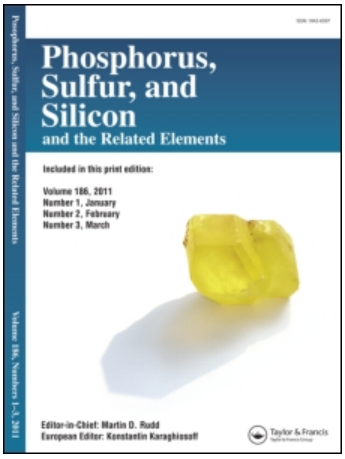


**Phosphorus, Sulfur, and Silicon and the Related Elements**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

# Synthesis and NMR Spectroscopic Study of New Furan-Derived Bis(Aminophosphonates)

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**To cite this Article** Kraicheva, I. , Finocchiaro, P. and Failla, S.(2007) 'Synthesis and NMR Spectroscopic Study of New Furan-Derived Bis(Aminophosphonates)', Phosphorus, Sulfur, and Silicon and the Related Elements, 182: 1, 57 — 64
**To link to this Article: DOI:** 10.1080/10426500600866903
**URL:** http://dx.doi.org/10.1080/10426500600866903

*Phosphorus, Sulfur, and Silicon*, 182:57–64, 2007

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500600866903

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# Synthesis and NMR Spectroscopic Study of New Furan-Derived Bis(Aminophosphonates)

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*The synthesis of two novel furyl-containing bis(aminophosphonates) 1,5-bis[N-methyl(dimethoxyphosphonyl)-1-(2-furyl)]diaminonaphthalene (**1**) and 1,5-bis[N-methyl(diethoxyphosphonyl)-1-(2-furyl)]diaminonaphthalene (**2**) through an addition of dialkyl phosphites to N,N′-difurfurylidene-1,5-naphthalenediamine is reported. The compounds have been characterized by elemental analysis, TLC, IR and NMR ($^{1}H$,$^{13}C$ and $^{31}P$) spectra. Some new $^{31}P$ NMR data of three previously described analogues (**3–5**) of the above bis(aminophosphonates) is also presented. The $^{31}P$ NMR study reveals that in most of the cases (**1,3–5**), the addition reaction is completely stereoselective, and only one diastereomer is formed. By the preparation of compound **2,** this reaction proceeds not completely stereoselectively with the predominant formation (in 90%) of one of the two possible diastereomers.*

**Keywords** Aminophosphonic acids; furan derivatives; NMR spectra; Schiff bases

## INTRODUCTION

Aminophosphonic acid derivatives possess a wide-range of potential for biomedical applications.[1–4] Numerous of them are used in therapy and diagnostic medicine.[1,3,5–9] Thus, some representatives find clinical applications in the treatment of bone disorders and cancer;[7,10,11] others are used as bone-seeking radiopharmaceuticals.[12]

The possibilities for pharmacological applications of the aminophosphonate derivatives due to their valuable properties have stimulated

Received August 5, 2005; accepted March 24, 2006.
Thanks are due to the UNESCO Division of Life Sciences for the financial support (GrantSC 206.579.0).
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the extensive research in this field.[1,2,13] Among this group of compounds bis(aminophosphonates) occupy an important place and recently much attention has been paid to various aspects of their chemistry – synthetic routes, structural and spectral characterization.[14–20] The addition of dialkyl phosphites to bis(imines) is a very useful procedure for their preparation.[14–16] The stereochemistry of the reaction attracts considerable interest, since it is known, that the absolute configuration at the $\alpha$-carbon atom of substituted phosphonic acids plays an important role in the biological activity of the molecule.[1,15,21]

In continuation of our studies on the preparation of furan-containing bis(aminophosphonates)[18,20,22–25] we report here the synthesis and NMR ($^{1}$H, $^{13}$C and $^{31}$P) spectroscopic characterization of two novel compounds derived from dialkyl phosphites and *N*, *N*′-difurfurylidene-1,5-naphthalenediamine. Some new $^{31}$P NMR data of other three bis(aminophosphonates), described earlier,[20,22,25] are also presented. The stereochemical aspects of the dialkyl phosphite addition to the corresponding bis(imines) in the two series are discussed. All compounds studied now possess two pharmacophoric groups—a furan ring and aminophosphonate moiety—and might be of particular interest as potential antitumor and antiviral agents.

