistry because of their application in the synthesis of organic products [24–31], especially in the synthesis of phosphorus ylides and naturally occurring products with biological and pharmacological attributes [32–34]. Some of the phosphorus ylides exhibited the dynamic ¹H NMR effect which provides good

G R A P H I C A L A B S T R A C T





Fig. 1. The reaction between 4-hydroxybenzaldehyde 1 and phenylisocyanate 2 lead to carbamate 3, it was employed in the presence of triphenylphosphine 4 and dimethyl acetylenedicarboxylate (DMAD) 5 for the synthesis of dimethyl-2-[4- formylphenyl phenylcarbamate-N-yl]-3-(triphenylphosphoranylidene) butandioate 6.

information regarding the interchangeable process of rotational isomers, which in turn provides important kinetic data [35–42].

In the present work, reaction between 4-hydroxybenzaldehyde **1** and phenylisocyanate **2** leads to 4-formylphenyl phenylcarbamate **3** then the product is utilizes as an NH source in the presence of triphenylphosphine **4** and dimethyl acetylenedicarboxylate (DMAD) **5** for the synthesis of dimethyl-2-[4-formylphenyl phenylcarbamate-*N*-yl]-3-(triphenylphosphoranylidene) butandioate **6** in excellent yield (Fig. 1). The experimental data of ¹H, ¹³C and ³¹P NMR indicate two rotational isomers of ylide **6** with the major *Z*-**6** and minor *E*-**6** forms. Herein, in order to further understand the mechanism of the interchangeable process around the C=C, C-C, HC-NC and OC-NC bonds, the rotational energy barrier (ΔG_{exp}^{\neq}) obtained by the dynamic ¹H NMR. The experimental data was also compared with the theoretical rotational barrier (ΔG_{calcd}^{\neq}) calculated using the DFT and ab initio methods.

Methods

Melting points and IR spectra of all compounds were measured on an Electro thermal 9100 apparatus and a JASCO FT-IR spectrometer, respectively. The ¹H, ¹³C, and ³¹P NMR spectra were obtained with a Bruker DRX-500 and 400 Avance instrument using CDCl₃ and acetone-d₆ as applied solvent TMS as internal standard at (400.1, 100.6, 161.9 MHz), respectively. Elemental analyses for C, H, and N were performed using a Heraeus CHN-O-Rapid analyzer. In addition, the mass spectra were recorded on an Agilent Technologies 5973 mass spectrometer operating at an ionization potential of 70 eV. Triphenylphosphine, dialkyl acetylenedicarboxylates and 4-formylphenyl phenylcarbamate were obtained from Fluka and used without further purification. In order to determine theoretical hindered internal rotational in the rotational interchangeable processes of the two Z- and E-isomers, first their structures were optimized using the ab initio and DFT methods at the HF/6-31G (d,p) and B3LYP/6-31G (d,p) levels of theory by the GAMESS program [43]. Then, relative energy versus dihedral angles was plotted by scanning method at the HF/6-31G (d,p) and B3LYP/6-31G (d,p) levels of theory, and all points in energy profile were fully optimized.

Experimental

To a magnetically stirred solution of 4-hydroxybenzaldehyde **1** (0.122 g, 1 mmol) and phenylisocyanate **2** under solvent-free condition at 6 h obtained carbamate **3**, then to a magnetically stirred solution of compounds with triphenylphosphine (0.26 g, 1 mmol) in 10 mL of dichloromethane, dimethyl acetylenedicarboxylate (0.14 g, 1 mmol) was added drop wise over a period of 10 min at room temperature. After approximately 24 h of stirring at room temperature, the product was filtered and washed with cold diethyl ether (3×5 mL). Dimethyl-2-[4-formylphenyl phenyl-carbamate-*N*-yl]-3-(triphenylphosphoranylidene) butandioate **6** was obtained in excellent yield (Fig. 1). The mechanism of this reaction has not been experimentally established; nevertheless an illustrative mechanism is shown in Fig. 2.

The structure of compound **6** was deduced from elemental analysis, IR, ¹H, ³¹P, ¹³C NMR and mass spectroscopy and no other product could be detected by NMR spectroscopy. The mass spectrum displayed a molecular ion peak at the appropriate m/z value. Any initial fragmentations involve partial or complete loss of the side chains and scission of the aromatic rings. The ¹H, ¹³C and ³¹P NMR spectra of ylide **6** are consistent with the presence of two isomers. The ylide moiety of this compound is strongly conjugated with the adjacent carbonyl group and the rotation around the partial double bond in the two *E*-**6** and *Z*-**6** geometrical isomers quite the reverse of rotation around the C=C bond (Fig. 3) and is



Fig. 2. A plausible mechanism for the synthesized product 6.



