

Synthesis, Characterization, Crystal Structure and Density Functional Investigation of dialkyl(phenyl((4-(phenyl diazenyl)phenyl) amino)methyl) Phosphonate

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ABSTRACT: The reaction of 4-phenylazo-phenylamine and benzaldehydes with dimethyl phosphite resulted in three new α -azoaminophosphonates in excellent yields. Molecular identification of synthesized compounds were probed using NMR, FT-IR, and elemental analysis techniques. The single crystal X-ray diffraction studies were used to determine the molecular structure of dimethyl [(4-methoxyphenyl ((4-phenyl diazenyl) phenyl) amino) methyl] phosphonate. The synthesized molecule was crystallized in the monoclinic space group P21/c with $a=11.213(2)$, $b=19.205(4)$, $c=11.429(2)$ Å, $\beta = 116.95(3)$, $V= 2193.8(8)$ Å³. Density functional theory calculation with B3LYP/6-311++G (2d, 2p) basis set has been used to determine geometry parameters and harmonic vibrational frequencies. The optimized geometrical parameters calculated by density functional theory show satisfactory agreement with experimental values.

KEYWORDS: α -Azoaminophosphonates; 4-phenylazo-phenylamine; Dimethylphosphite; Single crystal; Density functional theory.

INTRODUCTION

The α -amino phosphonates are the product of the multicomponent condensation reaction of aliphatic/aromatic aldehydes, amines, and alkyl phosphites. These compounds have applications in the agricultural, industrial, and medicinal chemistry fields [1-3]. A wide range of biological activities such as antibacterial, antiviral, antithrombotic, anti-cancer agents, peptidase, fungicidal, herbicide, insecticide, HIV protease, and inhibitors of UDP-galactopyranose

mutase has been reported for these compounds [1-9]. The nucleophilic addition of activated phosphite to imines is one of the most appropriate synthesis methods for α -amino phosphonates [10-12]. The direct reaction of aldehydes, amines, and dialkyl phosphites leads to the one-pot synthesis of tertiary amino phosphonates [13-16]. In this research, an azo-based amine (4-phenylazo phenylamine) was used to preparation of the new α -aminophosphonates.

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Furthermore, the DFT method was performed for optimizing the geometry of these products for determining the consistency of the theoretical and experimental data.

EXPERIMENTAL SECTION

Reagents and Techniques

Infrared absorption spectra were obtained on Shimadzu 8400 S spectrometer in KBr discs. The NMR spectra of synthesized compounds were recorded on a Bruker AV 400 MHz spectrometer in DMSO- d_6 as solvent. Carbon, hydrogen, and nitrogen analyses were performed on an Elementar Vario EL III analyzer. Melting points were measured by the Electrothermal 9300 apparatus. All chemical reagents and solvents were obtained from Merck Co. The 4-phenylazo-phenylamine compound has been prepared according to the method reported in the literature [15]. The experimental data of α -azoaminophosphonate (**2a-c**) are gathered on the supplementary Information.

General procedure for the synthesis of α -azoaminophosphonate (**2a-c**)

To a stirring solution of 4-phenylazo-phenylamine (0.20 g, 1 mmol), formic acid (15 μ L of 37% aqueous solution) and benzaldehydes (1 mmol) in Ethanol (15 mL), a solution of dimethylphosphite (1.20 mmol) was added. The mixture was stirred for 3 h at 60-70 °C. The solid product was filtered and washed with diethyl ether, dried, and crystallized. The products were soluble in Methanol, dimethylsulfoxide, N,N'-dimethylformamide.

Dimethyl [(phenyl((4-phenyldiazenyl)phenyl)amino)methyl]phosphonate (**2a**)

The yellow product crystallized from cyclohexane. Yield, 0.11 g (91%). m.p.138-139 °C. FT-IR, cm^{-1} : 3274 ν (bs, NH), 3083 ν (Ar-H), 2962, 2854 ν (C-H, O-CH₃), 1589 ν (N=N), 1487 ν (C=C), 1245 ν (P=O), 1230 ν (C-N), 1059, 1045 ν_{asym} (P-O, Stretching), 1026, 1018 ν_{sym} (P-O, Stretching), 684, 763. ¹H NMR ppm: 7.76-7.74(d, 2H, J=7.20 Hz), 7.69-7.67(d, 2H, J=8.80 Hz), 7.61-7.59(d, 2H, J=7.6 Hz), 7.55-7.51(t, 2H, J=7.60 Hz), 7.47-7.43(t, 1H, J=7.20 Hz and 1H, D₂O Exchangeable), 7.40-7.36(t, 2H, J=7.60 Hz), 7.32-7.28(t, 1H, 6.80 Hz), 7.02-7.00(d, 2H, J=8.80 Hz), 5.40-5.32(dd, 1H, J=10.40 Hz, CH), 3.72-3.69(d, 3H, J=10.40 Hz, CH₃) 3.54-3.52(d, 3H, J= 10.40 Hz, CH₃). ¹³C NMR ppm: 152.70, 151.01, 150.88, 144.17, 136.46, 130.38, 129.76, 128.78, 128.68, 128.62, 128.30,

125.07, 122.30, 113.63, 54.13, 53.99, 53.93, 53.84, 53.77. Anal. Calcd. for C₂₁H₂₂N₃O₃P: C, 63.79; H, 5.61; N, 10.63. Found: 63.74; H, 5.54; N, 10.56.