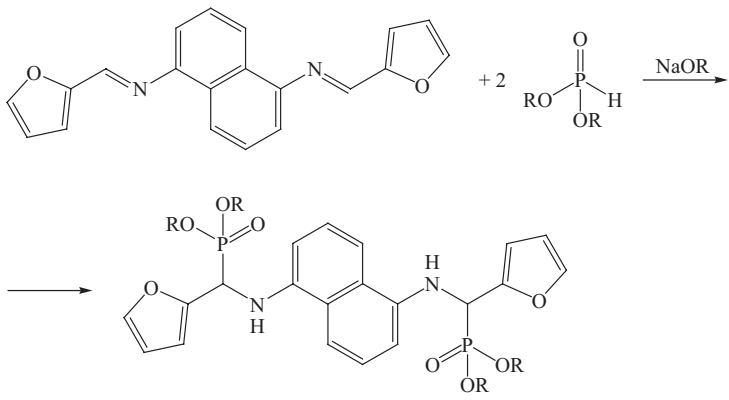


## RESULTS AND DISCUSSION

The Schiff base *N*,*N*′-difurfurylidene-1,5-naphthalenediamine has been described as early as 1965,[26] but no spectroscopic data about it is available so far. Therefore, we report here IR and NMR spectroscopic characteristics of this compound (see the Experimental section).

An addition of dimethyl and diethyl phosphite to *N*,*N*′-difurfurylidene-1,5-naphthalenediamine was performed, and two novel furan containing bis(aminophosphonates), 1,5-bis[*N*-methyl(dimethoxyphosphonyl)-1-(2-furyl)]diaminonaphthalene (**1**) and 1,5-bis[*N*-methyl(diethoxyphosphonyl)-1-(2-furyl)]diaminonaphthalene (**2**), were synthesized (Scheme 1). The reaction was carried out at an ambient temperature in the presence of sodium alkoxide as a catalyst. Products **1** and **2** are crystalline solids, which are soluble in organic solvents. One spot was found on the thin layer chromatograms for each of the two purified compounds. IR spectra of **1** and **2** display the expected[27,28] stretching absorption bands of the characteristic structural fragments in their molecules (see the Experimental section).

Of particular interest is the stereochemistry of the addition of dialkyl phosphites to bifunctional Schiff bases.[16,17] The reaction should result in the formation of two diastereomeric products: *meso* form (*R,S* ) and



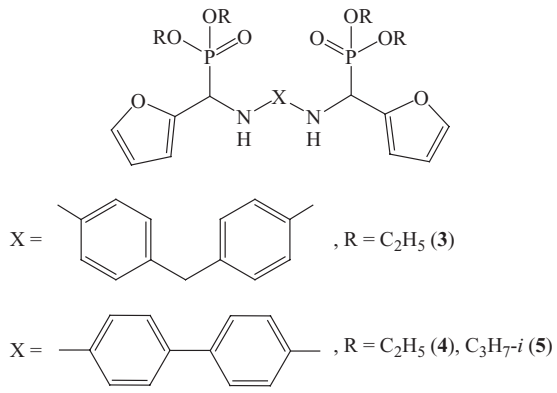

R = $CH_3$ (**1**), $C_2H_5$ (**2**)

**SCHEME 1**



a racemic mixture of two enantiomers (*R*, *R* and *S*, *S*).[14–17] In our case, the $^1H$, $^{13}C$, and $^{31}P$ NMR spectra of the purified compounds **1** and **2** show only one set of signals. This indicates the presence of only one of the two possible diastereomers in each of the recrystallized samples. The $^1H$ NMR spectra, recorded in DMSO-$d_6$ solution, exhibit the signals of the CHP and NH protons each as a doublet of doublets. One signal is also found for each of these protons in **1** and **2**, when the spectra are recorded in $CDCl_3$ solution. The methyl protons of the alkoxy group give two doublets (**1**) and two triplets (**2**), owing to the nonequivalence of the two OR groups.[15] The proton signals of the furan ring in both compounds are complicated due to the additional coupling with the $^{31}P$ nucleus.[20,29] The NMR signal of 3-H of the furan ring appears in the spectra as a pseudotriplet because of the sufficiently similar values of the coupling constants $^3J_{HH}$ and $^4J_{PH}$, just like in the case of 5-methylfuryl derived bis(aminophosphonates) reported earlier.[20] The NMR signal of 5-H of the furan ring is observed as a multiplet in the spectra of **1** and **2**, which are recorded in DMSO-$d_6$ solution. Under the same conditions, 4-H of the furan ring in compound **1** gives a threefold doublet. The long-range coupling of this proton to phosphorus, measured from the spectrum, is about 0.5 Hz.