Fig. 3. Interchangeable processes of rotational isomers for the synthesized ylide 6.

slow on the NMR time scale at ambient temperature. Selected ¹H, ¹³C and ³¹P NMR chemical shifts and coupling constants in the major and minor geometrical isomers of product **6** are shown in the below section.

Dimethyl 2-[(4-formylphenyl)phenylcarbamate-N-yl]-3-(triphenylphosphoranylidene)butandioate (6)

Orange powder, yeild: 0.61 g (95%), mp 127–129 °C. IR (KBr) (v_{max} , cm⁻¹): 1745, 1712, 1644 (C=O).

Major isomer Z-**6** (67%): ¹H NMR (400.22 MHz, δ, CDCl₃): 2.92 and 3.83 (6H, 2s, 2 OCH₃), 5.00 (1H, d, ${}^{3}J_{PH} = 20.0$ Hz, P=C–CH), 6.90–7.9 (23H, m, 3C₆H₅ and carbamate), 9.93 (1H, s, CHO). ¹³C NMR (100.63 MHz, δ, CDCl₃): 41.07 (d, ${}^{1}J_{PC} = 135.85$ Hz, P=C), 52.40 and 52.71 (2s, 2 OCH₃), 62.96 (P=C–CH, ${}^{2}J_{PC} = 17.1$ Hz), 125.34 (d, ${}^{1}J_{PC} = 91.6$ Hz, C_{ipso}), 128.67 (d, ${}^{3}J_{PC} = 12.1$ Hz, C_{metha}), 132.23 (d, ${}^{4}J_{PC} = 2.0$ Hz, C_{para}), 134.78 (d, ${}^{2}J_{PC} = 10.1$ Hz, C_{ortho}), 119.62, 125.14, 127.46, 128.14, 128.56, 131.39, 139.05 (7s, C_{arom}), 152.65 (s, C, Ar–O), 156.56 (s, C=O_{carbamat}), 168.61 (d, ${}^{3}J_{PC} = 13.08$ Hz, C=O), 172.87 (d, ${}^{3}J_{PC} = 14.08$ Hz, P–C=C). ³¹P NMR (162.01 MHz, δ, CDCl₃): 24.78 [s, (Ph₃P⁺-C)]. *Minor isomer E*-**6** (33%): ¹H NMR (400.22 MHz, δ, CDCl₃): 3.13 and 3.92 (6H, 2s, 2 OCH₃), 5.01 (1H, d, ${}^{3}J_{PH} = 20.0$ Hz, P=C–CH), 6.9–7.9 (23H, m, 3C₆H₅ and carbamate) 9.93 (1H, s, CHO). ¹³C NMR (100.63 MHz, δ, CDCl₃): 48.98 and 49.55 (2s, 2 OCH₃), 62.85 (d, ${}^{2}J_{PC} = 17.1$ Hz, P=C–CH), 126.52 (d, ${}^{1}J_{PC} = 92.2$ Hz, C_{ipso}), 127.87 (d, ${}^{3}J_{PC} = 12.1$ Hz, C_{metha}), 133.53 (d, ${}^{4}J_{PC} = 2.0$ Hz, C_{para}), 134.72 (d, ${}^{2}J_{PC} = 10.1$ Hz, C_{ortho}), 118.52, 125.04, 127.46, 126.12, 128.16, 133.27, 138.01 (7s, C_{arom}), 152.08 (s, CAr–O), 154.60 (s, CO_{carbamat}), 170.02 (d, ${}^{3}J_{PC} = 13.08$ Hz, C=O), 173.84 (d, ${}^{2}J_{PC} = 14.08$ Hz, P–C=C). ³¹P NMR (162.01 MHz, δ, CDCl₃): 24.78 [s, (Ph₃P⁺-C)].

