Crystal Structure of and *ab initio* Calculations on $[(C_6H_5)(CH_3)CH\text{-}NH]\text{-}P(O)(p\text{-}OC_6H_4CH_3)_2$, Syntheses and Spectroscopic Characterization of *N*-Benzyl Phosphoramidic Acid (4-Methylphenyl)ester Derivatives

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Some new *N*-benzyl phosphoramidic acid (4-methylphenyl)ester derivatives were synthesized and characterized by ^{1}H, ^{13}C, ^{31}P NMR and IR spectroscopy and elemental analysis. The structure of $[(C_6H_5)(CH_3)CH\text{-}NH]P(O)(p\text{-}OC_6H_4CH_3)_2$ (**2**) was investigated. This compound exists in polymeric zigzag chains in the crystalline lattice produced by hydrogen bonding built from two alternating independent molecules. NMR data indicate two diastereotopic *p*-cresol groups as confirmed by X-ray crystallography. *Ab initio* calculations were performed on the geometry of compound **2** at the UHF/6-311G** and B3LYP/6-311G** levels. The optimized structure of each independent molecule contains two different *p*-cresol groups, in agreement with the experimental results.

Key words: *N*-Benzyl Phosphoramidic Acid (4-methylphenyl)esters, X-Ray Crystallography, NMR, *ab initio* Calculations

Introduction

Phosphoramidic acid esters have attracted attention owing to their synthetic and biological value [1 – 4]. Of the numerous compounds known, structures have been determined only for a few molecules [5 – 7].

Gorenstein has reviewed the various effects that affect the ^{31}P chemical shifts in phosphoryl compounds [8]. Many authors have considered the substituent effects on the NMR and IR spectra of phosphoramidic acid esters [9 – 11]. *Ab initio* calculations were performed for an evaluation of the effects of different substituents on the NMR spectra [12 – 14].

In this study, we focus on two diastereotopic *p*-cresol groups in *N*-(α-methylbenzyl) phosphoramidic acid bis(4-methylphenyl)ester **2**, due to the chiral carbon atom in the amino group. We believe that this is the first example of diastereotopic groups that have been confirmed by X-ray single crystal structure determination techniques as well as NMR spectroscopy so far for a phosphoramidic acid ester. Also, we performed *ab initio* calculations on the geometry of compound **2** to compare the optimized structure of this molecule with the structure that was obtained from the X-ray crystallography. In addition, some new *N*-benzyl phosphoramidic acid (4-methylphenyl)ester derivatives were synthesized for comparison.

Results and Discussion

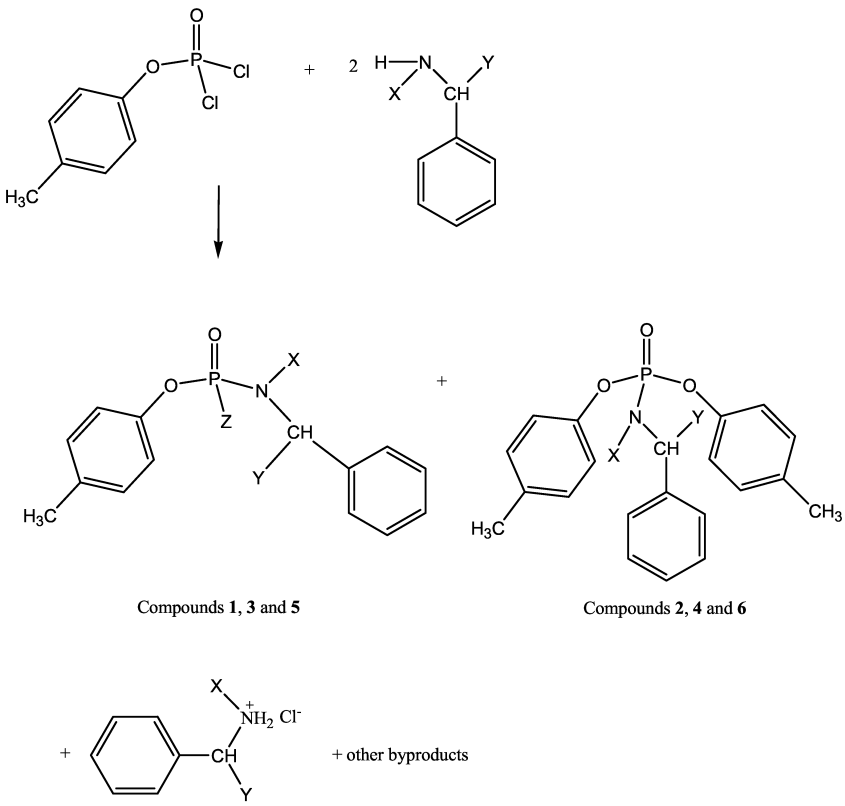
Syntheses of *N*-benzyl phosphoramidic acid (4-methylphenyl)ester derivatives with the constitution **1** – **6** were performed by the reaction of (4-tolyl) dichlorophosphate [15] with the appropriate benzylamines (Scheme 1).

Spectroscopic study

The ^{1}H NMR spectrum of compound **1** indicates two equivalent amine groups, but in compound **2**, two sets of peaks with equal intensity were observed for two *p*-cresol groups (the chiral carbon atom causes the two *p*-cresol groups to be diastereotopic) [16]. The ^{1}H NMR spectra of **1** and **2** show a broad peak for the amino protons.