Dimethyl [(4-methoxyphenyl ((4-phenyldiazenyl) phenyl) amino) methyl]phosphonate (**2b**)

The orange product crystallized from Ethanol. Yield, 0.16 g (78%). m.p.154-155 °C. FT-IR, cm^{-1} : 3261 ν (bs, NH), 3087 ν (Ar-H), 2925, 2856 ν (C-H, O-CH₃), 1589 ν (N=N), 1487 ν (C=C), 1245 ν (P=O), 1242 ν (C-N), 1047 ν_{asym} (P-O, Stretching), 1022 ν_{sym} (P-O, Stretching). ¹H NMR ppm: 7.77, 7.75(d, 2H, J=7.20 Hz), 7.69, 7.67(d, 2H, J=8.80 Hz), 7.54-7.50(m, 4H), 7.46, 7.42(t, 1H, J=7.20 Hz), 7.40, 7.36(dd, 1H, J=6.00 Hz, D₂O Exchangeable), 7.00, 6.96(d, 2H, J=8.80 Hz), 6.95, 6.93(d, 2H, J=8.80 Hz), 5.32-5.24(dd, 1H, J=10.00 Hz, CH), 3.74(s, 3H, OCH₃), 3.71-3.70(d, 3H, J=10.40 Hz, CH₃) 3.53, 3.51(d, 3H, J= 10.40 Hz, CH₃). ¹³C NMR ppm: 159.23, 152.80, 151.32, 151.20, 144.08, 129.95, 129.70, 128.42, 125.03, 122.32, 114.16, 113.65, 55.52, 53.84, 53.77, 53.69, 52.51, 51.99. Anal. Calcd. for C₂₂H₂₄N₃O₄P: C, 62.11; H, 5.69; N, 9.88. Found: 62.04; H, 5.62; N, 9.78.

Dimethyl [(4-nitrophenyl ((4-phenyldiazenyl) phenyl) amino) methyl]phosphonate (**2c**)

The yellow product crystallized from Ethanol. Yield, 0.20 g (83%). m.p.158-159 °C. FT-IR, cm^{-1} : 3217 ν (bs, NH), 3089 ν (Ar-H), 2923, 2856 ν (C-H, O-CH₃), 1591 ν_{asym} (N-O), 1589 ν (N=N), 1350 ν_{sym} (N-O), 1485 ν (C=C), 1245 ν (P=O), 1230 ν (C-N), 1043 ν_{asym} (P-O, Stretching), 1017 ν_{sym} (P-O, Stretching). ¹H NMR ppm: 8.81, 8.79(d, 2H, J=8.40 Hz), 8.02, 8.00(d, 2H, J=8.80 Hz), 7.94(s, 1H, D₂O Exchangeable), 7.92-7.90(d, 2H, J=5.6 Hz), 7.65-7.59(dd, 2H, J=8.80 Hz), 7.56, 7.54(d, 2H, J=8.40 Hz), 7.04, 6.95(m, 3H). 5.50-5.48(dd, 1H, J=10.10 Hz, CH), 3.73-3.71(d, 3H, J=10.10 Hz, CH₃) 3.53, 3.50(d, 3H, J= 10.10 Hz, CH₃). ¹³C NMR ppm: 161.22, 153.66, 152.47, 151.06, 142.70, 132.01, 129.99, 129.72, 124.35, 123.05, 122.84, 114.78, 54.31, 53.82, 53.73, 52.44, 52.36. Anal. Calcd. for C₂₁H₂₁N₄O₅P: C, 57.27; H, 4.81; N, 12.72. Found: 57.23; H, 4.77; N, 12.66.

Crystal structure analysis

The orange crystals of dimethyl[(4-methoxyphenyl((4-phenyldiazenyl)phenyl)amino) methyl] phosphonate (**2b**) were grown from ethanol at 25 °C. An STOE IPDS-2T

Table 1: Crystallographic and structure refinement data for 2b.