Results and discussion

Dynamic effect for the E-6 and Z-6 rotational isomers as a result of restricted rotational around the partial carbon–carbon double bond (process a, C=C) (Fig. 3)

Two doublets (δ = 5.03 and 5.04 ppm) are observed for the CH protons of major and minor isomers of compound **6** in the ¹H NMR spectrum in CDCl₃ solvent at ambient temperature which

Table 1

The key D ¹H NMR data and related thermodynamic parameters of activation estimated for restricted rotational process and the related theoretical data around the carboncarbon double bond C=C.

	$E_{\rm a}$ (kJ mol ⁻¹)	ΔS^{\neq} (kJ mol ⁻¹ K ⁻¹)	ΔH^{\neq} (kJ mol ⁻¹)	ΔG^{\neq} (kJ mol ⁻¹)	Δv (Hz)	$k_{c}(s^{-1})$	$T_{\rm c}$ (K)
Exprimental ⁱ	_	-	-	64 ± 2	48	107.56	308
Theoretical ^j	72.21	-0.017	69.65	75.00	-	-	308
Theoretical ^k	64.92	-0.021	62.36	68.93	-	-	308

ⁱ Data obtained from the ¹H NMR study.

^j Data obtained using ab initio method at HF/6-31G (d,p) level of theory.

^k Data obtained using DFT method at B3LYP/6-31G (d,p) level of theory.

appear as a broad doublet near 298 K. From the coalescence temperature of the proton resonances of the CH group and using the equation for the rate constant, the first-order rate constant (k)was calculated for the bond rotation in product **6** as 107.56 s^{-1} at 308 K. For this process, activation and kinetic parameters involving k_c and ΔG_{exp}^{\neq} and other activation parameters such as E_a , ΔH^{\neq} and ΔS^{\neq} calculated for ylide **6** are accumulated in Table 1. In order to determine the theoretical rotational energy barrier in the rotational interchangeable process (a) of the two Z- and E isomers in the ylide 6, their structures were first optimized at the HF/6-31G (d,p) and B3LYP/6-31G (d,p) levels of theory [44–47]. Then, the scanning method was employed at the same levels with a change in dihedral angle (OCCP) on the basis of 4 degrees rotation in each step. This gave the relative energy at each point in accord with 4 degrees rotation in a fully optimized process. Fig. 4 showed the optimized structures corresponding to the E-6, Z-6 isomers and TS. Then, the corresponding relative energies were plotted versus the dihedral angle (OCCP, Fig. 5). As can be seen in Fig. 5, a transition state (TS) has appeared at the top of this plot. Frequency calculations were employed for all states involving TS and the first negative frequency value (-70.93 and -71.25 Hz at HF/6-31G (d,p) and B3LYP/6-31G (d,p) levels, respectively) could be considered as good proof in confirming the TS structure. With respect to the relative energies obtained from Fig. 5, and relevant equations [35,40], values of E_a , ΔH^{\neq} , ΔG^{\neq} , ΔS^{\neq} were calculated for the restricted rotational process (a) around the C=C double bond at the HF/6-31G(d,p) and B3LYP/6-31G (d,p) levels of theory. Results are accumulated in Table 1 along with the experimental data that has been obtained from the dynamic ¹H NMR effects at the experimental temperature of 308 K. The results indicated that there is a good agreement between the experimental rotational energy barrier (ΔG_{exp}^{\neq} = 64 ± 2) and those obtained at the B3LYP/6-31G (d,p) level (ΔG_{calcd}^{\neq} = 68.93). It seems that the B3LYP/6-31G (d,p) is a suitable level for the calculation of restricted rotational process (a) around the C=C double bond in a huge molecule like the ylide **6** with large atoms such as 6 oxygen, 1 nitrogen and 1 phosphorus atoms and a large number of other atoms.



Fig. 5. Profile of relative energy in restricted rotational process around the C=C bond for the ylide **6** versus dihedral angel (OCCP) at the B3LYP/6-31G (d,p) level.

Dynamic effects for the rotational around the carbon–carbon single bonds (processes b and c, H–C–C–PPh3) (Fig. 3)

Herein, when the temperature was reduced with respect to the ambient temperature, the ¹H NMR spectrum of the *Z*-**6** isomer in CDCl₃ at +5 °C showed a resonance arising from the methoxy proton (H–C–C–P, 3JPH) which is broad in comparison with a corresponding doublet that was measured at the ambient temperature. When temperature was considerably reduced, the methoxy proton coalesces near the 296 K and a sharp signal resonance at 298 K, which is related to the rotational process around the carbon–carbon single bond (H–C–C–PPh3) in the *Z*-**6** isomer. The experimental data are reported in Table 2. It must be mentioned that the methoxy protons of *E*-**6** isomer coalescence near 291 K and appear as a sharp signal resonance at 293 K (Fig. 3, process b). These values are also reported in Table 2. In addition, as mentioned in the previous section, theoretical studies were investigated on the basis of rotation around the carbon–carbon single



Fig. 4. Optimized structures corresponding to the E-6, Z-6 isomers and TS.