All molecules **1** – **6** contain benzylic protons and the coupling patterns between these protons and the phosphorus atom are different. Where two benzylic protons are present, these are diastereotopic, which will result in different chemical shifts.

The quartet for the CH proton in **1** and **2** shows that there are no couplings with the phosphorus atom.



1 + **2**: X = H, Y = CH_3, Z = NH-CH(CH_3)C_6H_5

3 + **4**: X = C_2H_5, Y = H, Z = Cl

5 + **6**: X = *tert*-C_4H_9, Y = H, Z = Cl

Scheme 1. Preparation of molecules **1**–**6** (compounds **1**/**2**, **3**/**4**, and **5**/**6** are formed in the same transformation).

Compound **3** shows a doublet of quartets for the benzylic protons which is converted to a doublet of doublets in the $^1H\{^{31}P\}$ NMR spectrum. For molecule **5** a doublet peak was observed for the CH_2 protons. The ^1H NMR spectrum of compound **4** shows a doublet for the benzylic protons (arisen from the coupling with phosphorus atom), and the spectrum of **6** only a singlet peak.

^1H NMR spectra of some molecules with the skeleton $R^1R^2NP(O)(p\text{-}OC_6H_4CH_3)Cl$ (**A**) where R^1 = R^2 = alkyl or aryl, indicate a long range coupling between phosphorus and p-CH_3 protons with $^7J_{P-H}$ = 1.2 – 2.6 Hz [17]. Despite this, ^1H NMR spectra of **1**–**6** show no coupling between phosphorus and p-CH_3 protons, although the molecules **3** and **5** have the same structure as **A** with different amine substituents. Perhaps the high electron donation of amine groups and thus the formation of partial multiple bonds between phosphorus and nitrogen atoms cause the vanishing of $^7J_{P-H}$ [17].

The ^{31}P NMR spectra show that the substitution of a chlorine atom in compounds **3** and **5** by a p-cresol group (which produces molecules **4** and **6**) cause a large upfield shift of the phosphorus signal. This phenomenon was also observed upon substitution of an α-methylbenzyl amine group with a p-cresol group.

X-ray crystallography

To study the effect of the chiral carbon atom on the structure of molecule **2**, we used X-ray crystallography. Crystallographic data of compound **2** are given in Table 1. Selected bond lengths and angles are presented in Table 2. The unit cell of **2** contains two crystallographically independent molecules (labeled as P(1) and P(1A) for the corresponding

Table 1. Crystallographic data for *N*-(α-methylbenzyl) phosphoramidic acid bis(4-methylphenyl)ester (**2**).

Empirical formula	$C_{22}H_{24}NO_3P$
F. W.	381.39
Temperature	163 (2) K
Wavelength	0.71073 Å
Cryst system	monoclinic
Space group	$P2_1$
Unit cell dimensions	$a = 12.690$ (6) Å, $\alpha = 90.0°$
	$b = 7.432$ (4) Å, $\beta = 105.26$ (4)°
	$c = 22.504$ (11) Å, $\gamma = 90.0°$
V	2047.6 (18) Å^3
Z, calc. density	4, 1.237 Mg m^{-3}
Abs. coefficient	0.155 mm^{-1}
$F(000)$	808
crystal size	$0.6 \times 0.3 \times 0.2$ mm
θ range for data collection	2.11 to 25.06°
Limiting indices	$-4 \leq h \leq 15$,
	$0 \leq k \leq 8$,
	$-26 \leq l \leq 25$
Reflections collected	4190 / 3918 [R (int) = 0.0574]
Completeness to $\theta = 25.06$	99.5%
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3918 / 1 / 488
Goodness-of-fit on F^2	1.010
Final R indices [3184 refs	
with $I > 2\sigma(I)$]	$R1 = 0.0646$, $wR2 = 0.1752$
R Indices (all data)	$R1 = 0.0842$, $wR2 = 0.1826$
Absolute structure parameter	0.06 (17)
Extinction coefficient	0.008 (3)
Largest diff peak and hole	0.577 and -0.628 e·Å^{-3}

Table 2. Selected bond lengths (Å) and selected bond angles (deg) for compound **2**.

P(1)-O(1)	1.462(3)	O(2)-C(9)	1.393(6)
P(1)-O(2)	1.592(4)	O(3)-C(16)	1.425(6)
P(1)-O(3)	1.595(4)	O(3A)-C(16A)	1.394(5)
P(1)-N(1)	1.610(5)	O(2A)-C(9A)	1.406(5)
P(1A)-O(1A)	1.469(3)	N(1)-C(1)	1.469(6)
P(1A)-O(2A)	1.582(4)	N(1)-H(1B)	0.8601
P(1A)-O(3A)	1.605(3)	N(1A)-C(1A)	1.473(6)
P(1A)-N(1A)	1.614(5)	N(1A)-H(1NA)	0.8599
O(1)-P(1)-O(2)	116.4(2)	O(3A)-P(1A)-N(1A)	109.1(2)
O(1)-P(1)-O(3)	115.4(2)	C(9)-O(2)-P(1)	122.3(3)
O(2)-P(1)-O(3)	94.0(2)	C(16)-O(3)-P(1)	117.9(3)
O(1)-P(1)-N(1)	111.4(2)	C(16A)-O(3A)-P(1A)	123.4(3)
O(2)-P(1)-N(1)	110.1(2)	C(9A)-O(2A)-P(1A)	120.3(3)
O(3)-P(1)-N(1)	108.2(2)	C(1)-N(1)-P(1)	126.6(4)
O(1A)-P(1A)-O(2A)	115.9(2)	C(1)-N(1)-H(1B)	116.7
O(1A)-P(1A)-O(3A)	116.10(18)	P(1)-N(1)-H(1B)	116.7
O(2A)-P(1A)-O(3A)	93.64(19)	C(1A)-N(1A)-P(1A)	125.9(4)
O(1A)-P(1A)-N(1A)	110.5(2)	C(1A)-N(1A)-H(1NA)	117.0
O(2A)-P(1A)-N(1A)	110.4(2)	P(1A)-N(1A)-H(1NA)	117.0