Empirical formula	C ₂₂ H ₂₄ N ₃ O ₄ P
Formula weight	425.41
Temperature (K)	298(2) K
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P 2 ₁ /c
Crystal size (mm ³)	0.40 x 0.40 x 0.15
a (Å)	11.213(2)
b (Å)	19.205(4)
c (Å)	11.429(2)
α (°)	90
β (°)	116.95(3)
γ (°)	90
Volume (Å ³)	2193.8(8)
Z	4
Calculated density (Mg/m ³)	1.288
Absorption coefficient(mm ⁻¹)	0.158
θ Ranges for data collection (°)	2.12 - 24.99
F(000)	896
Index ranges	-12 ≤ h ≤ 13
	-22 ≤ k ≤ 22
	-13 ≤ l ≤ 13
Data collected	10391
Reflections collected / unique	16074/3860
Completeness to theta = 24.99	100.0 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3860 / 0 / 277
Final R ₁ / wR ₂ ^a (I>2σ(I))	0.0772/ 0.1294
Final R ₁ / wR ₂ ^a (all data)	0.1745/ 0.1577
Goodness-of-fit on F ² (S)	0.891
Largest diff. peak and hole (e Å ⁻³)	0.243, -0.327

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, wR_2 = [\sum (w(F_o^2 - F_c^2)^2) / \sum w(F_o^2)^2]^{1/2}$$

diffractometer with graphite monochromated Mo-Kα radiation was used for X-ray diffraction measurements at 298 K. The plate shape crystal was chosen and mounted on a glass fiber. The cell constants and orientation matrices were achieved by the least-squares refinement of diffraction data from 3860 unique reflections. The STOE X-AREA software package was used for obtaining the data in a series of ω scans in 1° oscillation and integrated[18]. The structure of **2b** was solved by direct methods and subsequent difference Fourier maps and then refined on F² by a full-matrix least-squares procedure using anisotropic displacement parameters[19]. The atomic factors were extracted from the international tables for X-Ray crystallography[20]. Refinements were done using the X-STEP32 crystallographic software package[21]. Table 1 shows the details of the crystal structure refinement of **2b**, respectively.

Computational method

Gaussian 03 package programs were used for quantum chemical calculations[22]. The gas phase geometries of **2b** were optimized with the density functional theory method and B3LYP/6-311++G(2d,2p) level and basis set. The frequency calculations were done and set in a manner that the enhanced structures matched the global minimum. The Gauss-View program was applied to complete the vibrational band assignments[21].

RESULTS AND DISCUSSION

Synthesis and structure

In a simple experimental procedure, a mixture of benzaldehyde derivative, 4-phenylazophenylamine [17, 24], dimethylphosphite, and formic acid in ethanol were heated at 60 °C for 3 hours. The corresponding dimethyl[(aryl((4-phenyldiazenyl)phenyl)amino)methyl] phosphonate (**2a-c**) were obtained in excellent yield (Fig. 1). The synthesized compounds have been characterized by infrared, NMR, and elemental analysis spectroscopy techniques. The structure of **2b** was determined by X-ray diffraction and computed using DFT method.

NMR spectra

¹H NMR spectra of **2a-c** exhibited D₂O exchangeable doublet of doublet signals for NH in the ranges of 7.92-7.40 ppm (Figs. S2). The O-CH₃ and C3-H proton signals were observed as the doublet of doublet peaks in the range of 3.70-3.73, 3.54-3.50, and 5.24-5.50 ppm, respectively. The protons of aromatic rings exhibited

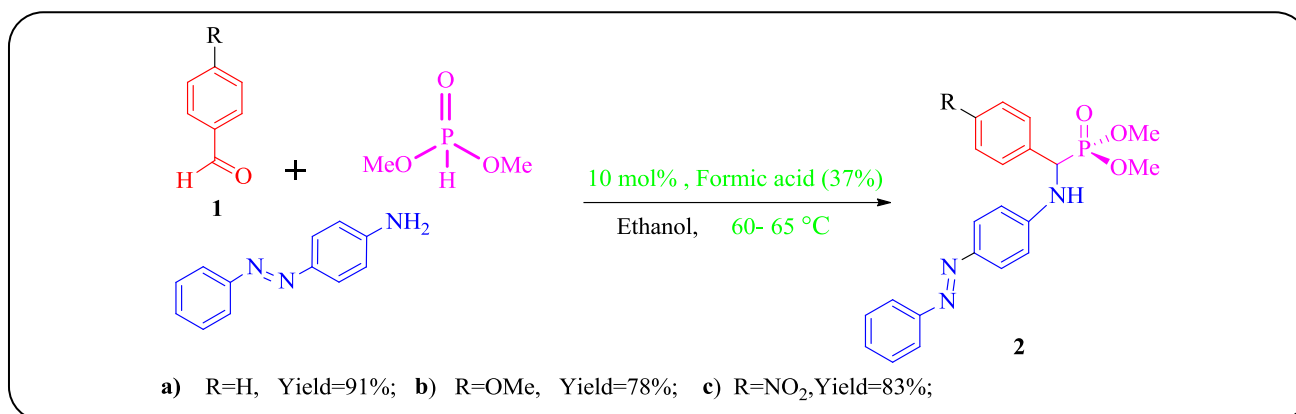


Fig. 1: The synthesis of α -azoaminophosphonate (2a-c).