In the $^{13}C\{^1H\}$ NMR spectra of **1** and **2**, the carbon atoms adjacent to the nitrogen atom and the carbon atoms of the furan ring show doublets, due to coupling with phosphorus.[30] The alkoxy methyl and methylene carbon atoms give rise to pairs of doublets because of the nonequivalence of the two alkyl ester groups, as well as of the signal splittings




**SCHEME 2**



resulting from the carbon–phosphorus two- and three-bond couplings,[30] respectively. Long-range couplings of phosphorus to the other carbon atoms of the naphthalene ring in **1** and **2** are not observed. Each of these carbon atoms gives a singlet in the chemical shift region reported for corresponding 1,5-diaminonaphthalene carbon atoms.[31,32]

The $^{31}P\{^{1}H\}$ NMR spectra of the recrystallized compounds **1** and **2** consist each of only one singlet (see the Experimental section). One signal is also observed in the $^{31}P\{^{1}H\}$ NMR spectra of the analogous purified addition products of dialkyl phosphites to bis(imines) **3–5**, described previously[20,22,25] (Scheme 2). In this study, we analyzed samples of the crude reaction products **1–5** by $^{31}P$ NMR spectroscopy. The spectra of the nonrecrystallized products **1** and **3–5** show a singlet, which indicates that only one diastereomer is formed during the reaction. Thus, the experiments reveal the complete stereoselectivity of the dialkyl phosphite addition to the bis(imines) in these cases. In the case of **2** the reaction mixture gives two phosphorus signals with unequal intensity and very similar chemical shifts—at 20.35 and 20.33 ppm (Figure 1a). The intensity ratio of the signals is 9:1. This observation indicates that in this case the diethyl phosphite addition to the *N*,*N*′-difurfurylidene-1,5-naphthalenediamine is not completely stereoselective and leads to the predominant formation (in 90%) of one of the diastereomers. Thus the crude product **2** is a mixture of the racemic and *meso* forms. In the spectrum of the purified sample **2** appears only the phosphorus NMR signal at 20.33 ppm (Figure 1b) assigned to the major diastereomer formed by the addition reaction.

