

## Synthesis of dimethyl-*N*-(1,6-dimethylphenylsulfonamino-*N*-yl)-3-(diphenoxyphosphoryl) butenedioate and assignment of the structure by VT-NMR and X-ray diffraction

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**Abstract:** A new class of sulfonamide phosphonate diester was synthesised and VT NMR of the compound by <sup>1</sup>H NMR technique investigated. The dynamic effect <sup>1</sup>H NMR of the compound attributed to rotational barrier around the C-N single bound. Then by the resulted data, the relevant thermodynamic parameter of activation energy was calculated.

**Keywords:** Sulfonamide phosphonate esters, Dynamic effect NMR, Rotational barrier, Thermodynamic parameters.

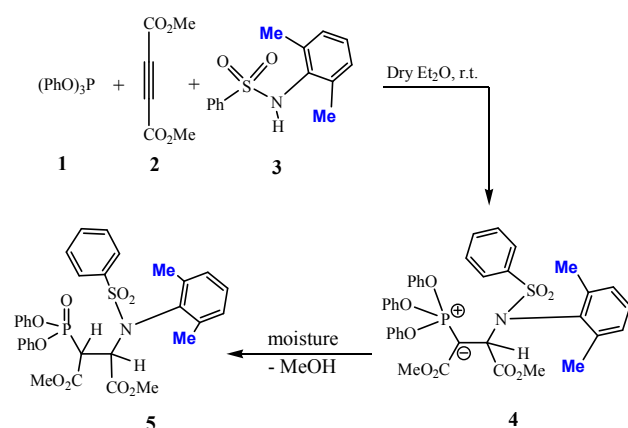
### Introduction

In pursuing our research for synthesis of phosphonate esters by using of triphenylphosphite as reagent in non polar solvent media (mixed of n-hexane and diethyl ether), some classes of phosphonate esters were synthesized [1-3]. Herein a new class of sulfonamide phosphonate ester was resulted (compound 5) which has two changeable methyl groups A and B (Scheme 1 and Fig. 1). The dynamic effect <sup>1</sup>H NMR of the following compound attributed to rotational barrier around the C-N single bound [4-9].

For this phenomenon, behavior of the molecule was monitored by <sup>1</sup>H-NMR technique at close variation of temperatures. Then by the resulted data, the relevant thermodynamic parameters were calculated.

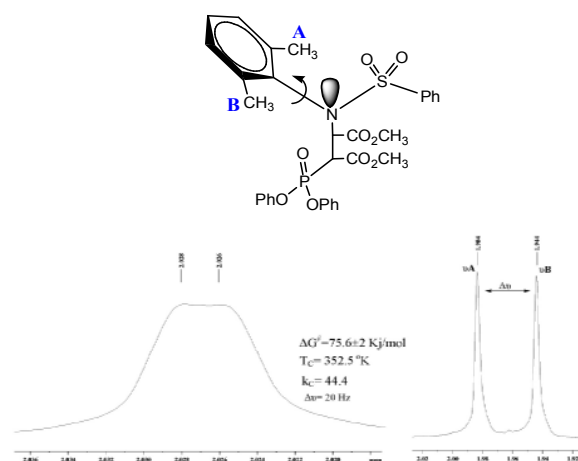
### Results and discussion

Herein to consideration of the dynamic NMR behaviour, the NMR tube that containing of compound 5, was placed in the probe of NMR heated up by slow increasing of temperature, from 298 to 360 K. Eventually the coalescence temperature was observed at TC= 352.5 K, and the activation energy ( $\Delta G^\ddagger$ ) of the rotation around C-N single bond calculated of  $75.6 \pm 2$  KJ/mol.