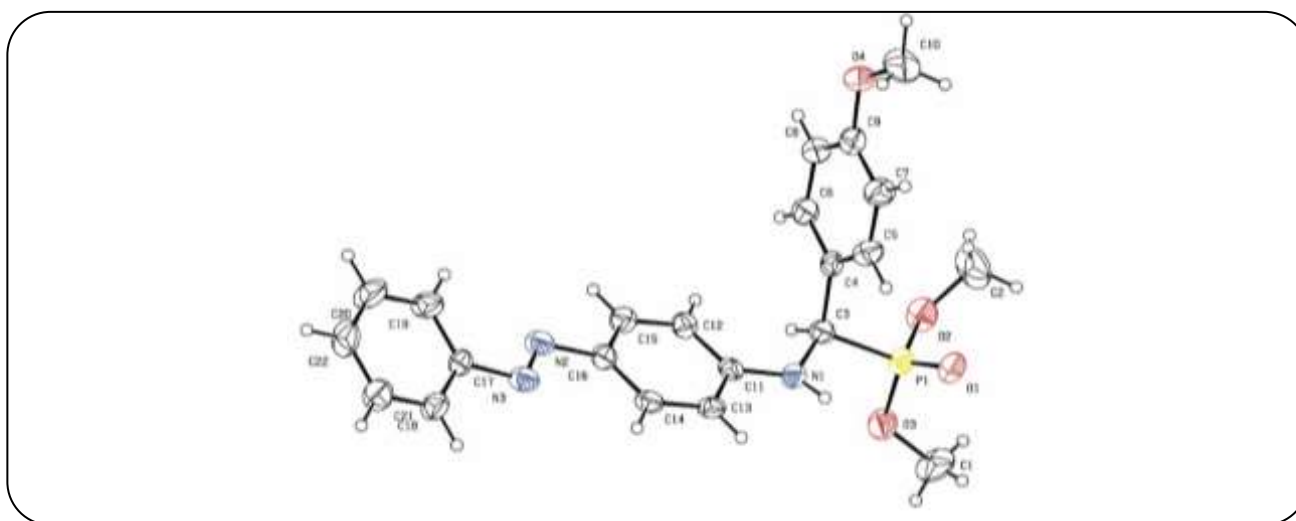


Fig. 2: Overall view of **2b**.

signals within a range of 7.24–8.79 ppm. The ¹³C NMR spectra of **2a-c** exhibited four signals for the CH₃ in the ranges of 53.99–51.99 ppm. The signals in the ranges of 54.31–53.84 ppm can be assigned to C3-H carbon. The other aromatic carbons signals were observed in the range of 161.22–113.63 ppm. Similarly, the FT-IR spectra supported these chemical shifts (Figs. S1–S3 in supporting data).

Single crystal X-ray diffraction analysis of **2b**

2b (C₂₂H₂₄N₃O₄P) was crystallized in the monoclinic space group P 21/c with Z= 4 in the unit cell (Fig. 2). The crystal structure parameters of the **2b** are a=11.213(2), b=19.205(4), c=11.429(2) Å, β=116.95(3), V=2193.8(8) Å³. The asymmetric unit in the crystal structure contains only one molecule (Fig. 2 and Table 1). The optimized parameters of **2b** have been obtained using the DFT/B3LYP/6-311G (2d,2p) basis set. The compared results of experimental and

theoretical for selected bond lengths, bond angles, and torsion angles are given in Table 2 (see Table S1 and Fig. S4 in supporting data). These results are arguing that theoretical results coincide well with the experimental characteristics. There are some structural features in the molecular structure. The bond angles (C16–N2–N3, N2–N3–C17, N3–C17–C18) and dihedral angle (C15–C16–N2–N3, C16–N2–N3–C17, N2–N3–C17–C18) between the benzene rings in the amino azobenzene framework is at the range of 112.8–115.9° and 169.9–179.8°, respectively. In addition, the C12–C11–N1 and C13–C11–N1 bond angles between the benzene ring and N₁H group are 123.4 and 118.4°, respectively. Therefore, the benzene rings along with N=N and NH groups in the amino azobenzene framework are fairly planar. Also, the C3–N1–C11, C3–N1–H1, and C11–N1–H1 bond angles are 122.8°, 117.3°, and 115.1°, respectively, showing that the N1 atom is essentially planar.

Table 2: Selected bond lengths (Å), bond angles, and torsion angles in comparison with calculated values of 2b.

Bond length (Å)	X-ray analysis	B3LYP/6-311++G(2d,2p)
P1-O1	1.448(3)	1.475
P1-O2	1.558(3)	1.609
P1-C3	1.804(4)	1.855
C3-C4	1.532(6)	1.517
C3-N1	1.453(5)	1.453
N1-C11	1.371(5)	1.379
C16-N2	1.438(6)	1.404
N2-N3	1.221(4)	1.256
N3-C17	1.453(5)	1.417
N1-H1	0.96(5)	1.004
C3-H3	0.980	1.090
bond angles (°)		
C1-O3-P1	119.3(3)	119.7
O1-P1-C3	115.0(2)	114.9
O2-P1-C3	104.33(19)	106.2
P1-C3-N1	109.7(3)	113.2
P1-C3-C4	108.3(3)	109.7
P1-C3-H3	108.2	104.0
N1-C3-C4	114.1(4)	112.5
C3-N1-H1	117(3)	114.9
C3-N1-C11	122.8(4)	125.4
N2-N3-C17	112.8(4)	115.1
N3-C17-C18	115.8(4)	115.6
Torsion angles		
C1-O3-P1-C3	-175.7(4)	176.4
O3-P1-C3-N1	64.5(4)	46.8
O3-P1-C3-C4	-170.5(3)	173.4
P1-C3-N1-C11	-173.7(3)	-100.5
C15-C16-N2-N3	177.3(4)	179.8
C16-N2-N3-C17	176.4(4)	179.9
N2-N3-C17-C18	169.9(4)	179.9