phosphorus atoms, Fig. 1). The torsion angles P(1)-O(3)-C(16)-C(17) and P(1A)-O(3A)-C(16A)-C(17A) are 87.8(6)° and 21.9(6)°, respectively (Table 1). The

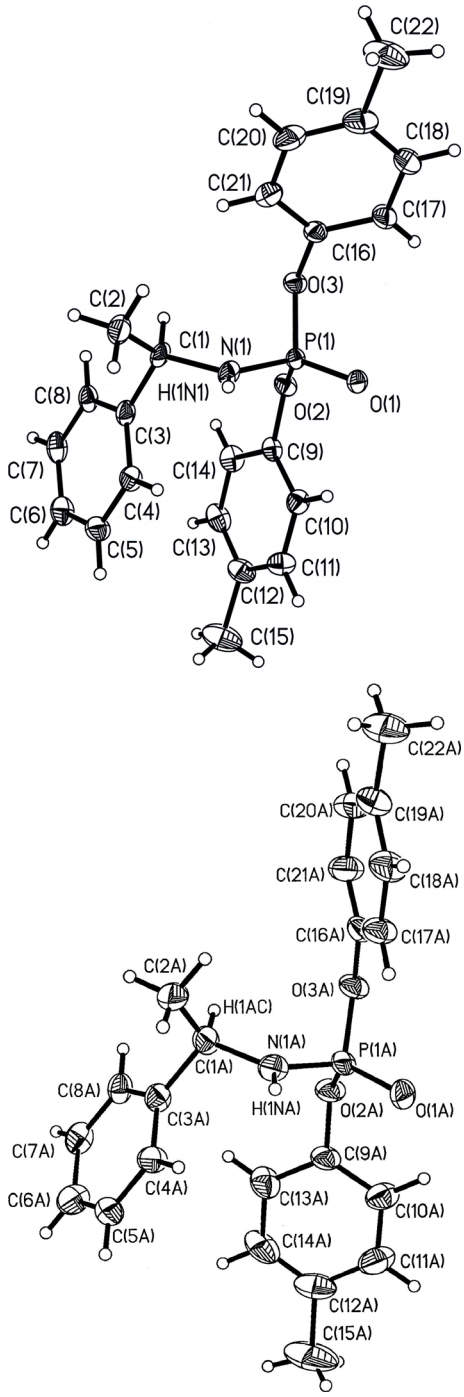


Fig. 1. Molecular structure and atom-labeling scheme for $[(C_6H_5)(CH_3)CH\text{-}NH]P(O)(p\text{-}OC_6H_4CH_3)_2$; the two crystallographically independent molecules are shown (50% probability ellipsoids).

Table 3. Selected torsion angles (deg) for compound **2**.

P(1)-O(3)-C(16)-C(17)	87.8(6)	P(1A)-N(1A)-C(1A)-C(2A)	−131.9(5)
P(1A)-O(3A)-C(16A)-C(17A)	21.9(6)	P(1)-N(1)-C(1)-C(3)	95.6(6)
P(1)-O(2)-C(9)-C(10)	−36.3(7)	P(1A)-N(1A)-C(1A)-C(3A)	106.4(5)
P(1A)-O(2A)-C(9A)-C(10A)	−76.1(6)	O(1)-P(1)-N(1)-C(1)	177.9(4)
P(1)-O(3)-C(16)-C(21)	−97.9(6)	O(1A)-P(1A)-N(1A)-C(1A)	177.9(4)
P(1A)-O(3A)-C(16A)-C(21A)	−159.9(4)	O(1)-P(1)-O(3)-C(16)	−46.9(4)
P(1)-O(2)-C(9)-C(14)	143.6(4)	O(1A)-P(1A)-O(3A)-C(16A)	−67.7(4)
P(1A)-O(2A)-C(9A)-C(14A)	110.0(5)	O(1)-P(1)-O(2)-C(9)	69.3(4)
P(1)-N(1)-C(1)-C(2)	−140.9(5)	O(1A)-P(1A)-O(2A)-C(9A)	50.7(4)

Table 4. Hydrogen bonds for compound **2** [Å and deg.]. Hydrogen bonds with H…A $< r(\mathrm{A}) + 2.000$ Å and ∠DHA > 110 deg.