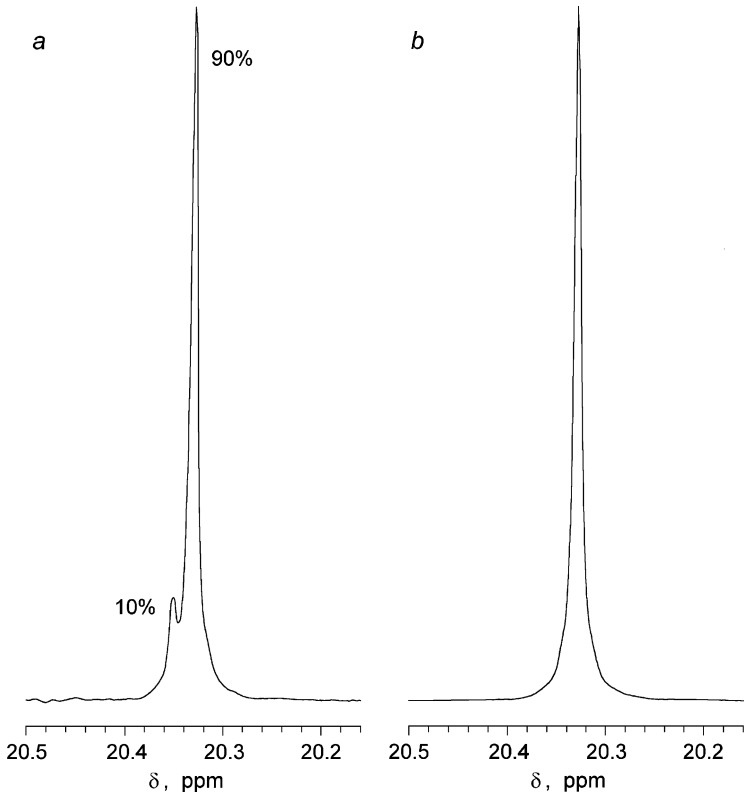



**FIGURE 1** $^{31}P\{^{1}H\}$ NMR spectrum of the crude (a) and the recrystallized (b) compound **2**.



## EXPERIMENTAL

Dimethyl phosphite (Sigma Aldrich Chemie GmbH, Steinhelm, Germany) and diethyl phosphite (Fluka Chemie AG, Buchs, Switzerland) were purified by vacuum distillation. All solvents were freshly distilled prior to use. The melting points of the products were determined on a Kofler microscope and are uncorrected. IR spectra were taken on a Bruker IFS 1113 spectrophotometer in KBr pellets. $^{31}P\{^{1}H\}$ and $^{1}H$ NMR spectra in $CDCl_3$ were recorded with a Varian-Inova 500 MHz spectrometer at r.t. using 85% $H_3PO_4$ as an external reference and tetramethylsilane (TMS) as an internal standard. $^{1}H$ (DMSO-$d_6$), $^{13}C\{^{1}H\}$, DEPT, and CH COSY ($CDCl_3$) NMR spectra were recorded on a Bruker DRX-250 250 MHz spectrometer at r.t. and TMS as an internal standard. TLC was perform on acid-washed

silica gel with a 254-nm fluorescent indicator on polyester 60Å (Sigma) at r.t. Samples were applied as $CHCl_3$ solutions. Chromatograms were developed ascendingly using benzene:methanol (10:1). Spots were detected under UV light and in an iodine-vapor atmosphere. The Schiff base *N*,*N*′-difurfurylidene-1,5-naphthalenediamine was prepared from furfural and 1,5-naphthalenediamine according to S. D. Warren Co.,[26] m.p. 176–177°C (literature m.p. 173–174°C[26]); IR (KBr pellet), $\tilde{\nu}$ ($cm^{-1}$): 1625 ($\nu_{C=N}$); 1598, 1580, 1557, 1504, 1478 ($\nu_{C=C(Ar,Fur)}$); 1029 ($\nu_{C-O-C}$); $^1$H NMR ($CDCl_3$), $\delta$(ppm), $J_{HH}$ (Hz): 8.37 (s, 2H, CH=N); 8.24 (d, $^3J = 8.0$, 2H, ArH-4,8); 7.67 (m, 2H, FurH-5); 7.47 (dd, $^3J = 8.3$ and 7.3, 2H, ArH-3,7); 7.08 (d, $^3J = 7.5$, 2H, ArH-2,6); 7.05 (d, $^3J = 3.5$, 2H, FurH-3); 6.60 (dd, $^3J = 3.5$ and 1.5, 2H, FurH-4). 4,4′-bis[*N*-methyl(diethoxyphosphonyl)-1-(2-furyl)]diaminodiphenylmethane **3** was prepared as described in Kraicheva et al.[22] Bis[*N*-methyl(diethoxyphosphonyl)-1-(2-furyl)]benzidine **4** and bis[*N*-methyl(diisopropoxyphosphonyl)-1-(2-furyl)]benzidine **5** were synthesized according to Kraicheva.[25] $^{31}$P NMR ($CDCl_3$), $\delta$(ppm); purified compound, crude product: **3**: 20.6 (s)[20], 20.5 (s); **4**: 20.5 (s)[20], 20.4 (s); **5**: 18.6 (s), 18.6 (s).



## 1,5-Bis[*N*-methyl(dimethoxyphosphonyl) -1-(2-furyl)]diaminonaphthalene (1)

*N*,*N*′-Difurfurylidene-1,5-naphthalenediamine (4.05 g, 12.90 mmol) and dimethyl phosphite (3.69 g, 33.55 mmol) were mixed and stirred, and a saturated methanolic $CH_3ONa$ solution was added dropwise. After stirring at an ambient temperature for 3 h, the reaction mixture was washed with water and filtered. The crude product was purified by recrystallization from benzene. The colorless crystalline powder obtained was dried in vacuo to constant weight.