Moreover, the P1-C3-N1, P1-C3-C4, and N1-C3-C4 bond angles centered on C3 are all between 109.7(3), 108.3(3), and 114.1(4), respectively. These results indicate that the phosphonate group, 4-methoxybenzene ring, hydrogen (C3-H), and N1 have tetrahedral configurations about the C3 atom in the non-planar molecular structure. As Table 2 shows some of the calculated parameters such as the dihedral angle of optimized parameters are slightly different from the experimental ones. It noted that the calculated results correspond to the gas phase whereas experimental results belong to the solid state.

Fourier transforms infrared spectroscopic analysis

The vibrational frequencies of dimethyl[(aryl)((4-phenyldiazenyl)phenyl)amino)methyl] phosphonate (**2a-c**) were measured in the 4000-400 cm^{-1} . The spectra show the bands within a range of 3217-3274, 3194-3182, 3089-3083, and 3073-3065 cm^{-1} indexed to (N-H), (Ar-H), (O-CH₃) and (C₃-H), in the respective order. The stretching vibration at 1589 and 1487-1485 cm^{-1} are attributed to (N=N) and (C=C), respectively. Also, stretching vibration of the (C-N) and (P=O) appeared at the 1230-1242 and 1245 cm^{-1} , respectively. The vibrations observed at 1047-1043 and 1022-1017 cm^{-1} region are assigned for ν_{as} and ν_{s} of the O-P-O group. Fig. 3 shows the experimental and calculated infrared spectra of **2b**. In addition, some vibrational assignments and infrared intensities are given in Table 3. The calculated vibrational frequencies of some bonds display significant redshifts for stretching frequencies. The stretching vibrational of N-H appears at 3274 cm^{-1} , which has a reasonable deviation from the experimental value (3500-3300 cm^{-1}).

The aromatic C-H stretching vibrations were detected at 3182 cm^{-1} and were computed at 3188 and 3180 cm^{-1} . The calculated ν_{as} of CH₃ stretching vibrations were detected at 3134, 3126, 3120 cm^{-1} , whereas ν_{s} stretching mode was found at 3051, 3049, and 3017 cm^{-1} . These stretching vibrations were found at 3132 and 3050 cm^{-1} in the experimental IR spectra. The modes of aromatic C-H out-of-plane and in-plane bending are distinguished in the 1000-600 cm^{-1} and 1475-1000 cm^{-1} regions (usually mixed with C-C modes) [25, 26].

The experimental values of out-of-plane bending modes were observed at 945 and 763 cm^{-1} and calculated at 941 and 764. However, the in-plane bending frequencies were detected at 1163 cm^{-1} and computed at 1159 cm^{-1} .

Table 3: The selected experimental and calculated wave numbers (cm^{-1}) for compound **2b** calculated by B3LYP/6-311++G (2d, 2p) method.

Experimental ν	Theoretical		Vibrational assignment ^b
	ν	Int. ^a	
3274	3637	80	νNH
3194	3197	21	$\nu\text{CH(Ar)}$
3182	3188	22	
	3180	5	
3132	3134	21	$\nu_{\text{as}}\text{CH}_3$
	3126	23	
	3120	13	
3066	3063	8	$\nu\text{C3-H}$
3050	3051	66	$\nu_s\text{CH}_3$
	3049	47	
	3017	54	
1589 1564	1613	15	$\nu\text{C=C} + \nu\text{N=N}$
	1552	96	
	1545	535	
	1535	16	
1476	1480	2	$\beta_s\text{CH}_3 + \beta_{\text{as}}\text{CH}_3$
	1477	1	
	1474	9	
1444	1471	195	$\nu\text{C=C} + \nu\text{N=N} + \beta\text{N-H} + \beta\text{P-C}$
	1449	13	
1311	1320	94	$\nu\text{C-N} + \beta\text{C3-H} + \beta\text{CCC(Ar)}$
1245	1258	110	$\nu\text{P=O} + \nu\text{C-C}$
	1232	60	
1163	1159	233	$\nu\text{C-N} + \beta\text{CH} + \alpha\text{CH(aliph)}$
1059	1055	420	$\nu\text{P-O-C} + \beta\text{CCC(Ar)}$
1026	1038	342	
	1029	2	
945	941	4	$\gamma\text{H-C=C}$
844	842	66	$\nu\text{P-O-C} + \beta\text{CCC(Ar)}$
763	764	21	$\gamma\text{(H-C=C)} + \nu\text{P-C} + \delta\text{CH}_3$
684	689	16	$\nu\text{P-C}$

a. Calculated infrared intensities in km/mol .