D-H	*d* (D-H)	*d* (H…A)	∠ DHA	*d* (D…A)	A
N1-H1B	0.860	1.999	165.44	2.839(6)	O1A $[x, y+1, z]$
N1A-HINA	0.860	1.964	171.08	2.817(6)	O1

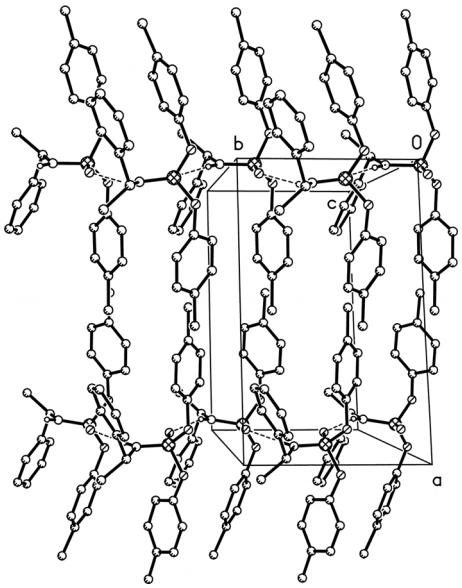


Fig. 2. A view of the unit cell packing for compound **2**.

P(1)-O(1) and P(1A)-O(1A) bond lengths are 1.462(3) and 1.469(3) Å, in agreement with normal double bond lengths (1.45 Å) [4]. The P-O bond lengths (between phosphorus and oxygen atoms of *p*-cresol groups) are about 1.60 Å (Table 2) which are slightly smaller than the standard P-O single bond length (1.64 Å) [4]. The P(1)-N(1) and P(1A)-N(1A) bond lengths are 1.610(5) and 1.614(5) Å, which are between the single and double bond lengths (1.77 and 1.57 Å, respectively) [4]. The angles P(1)-N(1)-C(1), C(1)-N(1)-H(1B) and P(1)-N(1)-H(1B) are 126.6(4)°, 116.7° and 116.7° and the angles P(1A)-N(1A)-C(1A), C(1A)-N(1A)-H(1NA) and P(1A)-N(1A)-H(1NA) are 125.9(4)°, 117.0° and 117.0°, respectively. The environment of the nitrogen atoms is practically planar. The sum of the surrounding angles for N(1) and N(1A) are 360° and 359.9°, respectively.

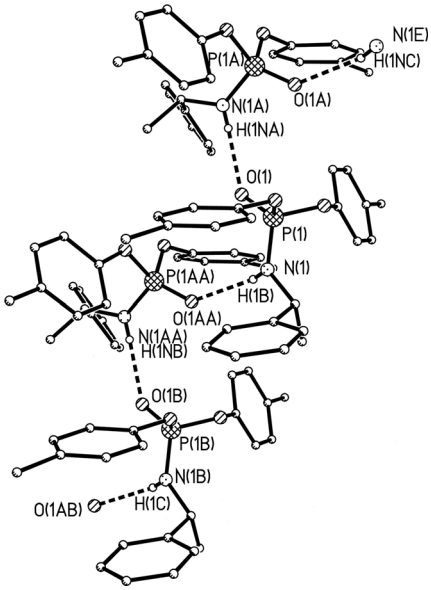


Fig. 3. Intermolecular hydrogen bond in compound **2**.

The phosphorus atoms P(1) and P(1A) have a distorted tetrahedral configuration with angles in the range 116.4(2)° – 94.0(2)° (the maximum and minimum values of angles for the molecule labeled with P(1) are observed for O(1)-P(1)-O(2) and O(2)-P(1)-O(3), respectively). In the other molecule, they are in the region 116.10(18)° – 93.64(19)°, for the angles of O(1A)-P(1A)-O(3A) and O(2A)-P(1A)-O(3A).

In the crystal lattice of **2**, infinite zigzag chains are built from two alternating crystallographically independent molecules (Fig. 2). Neighboring molecules are connected *via* two different kinds of intermolecular hydrogen bonds (see Table 4). The molecule labeled with A provides O(1A) as an acceptor and forms the N1-H1B…O(1A) hydrogen bond. The other hydrogen bond is produced by O(1) as an acceptor [(N(1A)-H(1NA)…O(1)] (Fig. 3).

Table 5. Selected bond lengths (Å) and angles (deg) for the optimized structures of conformer P(1) of compound **2** with UHF/6-311G** and B3LYP/6-311G**.

	UHF/6-311G**	B3LYP/6-311G**		UHF/6-311G**	B3LYP/6-311G**
P(1)-O(1)	1.444	1.472	O(2)-C(9)	1.378	1.396
P(1)-O(2)	1.589	1.628	O(3)-C(16)	1.375	1.394
P(1)-O(3)	1.583	1.621	C(1)-C(2)	1.527	1.531
P(1)-N(1)	1.631	1.652	C(1)-C(3)	1.525	1.527
C(12)-C (15)	1.511	1.510	N(1)-C(1)	1.472	1.481
C(19)-C(22)	1.511	1.51	N(1)-H(1B)	0.996	1.011
O(1)-P(1)-O(2)	116.6	117.9	C(9)-O(2)-P(1)	125.1	123.4
O(1)-P(1)-O(3)	112.1	111.4	C(16)-O(3)-P(1)	127.8	125.7
O(2)-P(1)-O(3)	99.1	98.2	C(1)-N(1)-P(1)	124.7	124.0
O(1)-P(1)-N(1)	113.3	113.6	C(1)-N(1)-H(1B)	115.8	115.8
O(2)-P(1)-N(1)	104.9	103.9	P(1)-N(1)-H(1B)	118.9	118.8
O(3)-P(1)-N(1)	109.7	110.5	N(1)-C(1)-C(2)	111.6	112.1

In both independent molecules, the two *p*-cresol groups are not symmetry related due to the presence of an asymmetric carbon atom in the molecule. The P(1A)-O(2A) and P(1A)-O(3A) bond lengths are 1.582(4) and 1.605(3). Similar results are obtained for P(1)-O(2) and P(1)-O(3) (Table 2, also compare the P(1)-O(2)-C(9) and P(1)-O(3)-C(16) and other corresponding angles in the other molecule).