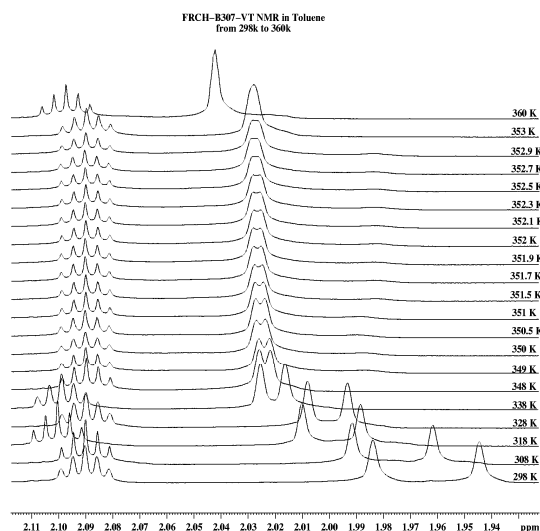


**Scheme 1.** Main reaction with the intermediate and final product.

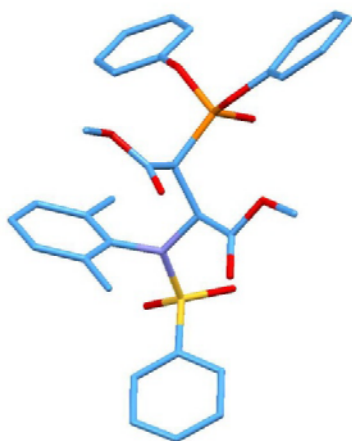
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**Figure 1.** Coalescence point and difference between the resonance frequencies of the nuclei in position A and B of compound **5** in the  $^1\text{H}$  NMR, the collected spectra relevant the dynamic effects was showed as the following VT NMR (see Figure 2).



**Figure 2.** Variation temperature  $^1\text{H}$  NMR of compound **5** from 298 to 360 K.



**Figure 3.** X-ray single crystalline structures of compound **5**. The structure of the molecule was characterized by  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$ -NMR, IR, mass, and X-ray diffraction (Figure 3 and Experimental section).

### Conclusion

In conclusion, the observed dynamic NMR effect of compound **5** arises from rotational barrier around the C-N single bond. Also other factor for this inversion would be attributed to inversion of pyramidal amine group, but the rotation barrier is the main reason for this phenomenon. Furthermore the reaction of dialkyl acetylenedicarboxylates with triphenylphosphite in

the acid-presence of NH such as sulphonamide also leads to a facile synthesis of some functionalized phosphonate ylides and phosphonate esters. Performing of the reaction under neutral conditions and the reagents is more advantageous of this methodology for synthesis of the new class of sulphonamide phosphonate esters.

### Experimental

#### General procedure

To a magnetically stirred solution of dialkyl acetylenedicarboxylate **2** (2 mmol) and sulfonamide **3** (2 mmol) was added triphenylphosphite **1** (0.62 g, 2 mmol) slowly at room temperature in dry diethyl ether as a solvent. The reaction mixture was stirred for 2 hours at room temperature. The resultant precipitate was collected and washed with cooled *n*-hexane and diethyl ether (3×5 mL) to yield the phosphonate ylide **4**. If few drops of distilled water added to the reaction mixture, then leaving the reaction mixture in an exposed vessel to air for a week, the phosphonate ester **5** is resulted. The work-up followed removal of the solvent under reduced pressure and the resultant yellow residue was collected and crystallized from ether/*n*-hexane (4:1).