b. Abbreviation: ν stretching, β bending, α scissoring, δ rocking, γ out of plane, s symmetry, as asymmetry

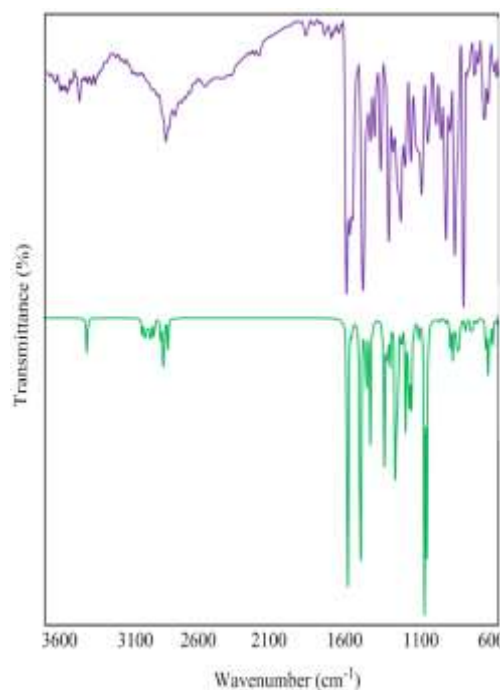


Fig. 3: The experimental (top) and calculated (bottom) FT-IR spectrum of **2b**

The stretching vibration of N=N bond in the experimental IR spectrum was appeared at 1589 cm^{-1} and calculated at $1613, 1552, 1545,$ and 1535 cm^{-1} (usually mixed with the aromatic C=C stretching mode). The C=C stretching vibrations were observed at 1487 cm^{-1} , while the matching computed values were 1488 cm^{-1} [26, 27]. The stretching absorption calculation of C-N shows three bands at $1362, 1266,$ and 1103 cm^{-1} , which matched the experimental values at $1311, 1230,$ and 1108 cm^{-1} [28]. The experimental infrared spectrum shows strong bonds at 1059 and 1026 cm^{-1} assigned for ν_{as} and ν_s of the O-P-O group and computed at 1055 and 1038 . The calculated C-C-C deformation frequencies of aromatic rings were detected at $1320, 1038,$ and 1029 cm^{-1} (mixed with aromatic C-H torsion, C-N and P-O-C, in the respective order). These values corresponded at 1311 and 1026 cm^{-1} in experimental values. The computed frequencies coincided very well with the experimental data. The calculated frequencies showed a good agreement with experimental data.

The proposed mechanism

The suggested mechanism for the synthesis of azo- α -aminophosphonate by aqueous formic acid is shown