Quantum chemical calculations

To further investigate molecule **2** and to compare the experimental and theoretical data, *ab initio* calculations were performed to optimize the geometry of two conformers of molecule **2** on the UHF/6-311G** and B3LYP/6-311G** levels, using the Gaussian 98 program [18]. There are some differences in the corresponding bond angles and in the particular torsion angles; however, the corresponding bond lengths are nearly identical (Tables 5 – 7). Fig. 4 shows the optimized structures obtained for two independent molecules labeled with P(1) (up), and P(1A) (down). The calculated results are generally in good agreement with the experimental ones. The gas phase minimum energy for conformer labeled with P(1) at UHF and B3LYP levels are −920677.4746 and −925546.2101 kcal.mol^{-1} and that of conformer labeled with P(1A) are −920678.5012 and −925547.1244 kcal.mol^{-1}, respectively. Therefore, conformer P(1A) is more stable than conformer P(1) as 1.027 kcal.mol^{-1} at UHF method and 0.914 kcal.mol^{-1} at DFT level.

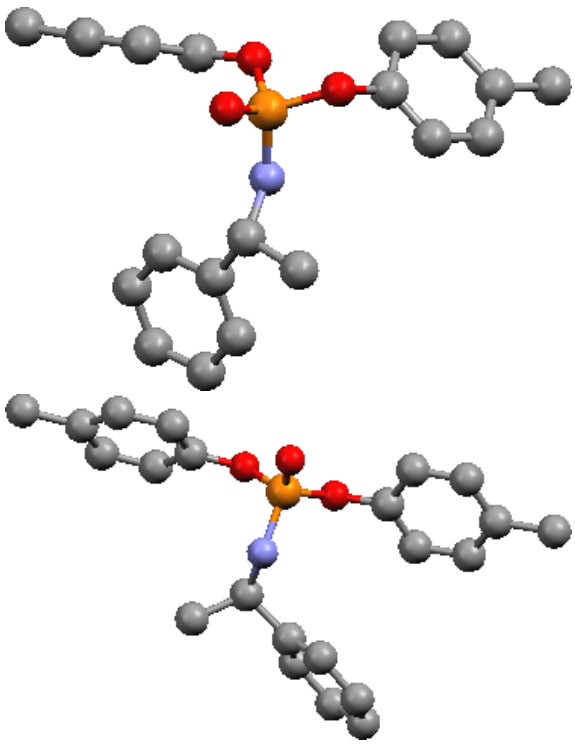


Fig. 4. Optimized structures for **2**, two independent molecules [up, P(1) and down, P(1A)] with UHF/6-311G** and B3LYP/6-311G**, H atoms are omitted for clarity.

Experimental Section

X-ray measurements

X-ray data were collected on a Bruker SMART 1000 CCD single crystal diffractometer with graphite monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). The structure was refined with SHELXL-97 [19] by a full-matrix least-squares procedure on F^2. The crystallographic information file (CIF) has been deposited at the Cambridge Crystallographic Database Center as a supplementary publication No CCDC 224962.

Spectroscopic measurements

^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker Avance DRS 500 spectrometer. ^{1}H and ^{13}C chemical shifts were determined relative to internal TMS, ^{31}P chemical shifts relative to 85% H_3PO_4 as external standard. Infrared (IR) spectra were recorded on a Shimadzu model IR-60 spec-

Table 6. Selected bond lengths (Å) and angles (deg) for the optimized structures of conformer P(1A) of compound **2** with UHF/6-311G** and B3LYP/6-311G**.

	UHF/6-311G**	B3LYP/6-311G**		UHF/6-311G**	B3LYP/6-311G**
P(1A)-O(1A)	1.448	1.477	O(2A)-C(9A)	1.377	1.394
P(1A)-O(2A)	1.585	1.624	O(3A)-C(16A)	1.382	1.399
P(1A)-O(3A)	1.577	1.615	C(1A)-C(2A)	1.532	1.537
P(1A)-N(1A)	1.632	1.654	C(1A)-C(3A)	1.524	1.526
C(12A)-C(15A)	1.511	1.510	N(1A)-C(1A)	1.459	1.469
C(19A)-C(22A)	1.511	1.510	N(1A)-H(1NA)	0.995	1.009
O(1A)-P(1A)-O(2A)	116.4	117.3	C(9A)-O(2A)-P(1A)	126.3	123.8
O(1A)-P(1A)-O(3A)	116.6	117.7	C(16A)-O(3A)-P(1A)	126.5	123.7
O(2A)-P(1A)-O(3A)	95.6	93.6	C(1A)-N(1A)-P(1A)	127.7	127.0
O(1A)-P(1A)-N(1A)	111.3	111.8	C(1A)-N(1A)-H(1NA)	117.4	117.5
O(2A)-P(1A)-N(1A)	107.2	107.0	P(1A)-N(1A)-H(1NA)	114.3	114.5
O(3A)-P(1A)-N(1A)	108.4	107.6	N(1A)-C(1A)-C(2A)	109.5	109.5

Table 7. Selected torsion angles (deg) for the optimized structures of two conformers of compound **2** with UHF/6-311G** and B3LYP/6-311G**.