Table 2

The key D ¹ H NMR data and related thermodynamic parameters of activation estimated for rotational process and the related theoretical data around the carbon-carbon sing
bond C–C.

	Ea (kJ mol ⁻¹)	ΔS^{\neq} (kJ mol ⁻¹ K ⁻¹)	ΔH^{\neq} (kJ mol ⁻¹)	ΔG^{\neq} (kJ mol ⁻¹)	Δv (Hz)	$k_{\rm c} ({ m s}^{-1})$	$T_{\rm c}$ (K)
Exprimental ⁱ	-	-	-	41 ± 2	44	98.68	203
Exprimental ^j	-	-	-	39 ± 2	44	89.71	193
Theoretical ^k	79.14	-0.005	77.46	78.93	-	-	203
Theoretical	47.51	-0.011	45.82	48.10	-	-	203

Data obtained from the ¹H NMR study for *Z*-**6**. Data obtained from the ¹H NMR study for *E*-**6**.

^k Data obtained using ab initio method at HF/6-31(d,p) level of theory for Z-6.

¹ Data obtained using DFT method at B3LYP/6-31G (d,p) level of theory for Z-6.



Fig. 6. Profile of relative energy in rotational process around the C-C bond for the Z-6 versus dihedral angel (CCCP) at the B3LYP/6-31G (d,p) level.

Table 3 The key D¹H NMR data and related thermodynamic parameters of activation estimated for rotational process and the related theoretical data around the nitrogen-carbon single bonds HC-NC

	Ea (kJ mol ⁻¹)	ΔS^{\neq} (kJ mol ⁻¹ K ⁻¹)	ΔH^{\neq} (kJ mol ⁻¹)	ΔG^{\neq} (kJ mol ⁻¹)	$\Delta v(Hz)$	$k_{\rm c} ({\rm s}^{-1})$	<i>T</i> _c (K)
Exprimental ⁱ	88.79	0.140	87.77	50 ± 2	12	26.91	233
Exprimental ^j	27.30	-0.098	26.47	47 ± 2	16	35.88	221
Theoretical ^k	24.04	-0.330	22.10	29.62	-	-	233
Theoretical ¹	37.98	-0.020	36.04	40.76	-	-	233

ⁱ Data obtained from the ¹H NMR study for Z-6.

Data obtained from the ¹H NMR study for E-6.

Data obtained using ab initio method at HF/6-31 (d,p) level of theory for Z-6.

¹ Data obtained using DFT method at B3LYP/6-31G (d,p) level of theory for Z-6.

bond in the Z-6 isomer (H-C-C-PPh3, process b) using the HF/6-31G (d,p) and B3LYP/6-31G(d,p) levels of theory. Then, relative energies were plotted against dihedral angle (CCCP, Fig. 6). As can be seen in Fig. 6, three transition states $(TS_1, TS_2 \text{ and } TS_3)$ with negative frequency values had been appeared on the tops of this plot. Rotational energy barriers (ΔG_{calcd}^{\neq}) at *TS*_s points exhibited that TS₃ has a higher value; hence, this process was chosen as a main rotational barrier. All theoretical calculations are reported in Table 2. As can be seen, the B3LYP/6-31G (d,p) is a better level than HF/6-31G (d,p).