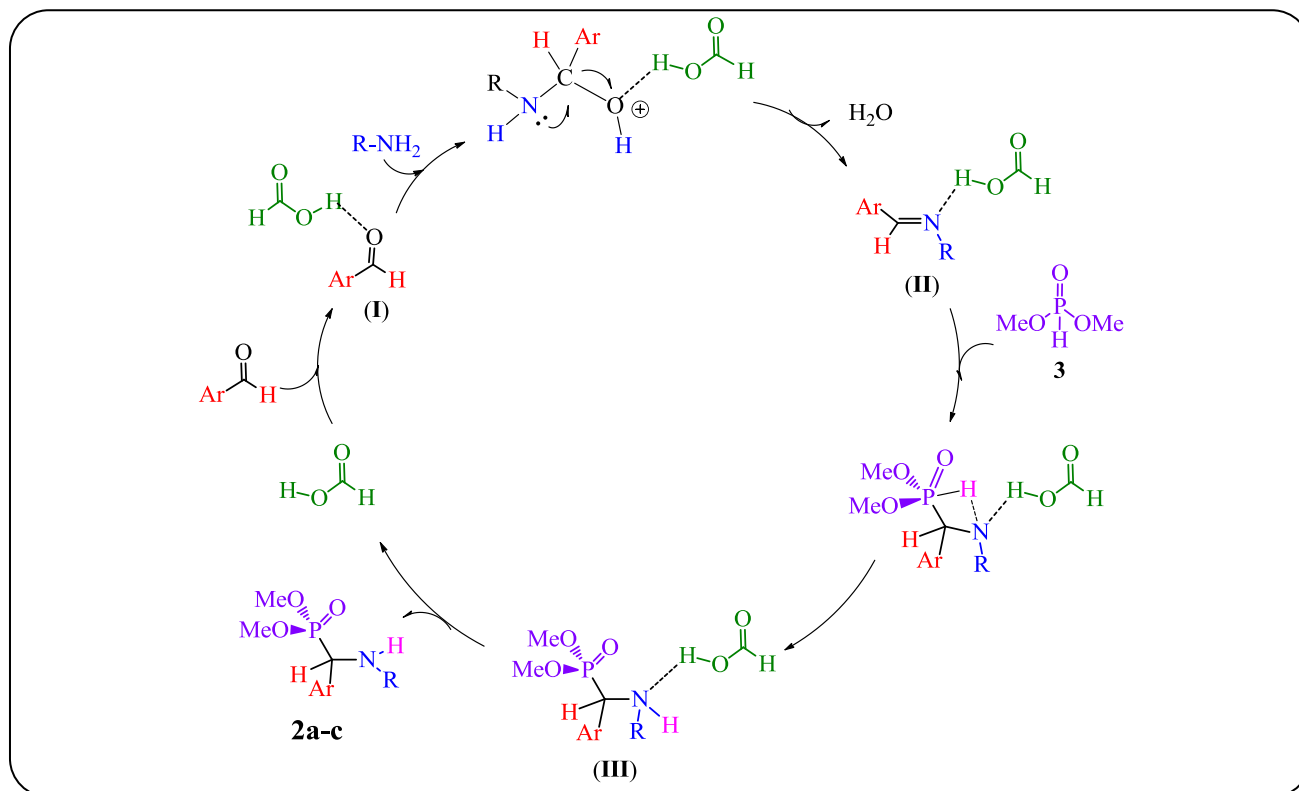


Fig. 4: The proposed mechanism for synthesis of α -azoaminophosphonate (**2a-c**) in aqueous formic acid as organocatalyst.

In Fig. 4 [13]. The first step is the activation of carbonyl groups in aldehydes by hydrogen bond interaction with formic acid (**I**). Second, an imine intermediate (**II**) was obtained by the addition of an amine to activated carbonyl. The formation of the imine intermediate by formic acid was reported in our former research [13]. Also, the addition of nucleophilic phosphonate **3** to imine intermediate (**II**) causes the formation of α -azoaminophosphonates (**2a-c**).

CONCLUSIONS

The present work reports the synthesis of α -azoaminophosphonates compounds dimethyl(aryl((4-(phenyldiazenyl)phenyl)amino)methyl)phosphonate (**2a-c**). The identity of the crystal structure was confirmed using a single crystal X-ray diffraction technique and the crystals belong to the monoclinic system with $P2_1/c$ space group. The comparison of calculated and experimental parameters showed good agreement between them. The amino azobenzene framework is essentially planar with the angle of 20.28° between two phenyl rings. Also, the N_1 atom is essentially planar. In the non-planar structure of **2b**, the phosphonate group, 4-methoxybenzene ring, hydrogen (C_3-H) and N_1 are tetrahedral configurations about the C_3 atom.

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REFERENCES

- [1] Schug K.A., Lindner W., [Noncovalent Binding Between Guanidinium and Anionic Groups: Focus on Biological-and Synthetic-Based Arginine/ Guanidinium Interactions with Phosph\[on\]ate and Sulf\[on\]ate Residues](#), *Chem. Rev.* **105**: 67-114 (2005).
- [2] Palacios F., Alonso C., Santos J.M., [Synthesis of \$\beta\$ -Aminophosphonates and-Phosphinates](#), *Chem. Rev.* **105**: 899-932(2005).
- [3] Kukhar V.P., Hudson H.R., [Aminophosphonic and Aminophosphinic Acids: Chemistry and Biological Activity](#), John Wiley & Sons Ltd, June 2000. ISBN: 978-0-471-89149-9.
- [4] Moonen K., Laureyn I., Stevens C.V., [Synthetic Methods for Azaheterocyclic Phosphonates and Their Biological Activity](#), *Chem. Rev.*, **104**: 6177-6216 (2004).