	UHF/6-311G**	B3LYP/6-311G**		UHF/6-311G**	B3LYP/6-311G**
P(1)-O(3)-C(16)-C(17)	82.2	82.0	P(1A)-O(3A)-C(16A)-C(17A)	−57.2	−54.9
P(1)-O(2)-C(9)-C(10)	−121.8	−128.9	P(1A)-O(2A)-C(9A)-C(10A)	43.7	43.3
P(1)-O(3)-C(16)-C(21)	−100.7	−101.8	P(1A)-O(3A)-C(16A)-C(21A)	126.2	129.0
P(1)-O(2)-C(9)-C(14)	60.4	53.9	P(1A)-O(2A)-C(9A)-C(14A)	−138.6	−139.7
P(1)-N(1)-C(1)-C(2)	−88.1	−85.8	P(1A)-N(1A)-C(1A)-C(2A)	−131.6	−129.9
P(1)-N(1)-C(1)-C(3)	144.0	146.0	P(1A)-N(1A)-C(1A)-C(3A)	103.6	105.1
O(1)-P(1)-N(1)-C(1)	−14.6	−19.2	O(1A)-P(1A)-N(1A)-C(1A)	173.8	173.7
O(1)-P(1)-O(3)-C(16)	176.1	175.8	O(1A)-P(1A)-O(3A)-C(16A)	43.0	46.5
O(1)-P(1)-O(2)-C(9)	−58.3	−57.7	O(1A)-P(1A)-O(2A)-C(9A)	−57.0	−55.1
O(1)-P(1)-N(1)-H(1)	174.7	174.7	O(1A)-P(1A)-N(1A)-H(1NA)	3.0	5.4

trometer. Elemental analysis was performed using a Heraeus CHN-O-RAPID apparatus.

Syntheses

*N,N'-Bis(α-methylbenzyl)phosphoramidic acid (4-methylphenyl)ester (**1**) and N-(α-methylbenzyl) phosphoramidic acid bis(4-methylphenyl)ester (**2**)*

α-Methylbenzyl amine (1.21 g, 10 mmol) was added to a solution of (4-tolyl) dichlorophosphate (1.125 g, 5 mmol) in dry benzene (20 ml) and stirred at −10 °C for 6 hours. After filtration, the solvent was evaporated and the oily residue was separated by column chromatography [silica gel; *n*-hexane/ethyl acetate (1:2)] to give compounds **1** (0.83 g, 42%) and **2** (0.37 g, 19%).

1: M. p. 78 °C. – IR (film): $\tilde{\nu}$ = 3205 (NH), 3020, 1501, 1441, 1384, 1213 (P=O), 1116, 1084, 1034, 960, 914, 835, 755, 695, 604, 561, 511, 481 cm^{-1}. – ^1H NMR (500.13 MHz, acetone): $\delta = 1.39$ (t, $^3J_{H-H} = 7.5$ Hz, 6 H, 2 CH_3), 2.22 (s, 3 H, *p*-CH_3), 4.46 (oct, $J_{(H-H,P-H)} = 7.1$ Hz, 2 H, 2 CH), 6.99 – 7.38 (m, 12 H, Ar-H). – $^1H\{^{31}P\}$ NMR (500.13 MHz, acetone): $\delta = 1.39$ (t, $^3J_{H-H} = 7.5$ Hz, 6 H, 2 CH_3), 2.22 (s, 3 H, *p*-CH_3), 4.46 (sext, $J_{H-H} = 7.2$ Hz, 2 H, 2 CH), 6.99 – 7.38 (m, 12 H, Ar-H). – ^1H NMR (500.13 MHz, $CDCl_3$): $\delta = 1.39$ (q, $^3J_{H-H} = 6.7$ Hz, 6 H, 2 CH_3), 2.27 (s, 3 H, *p*-CH_3), 2.91 (s, 2 H, NH), 4.40 (quin, $J_{H-H} = 6.1$ Hz, 2 H, 2 CH). – $^{13}C\{^1H\}$ NMR (125.77 MHz, acetone): $\delta = 19.97$ (s, *p*-CH_3), 25.10 (q, $^3J_{P-C}$ = 5.6 Hz), 51.14 (d, $^2J_{P-C} = 8.7$ Hz), 120.36 (d, $J_{P-C} = 4.8$ Hz), 126.18 (d, $J_{P-C} = 3.9$ Hz), 126.40 (d, $J_{P-C} = 4.8$ Hz), 128.11 (d, $J_{P-C} = 5.4$ Hz), 129.52 (s), 132.63 (s), 146.33 (d, $J_{P-C} = 5.7$ Hz), 146.42 (d, $J_{P-C} = 5.0$ Hz), 149.92 (d, $J_{P-C} = 6.4$ Hz). – ^{31}P NMR (202.46 MHz, acetone): $\delta = 9.59$ (t, $J_{P-H} = 9.0$ Hz). – $C_{23}H_{27}N_2O_2P$ (394.4): calcd. C 70.03, H 6.90, N 71.02; found C 70.01, H 6.81, N 7.08.