Dynamic effects for the restricted rotational around the nitrogencarbon single bonds (processes d and e, N-C-COOCH3) (Fig. 3)

More investigations were made for the rotation around the carbon-nitrogen single bonds in the Z-6 and E-6 isomers and the results are summarized in Tables 3. The same procedure was employed as in the previous sections and theoretical study was investigated on the basis of rotation around the carbon-nitrogen single bond (HC--NC) only for Z-6 isomer at the HF/6-31G (d,p) and B3LYP/6-31G(d,p) levels of theory. Then, relative energy versus dihedral angle (CNCC) was plotted in Fig. 7. As can be seen, three transition states $(TS_1, TS_2 \text{ and } TS_3)$ have appeared on this plot. Frequency calculations were employed for all TSs and ground states and TS structures were confirmed. Rotational energy barrier $(\Delta G_{calcd}^{\neq})$ for all TSs exhibited that TS₂ has a higher value and hence TS₂ was chosen as a main rotational barrier. Theoretical data $(\Delta G_{calcd}^{\neq})$ reported in Table 3 indicate that there is a good agreement between the experimental rotational barrier (ΔG_{exp}^{\neq}) and the obtained data at B3LYP/6-31G (d,p) level of theory.

Dynamic effects for the restricted rotational around the carbonnitrogen single bond (processes f and g, OC-NC) (Fig. 3)

Through investigation of the 1 H NMR spectra of product **6**, the dynamic ¹H NMR effect has been observed which is attributed to restricted rotational process around the carbon-nitrogen bond (Fig. 3, processes f and g) the experimental data are accumulated



Fig. 7. Profile of relative energy in rotational process around the HC-NC bond for the Z-6 versus dihedral angel (CNCC) at the B3LYP/6-31G (d,p) level.

 Table 4

 The key D ¹H NMR data and related thermodynamic parameters of activation estimated for rotational process and the related theoretical data around the nitrogen-carbon single bond OC-CN.

	$E_{\rm a}$ (kJ mol ⁻¹)	ΔS^{\neq} (kJ mol ⁻¹ K ⁻¹)	ΔH^{\neq} (kJ mol ⁻¹)	ΔG^{\neq} (kJ mol ⁻¹)	Δv (Hz)	$k_{\rm c}({ m s}^{-1})$	$T_{\rm c}$ (K)
Exprimental ⁱ	51.38	0.012	58.99	63 ± 2	24	53.82	296
Exprimental ^j	54.54	0.011	62.18	63 ± 2	20	44.85	291
Theoretical ^k	29.57	-0.046	27.11	40.80	-	-	296
Theoretical ¹	37.07	-0.049	34.61	49.18	-	-	296

ⁱ Data obtained from the ¹H NMR study for Z-6.

^j Data obtained from the ¹H NMR study for E-6.

^k Data obtained using ab initio method at HF/6-31G (d,p) level of theory for Z-6.

¹ Data obtained using DFT method at B3LYP/6-31G (d,p) level of theory for Z-6.



Fig. 8. Profile of relative energy in rotational process around the OC-NC bond for the Z-6 versus dihedral angel (CNCO) at the B3LYP/6-31G (d,p) level.

in Table 4. The same procedure was employed as previous sections. Then, relative energy versus dihedral angle (OCNO) was plotted in Fig. 8. As can be seen, two transition states (TS_1 and TS_2) have appeared on this plot. As a result, all theoretical data with respect to TS_1 reported in Table 4. Herein, B3LYP/6-31G (d,p) was also recognized as a suitable level.

Conclusion

Four rotational processes around the C=C, C-C, HC-NC and OC-NC bonds were investigated using dynamic ¹H NMR and theoretical calculations at the HF/6-31G (d,p) and B3LYP/6-31G(d,p) levels of theory.

The experimental and theoretical data, taken together, indicated that the rotational energy barrier around the C=C bond is considerably high, and observation of the two rotational isomers, *E*-**6** and *Z*-**6**, is impossible (seen as a single isomer) at high temperature, since the rate of rotation ($k = 107.56 \text{ S}^{-1}$) around the C=C bond is too fast on the NMR time scale. Herein, the B3LYP/ 6-31G (d,p) 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 ylide **6** that suffers from crowds of atoms during the interchangeable rotational processes. Application of a solvent in the presence of a huge molecule caused so many complications that it became an unsuccessful performance. In total, our attempts failed to employ solvents media. Under this condition (huge molecules with a large number of atoms such as seven oxygen, one nitrogen and one phosphorus atoms and other atoms along with solvents media), employment of structure optimization was impossible.

The results also showed the rotational energy barrier around the OC—NC single bond is higher than the C—C, HC—NC single bonds. It seems that participation of lone pair of nitrogen atom in resonance with conjugated carbon causes a partial double bond character. Herein, the B3LYP/6-31G (d,p) level provides the more reasonable results in comparison with HF/6-31G (d,p) level.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2015.02.084.

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