- [5] Pan W., Ansiaux C., Vincent S.P., [Synthesis of acyclic Galactitol-and lyxitol-Aminophosphonates as Inhibitors of UDP-Galactopyranose Mutase](#), *Tetrahedron Lett.*, **48**: 4353-4356(2007).
- [6] Duke S.O., Powles S.B., [Glyphosate: A Once-in-a-Century Herbicide](#), *Pest Manag. Sci.*, **64**: 319-325(2008).
- [7] Small D.M., Coombes J.S., Bennett N., Johnson D.W., Gobe G.C., [Oxidative stress, Anti-Oxidant Therapies and Chronic Kidney Disease](#), *Nephrology*, **17(4)**: 311-321(2012).
- [8] Drag M., Grembecka J., Pawelczak M., Kafarski P., [\$\alpha\$ -Aminoalkylphosphonates as a Tool in Experimental Optimization of P1 Side Chain Shape of Potential Inhibitors in S1 Pocket of Leucine-and Neutral Aminopeptidases](#), *Eur. J. Med. Chem.*, **40**: 764-771(2005).
- [9] Kirby A.J., Warren S.G., "The Organic Chemistry of Phosphorus", Elsevier Pub. Co. (1967).
- [10] Atmani A., Combret J.C., Malhiac C., Mulengi J.K., [\$\beta\$, \$\gamma\$ -Unsaturated \$\alpha\$ -Aminophosphonates: Synthesis and Reactivity](#), *Tetrahedron Lett.*, **41**: 6045-6048 (2000).
- [11] Ordóñez M., Viveros-Ceballos J.L., Sayago F.J., Cativiela C., [Stereoselective Synthesis of \$\alpha\$ -amino-H-Phosphinic Acids and Derivatives](#), *Synthesis*, **49**: 987-997 (2017).
- [12] Chandrasekhar S., Prakash S.J., Jagadeshwar V., Narsihmulu C., [Three Component Coupling Catalyzed by TaCl₅-SiO₂: Synthesis of \$\alpha\$ -amino Phosphonates](#), *Tetrahedron Lett.*, **42**: 5561-5563 (2001).
- [13] Mohammadiyan E., Ghafari H., Kakanejadifard A., [A New Procedure for Synthesis of \$\alpha\$ -Aminophosphonates by aqueous Formic Acid as an Effective and Environment-Friendly Organocatalyst](#), *J. Chem. Sci.*, **129**: 1883-1891(2017).
- [14] Heydari A., Karimian A., Ipaktschi J., [Lithium Perchlorate/Diethylether Catalyzed Aminophosphonation of Aldehydes](#), *Tetrahedron Letters.*, **39**: 6729-6732 (1998).
- [15] Palacios F., Aparicio D., Lopez Y.L., de los Santos J.M., [Addition of Amine Derivatives to Phosphorylated 1,2-diaza-1,3-butadienes. Synthesis of \$\alpha\$ -Aminophosphonates](#), *Tetrahedron Letters*, **45**: 4345-4348 (2004).
- [16] Hamed M.A., Shaban E., Kafafy H., El Gokha A.A.A., El Sayed I., [Synthesis and Characterization of Novel Azo Disperse Dyes Containing \$\alpha\$ -amino Phosphonate and Their Dyeing Performance on Polyester Fabric](#), *Egypt. J. Chem.*, 89-95 (2017).
- [17] Mirazizi F., Bahrami A., Haghbeen K., Shahbani Zahir H., Bakavoli M., Legge R. L., [Rapid and Direct Spectrophotometric Method for Kinetics Studies and Routine Assay of Peroxidase Based on Aniline Diazo Substrates](#), *J. Enzyme Inhibit. Med. Chem.*, **31**: 1162-1169 (2016).
- [18] Stoe C., "X-SHAPE: Program for Crystal Optimization for Numerical Absorption Correction, Version 2.05", Stoe & Cie GmbH: Darmstadt, Germany, DOI (2005).
- [19] Sheldrick G.S., "SHELXS-97 and SHELXL-97, Program for Crystal Structure Solution and Refinement", University of Göttingen, Germany, (1997).
- [20] Prince E., Wilson A., "International Tables for X-Ray Crystallography", Vol. C, Kluwer Academic Publisher, Dordrecht, The Netherlands, (1995).
- [21] Stoe C., "X-STEP32, Crystallographic Package, Version 1.07 b", Stoe & Cie GmbH: Darmstadt, Germany, DOI (2000).
- [22] Frisch M., Trucks G., Schlegel H.B., Scuseria G., Robb M., Cheeseman J., Montgomery Jr J., Vreven T., Kudin K., Burant J., "Gaussian 03, Revision C. 02", Gaussian Inc, Wallingford, ct, **26** (2004).
- [23] Dennington R., Keith T., Millam J., Eppinnett K., Hovell W.L., Gilliland R., "GaussView", Version, (2003).
- [24] Omidi S., Khojasteh V., Kakanejadifard A., Ghasemian M., Azarbani F., [Synthesis, Characterization, Spectroscopy And Biological Activity of 4-\(\(3-formyl-4-hydroxyphenyl\) azo\)-1-alkylpyridinium Salts](#), *J. Chem. Sci.*, **130**:114, 1-9 (2018).
- [25] Govindasamy P., Gunasekaran S., [Experimental and Theoretical Studies of \(FT-IR, FT-Raman, UV-Visible and DFT\) 4-\(6-methoxynaphthalen-2-yl\) butan-2-one](#), *Spec. Chim. Acta. A.*, **149**: 800-811 (2015).
- [26] Govindarajan M., Ganasan K., Periandy S., Mohan S., [DFT \(LSDA, B3LYP and B3PW91\) Comparative Vibrational Spectroscopic Analysis of A-Acetonaphthone](#), *Spec. Chim. Acta. A.*, **76**: 12-21 (2010).

- [27] Teimouri A., Chermahini A.N., Taban K., Dabbagh H.A., Experimental and CIS, TD-DFT, AB Initio Calculations of Visible Spectra and The Vibrational Frequencies of Sulfonyl Azide-Azoic Dyes, *Spec. Chim. Acta. A.*, **72**: 369-377 (2009).
- [28] Alam M.S., Lee D.-U., Spectral (FT-IR, FT-Raman, UV, and fluorescence), DFT, and Solid State Interaction Analyses of (E)-4-(3, 4-dimethoxybenzylideneamino)-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-one, *J. Mol. Struc.*, **1128**: 174-185 (2017).