2: M. p. 90 °C. – IR (film): $\tilde{\nu}$ = 3150 (NH), 3025, 2895, 1496, 1463, 1439, 1250 (P=O), 1195, 1160, 1123, 985, 934, 813, 758, 694, 566, 497 cm^{-1}. – ^1H NMR (500.13 MHz, $CDCl_3$): $\delta = 1.46$ (d, $J_{H-H} = 6.7$ Hz, 3 H, CH_3), 2.27 (s, 3 H, *p*-CH_3), 2.30 (s, 3 H, *p*-CH_3), 3.52 (s, 1 H, NH), 4.57 (q, $J_{H-H} = 6.5$ Hz, 1 H, CH), 6.92 (d, $^3J_{H-H} = 8.2$ Hz, 2 H_{meta}), 7.01 (d, $^3J_{H-H} = 8.2$ Hz, 2 H_{ortho}), 7.09 (s, 4 H), 7.13 – 7.29 (m, 5 H, Ar-H). – $^{13}C\{^1H\}$ NMR (125.77 MHz, $CDCl_3$): $\delta = 20.72$ (d, $^3J_{P-C} = 4.6$ Hz, CH_3), 24.91 (s, *p*-CH_3), 24.97 (s, *p*-CH_3), 51.97 (s, CH), 119.97 (t, $^3J_{P-C} = 4.3$ Hz), 125.96 (s), 127.24 (s), 128.53 (s), 129.95 (s), 130.10 (s), 134.27 (s), 134.39 (s), 144.25 (s), 144.29 (s), 148.55 (d,

$^2J_{P-C} = 6.8$ Hz), 148.74 (d, $J_{P-C} = 6.8$ Hz). – ^{31}P NMR (202.46 MHz, $CDCl_3$): $\delta = -1.79$ (s). – $C_{22}H_{24}NO_3P$ (381.4): calcd. C 69.28, H 6.34, N 3.67; found C 69.22, H 6.27, N 3.64.

*N-Ethylbenzyl phosphoramidochloridic acid (4-methylphenyl)ester (**3**) and N-ethylbenzyl phosphoramidic acid bis(4-methylphenyl)ester (**4**)*

To a solution of (4-tolyl) dichlorophosphate (1.125 g, 5 mmol) in dry acetonitrile (25 ml), *N*-ethylbenzylamine (1.35 g, 10 mmol) was added dropwise at −5 °C and the mixture stirred for 5 hours. After filtration, the solvent was removed under vacuum and the oily residue was purified by column chromatography [silica gel; *n*-hexane/ethyl acetate (3.5:1)]. Two compounds **3** (0.63 g, 39%) and **4** (0.36 g, 18%) were obtained in this procedure.

3: IR (film): $\tilde{\nu} = 3015$ (NH), 2805, 1593, 1494, 1367, 1260, 1189 (P=O), 1123, 1035, 939, 815, 756, 716, 691, 595, 529, 489 cm^{-1}. – ^{1}H NMR (500.13 MHz, $CDCl_3$): $\delta = 1.14$ (t, $^3J_{H-H} = 7.1$ Hz, 3 H, CH_3), 2.30 (s, 3 H, *p*-CH_3), 3.17 (doct, $J_{(H-H,P-H)} = 7.1$ Hz, 2 H, CH_2), 4.43 (dq, $J_{(H-H,P-H)} = 11.6$ Hz, 2 H, CH_2-Ar), 7.10 – 7.33 (m, 9 H, Ar-H). – ^{1}H{^{31}P} NMR (500.13 MHz, $CDCl_3$): $\delta = 1.14$ (t, $^3J_{H-H} = 7.1$ Hz, 3 H, CH_3), 2.30 (s, 3 H, *p*-CH_3), 3.17 (dsext, $J_{H-H} = 7.1$ Hz, 2 H, CH_2), 4.43 (dd, $J_{H-H} = 15.3$ Hz, 2 H, CH_2-Ar), 7.10 – 7.33 (m, 9 H, Ar-H). – ^{13}C{^{1}H} NMR (125.77 MHz, $CDCl_3$): $\delta = 12.67$ (d, $^3J_{P-C} = 1.8$ Hz, CH_3), 20.85 (s, *p*-CH_3), 40.38 (d, $^2J_{P-C} = 3.6$ Hz, CH_2), 49.02 (d, $^2J_{P-C} = 4.6$ Hz, CH_2-Ar), 120.38 (d, $^3J_{P-C} = 5.5$ Hz), 127.85 (s), 128.36 (s), 128.69 (s), 130.39 (s), 135.55 (s), 136.37 (d, $J_{P-C} = 5.2$ Hz), 147.95 (d, $^3J_{P-C} = 8.4$ Hz). – ^{31}P NMR (202.46 MHz, $CDCl_3$): $\delta = 12.12$ (quin, $J_{P-H} = 13.1$ Hz). – $C_{16}H_{19}NO_2PCl$ (323.8): calcd. C 59.36, H 5.92, N 4.33; found C 59.31, H 5.82, N 4.31.