#### Dimethyl-*N*-(1,6-dimethylphenylsulfonamino-*N*-yl)-3-(diphenoxyphosphoryl) butenedioate (**5**):

Colorless crystals, 0.53 g, yield 70%, m.p. 168-170 °C. IR (KBr) ( $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 2951 ( $\text{SO}_2$ ), 1781 and 1750 (2 C=O of esters), 1591 (C=C). MS, ( $m/z$ , %): 637 ( $\text{M}^+$ , 80), 544 ( $\text{M}^+$ -OPh, 95), 45160 ( $\text{M}^+$ -2Oph, 55). Anal. Calcd for  $\text{C}_{32}\text{H}_{32}\text{NO}_9\text{PS}$  C, 60.28; H, 5.06; N, 2.20; Found: C, 60.65; H, 5.40; N, 2.18.  $^1\text{H}$  NMR (500.1 MHz,  $\text{CDCl}_3$ ): 1.78, 1.79 (2×s, 6H, 2CH<sub>3</sub>), 3.5(s, 3H, OCH<sub>3</sub>), 3.6 (s, 3H, OCH<sub>3</sub>), 3.75 (dd, 1H,  $^2J_{\text{PH}} = 17$  Hz,  $^3J_{\text{HH}} = 12$  Hz), 5.7 (dd, 1H,  $^3J_{\text{PH}} = 15$  Hz,  $^3J_{\text{HH}} = 1.5$  Hz), 6.9-7.7 (m, 18H, Aromatic region).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  18.7, 19.7 (2×s, 2CH<sub>3</sub>), 46.5 (d,  $^1J_{\text{CP}} = 130.9$  Hz, P- $^{13}\text{C}$ ), 52.6, 52.9 (2×s, 2OCH<sub>3</sub>), 60.4 (d,  $^2J_{\text{CP}} = 4$  Hz, P-CH- $^{13}\text{C}$ ), 120.3 (d,  $^3J_{\text{CP}} = 4.9$  Hz, C<sub>ortho</sub> of C<sub>6</sub>H<sub>5</sub>), 120.6, 121 (d,  $^3J_{\text{CP}} = 4.3$  Hz, C<sub>ortho</sub> of C<sub>6</sub>H<sub>5</sub>), 125.5, 125.6 (2 C<sub>para</sub> of 2C<sub>6</sub>H<sub>5</sub>), 128.4, 129.0 (2C<sub>meta</sub> of 2C<sub>6</sub>H<sub>5</sub>), 129.4, 129.5, 129.8, 130.1, 132.9, 134.2, 137.9, 140.1, 141.9, 142.4, 149.9 (d,  $^2J_{\text{CP}} = 7.7$  Hz, C<sub>ipso</sub> of C<sub>6</sub>H<sub>5</sub>), 150.5(d,  $^3J_{\text{CP}} = 9.5$  Hz, C<sub>ipso</sub> of C<sub>6</sub>H<sub>5</sub>), 165.3 (d  $^2J_{\text{CP}} = 5.5$  Hz, C=O ester), 169.3 (s, C=O ester).

#### X-Ray crystallography (**5**): Crystal/refinement details:

The X-ray diffracted intensities were measured from a single crystal (**5**) of 0.33 x 0.23 x 0.11 mm at about

100 K on an Oxford Diffraction Xcalibur-S CCD diffractometer using monochromatized Mo-K $\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ .) Data were corrected for Lorentz and polarization effects and absorption correction applied using multiple symmetry equivalent reflections. The structure were solved by direct method and refined on  $F^2$  using SHELX-97 crystallographic package. A full matrix least-squares refinement procedure was used, minimizing  $w(F_o^2 - F_c^2)$ , with  $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$ , where  $P = (F_o^2 + 2F_c^2)/3$ . Agreement factors ( $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ ,  $wR2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$  and  $GOF = \{\sum [w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$  are cited, where  $n$  is the number of reflections and  $p$  the total number of parameters refined). All non-hydrogen atoms were refined anisotropically using all reflections. Positions of hydrogen atoms were localized from difference Fourier synthesis and their atomic parameters were constrained to the bonded atoms during refinement.

$C_{32}H_{32}NO_9PS$ ,  $M = 637.62$ ,  $F(000) = 1336 e$ , triclinic,  $P-1$  (No. 2),  $Z = 4$ ,  $T = 100(2) \text{ K}$ ,  $a = 8.2746(1)$ ,  $b = 16.2970(2)$ ,  $c = 23.2316(4) \text{ \AA}$ ,  $\alpha = 80.451(1)$ ,  $\beta = 89.518(1)$ ,  $\lambda = 87.915(1)^\circ$ ,  $V = 3087.35(8) \text{ \AA}^3$ ;  $D_c = 1.372 \text{ g cm}^{-3}$ ;  $\mu_{Mo} = 0.213 \text{ mm}^{-1}$ ;  $\sin\theta/\lambda_{max} = 0.7035$ ;  $N(\text{unique}) = 17954$  (merged from 91069,  $R_{int} = 0.0516$ ,  $R_{sig} = 0.0669$ ),  $N_o$  ( $I > 2 \sigma(I)$ ) = 12181;  $R = 0.0690$ ,  $wR2 = 0.1781$  ( $A, B = 0.04, 4.7$ ),  $GOF = 1.002$ ;  $|\Delta\rho_{max}| = 0.89(8) e \text{ \AA}^{-3}$ , CCDC 715537.

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