4: IR (film): $\tilde{\nu} = 3010$ (NH), 1597, 1495, 1446, 1375, 1269, 1219 (P=O), 1190, 1132, 1037, 918, 616, 723, 693, 632, 594, 554, 491 cm^{-1}. – ^{1}H NMR (500.13 MHz, $CDCl_3$): $\delta = 1.03$ (t, $^3J_{H-H} = 7.1$ Hz, 3 H, CH_3), 2.33 (s, 6 H, 2 *p*-CH_3), 3.15 (sext, $J_{H-H} = 7.1$ Hz, CH_2, 2 H), 4.47 (d, $^3J_{P-H} = 9.9$ Hz, CH_2-Ar, 2 H), 7.13 – 7.27 (m, 13 H, Ar-H). - ^{1}H{^{31}P} NMR (500.13 MHz, $CDCl_3$): $\delta = 1.03$ (t, $^3J_{H-H} = 7.1$ Hz, 3 H, CH_3), 2.33 (s, 6 H, 2 *p*-CH_3), 3.15 (q, $J_{H-H} = 6.9$ Hz, CH_2, 2 H), 4.47 (s, CH_2-Ar, 2 H), 7.13 – 7.27 (m, 13 H, Ar-H). – ^{13}C{^{1}H} NMR (125.77 MHz, $CDCl_3$): $\delta = 12.99$ (s, 1 C, CH_3), 20.79 (s, 2 C, 2 *p*-CH_3), 39.70 (d, $^2J_{P-C} = 3.5$ Hz, CH_2), 48.79 (d, $^2J_{P-C} = 4.9$ Hz, CH_2), 120.13 (d, $^3J_{P-C} = 4.8$ Hz), 127.43 (s), 128.41 (d, $^2J_{P-C} = 6.5$ Hz), 130.13 (s), 130.31 (s), 134.33 (s), 137.32 (d, $J_{P-C} = 4.0$ Hz), 148.94 (d, $J_{P-C} = 6.8$ Hz). – ^{31}P NMR (202.46 MHz, $CDCl_3$): $\delta = 1.37$ (quin, $^3J_{P-H} = 10.8$ Hz). – $C_{23}H_{26}NO_3P$ (395.5): calcd. C 69.85, H 6.63, N 3.54; found C 69.83, H 6.54, N 3.52.

*N-tert-Butylbenzyl phosphoramidochloridic acid (4-methylphenyl)ester (**5**) and N-tert-butylbenzyl phosphoramidicacid bis(4-methylphenyl)ester (**6**)*

A solution of *N-tert*-butylbenzylamine (1.63 g, 10 mmol) in dry benzene (10 ml) was added dropwise at −5 °C to a solution of (4-tolyl) dichlorophosphate (1.125 g, 5 mmol) in dry acetonitrile (25 ml) and the mixture stirred for 3 hours. After filtration, the solvent was removed under vacuum and the oily residue was purified by column chromatography [silica gel; *n*-hexane/ethyl acetate (6:1)]. Two compounds **5** (0.81 g, 46%) and **6** (0.36 g, 17%) were obtained in this procedure.

5: IR (film): $\tilde{\nu} = 3330$ (NH), 2890, 2620, 1873, 1716, 1593, 1492, 1445, 1280, 1257 (P=O), 1187, 1159, 1098, 1043, 956, 812, 706, 552, 487 cm^{-1}. – ^{1}H NMR (500.13 MHz, $CDCl_3$): $\delta = 1.25$ (s, 9 H, 3 CH_3), 2.28 (s, 3 H, *p*-CH_3), 3.91 (d, 2 H, CH_2), 7.01 – 7.14 (m, 9 H, Ar-H). – ^{13}C{^{1}H} NMR (125.77 MHz, $CDCl_3$): $\delta = 14.16$ (s, 1 C), 20.76 (s, 3 C, 3 CH_3), 29.74 (s, CH_2), 31.97 (s, *p*-CH_3), 119.75 (d, $J_{P-C} = 4.6$ Hz), 119.87 (d, $J_{P-C} = 4.8$ Hz), 120.02 (d, $J_{P-C} = 4.6$ Hz), 130.01 (s), 130.26 (s), 134.34 (s), 148.39 (d, $^3J_{P-C} = 7.4$ Hz), 148.80 (d, $^3J_{P-C} = 6.8$ Hz). – ^{31}P NMR (202.46 MHz, $CDCl_3$): $\delta = -10.42$ (s). – $C_{18}H_{23}NO_2PCl$ (351.8): calcd. C 61.45, H 6.59, N 3.98; found C 61.40, H 6.51, N 3.32.

6: IR (film): $\tilde{\nu} = 2925$ (NH), 2856, 1891, 1595, 1503, 1384, 1303, 1185 (P=O), 1160, 1102, 961, 824, 698, 563, 499 cm^{-1}. – ^{1}H NMR (500.13 MHz, $CDCl_3$): $\delta = 1.13$ (s, 9 H, 3 CH_3), 2.27 (s, 6 H, 2 *p*-CH_3), 3.69 (s, 2 H, CH_2), 7.10 – 7.34 (m, 13 H, Ar-H). – ^{13}C{^{1}H} NMR (125.77 MHz, $CDCl_3$): $\delta = 19.80$ (s, 3 C, 3 CH_3), 28.31 (s, 2 C, 2 *p*-CH_3), 28.50 (s, 1 C, CH_2), 46.58 (s, 1 C), 119.78 (d, $^3J_{P-C} = 4.8$ Hz), 126.39 (s), 128.00 (s), 128.16 (s), 130.31 (s), 135.21 (s), 148.54 (s), 148.59 (s). – ^{31}P NMR (202.46 MHz, $CDCl_3$): $\delta = -16.78$ (s). – $C_{25}H_{30}NO_3P$ (423.5): calcd. C 70.90, H 7.14, N 3.31; found C 70.90, H 7.12, N 3.28.

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