Yield: 3.52 g (51%); m.p. 209–210°C; $R_f = 0.52$. Anal. calcd. (%) for $C_{24}H_{28}N_2O_8P_2$: C, 53.93; H, 5.24; N, 5.24. Found: C, 53.81; H, 5.13; N, 5.17. IR (KBr pellet), $\tilde{\nu}$ ($cm^{-1}$): 3287 ($\nu_{NH}$); 1596, 1532, 1495 ($\nu_{C=C(Ar,Fur)}$); 1247 ($\nu_{P=O}$); 1058, 1029 ($\nu_{P-OMe,C-O-C}$). $^1$H NMR, $\delta$(ppm), $J_{HH}$ (Hz), $J_{PH}$ (Hz). Solvent DMSO-$d_6$: 7.62 (m, 2H, FurH-5); 7.44 (d, $^3J = 8.5$, 2H, ArH-4,8); 7.25 (pseudo-t, $^3J = 8.0$, 2H, ArH-3,7); 6.83 (d, $^3J = 7.7$, 2H, ArH-2,6); 6.58 (pseudo-t, $^3J$, $^4J = 3.0$, 2H, FurH-3); 6.42 (ddd, $^3J = 3.2$ and 1.9, $^5J = 0.5$, 2H, FurH-4); 5.65 (dd, $^3J = 9.9$ and 4.8, 2H, NH); 5.43 (dd, $^2J = 24.0$, $^3J = 9.9$, 2H, CHP); 3.72 and 3.61 (2d, $^3J = 10.6$ and 10.6, 12H, $CH_3$). Solvent $CDCl_3$: 7.42 (d, $^3J = 8.3$, 2H, ArH-4,8); 7.40 (dd, $^3J = 1.9$, $^4J = 0.8$, 2H, FurH-5); 7.29 (pseudo-t, $^3J = 8.3$, 2H, ArH-3,7); 6.65 (d, $^3J = 7.5$, 2H, ArH-2,6); 6.42 (pseudo-t, $^3J$, $^4J = 3.3$, 2H, FurH-3); 6.32 (dd, $^3J = 3.2$ and 1.9, 2H, FurH-4); 5.17 (pseudo-t, $^3J = 7.8$, 2H, NH); 5.08 (dd, $^2J = 23.5$, $^3J = 9.0$, 2H,

CHP); 3.83 and 3.66 (2d, $^3J = 10.7$ and 10.6, 12H, $CH_3$). $^{31}P\{^1H\}$ NMR (200 MHz, $CDCl_3$), $\delta$(ppm): 22.7. $^{13}C\{^1H\}$ NMR (62.90 MHz, $CDCl_3$), $\delta$(ppm), $J_{PC}$ (Hz): 148.7 (d, $^2J = 2.5$, FurC-2); 142.7 (d, $^4J = 3.2$, FurC-5); 141.5 (d, $^3J = 13.3$, ArC-1,5); 125.5 (ArC-3,7); 124.8 (ArC-9,10); 111.3 (ArC-4,8); 110.8 (d, $^4J = 2.4$, FurC-4); 109.0 (d, $^3J = 7.3$, FurC-3); 107.1 (ArC-2,6); 54.2 and 53.8 (2d, $^2J = 6.9$ and 6.8, $CH_3$); 50.1 (d, $^1J = 160.2$, CHP).

## 1,5-Bis[*N*-methyl(diethoxyphosphonyl) -1-(2-furyl)]diaminonaphthalene (2)

**2** was prepared from *N,N′*-difurfurylidene-1,5-naphthalenediamine (4.05 g, 19.90 mmol) and diethyl phosphite (4.63 g, 33.55 mmol) using $C_2H_5ONa$ as a catalyst following the procedure given for **1**.

Yield: 4.80 g (63%); m.p. 194–195°C; $R_f = 0.66$. Anal. calcd. (%) for $C_{28}H_{36}N_2O_8P_2$: C, 56.95; H, 6.10; N, 4.75. Found: C, 56.81; H, 6.03; N, 4.68. IR (KBr pellet), $\tilde{\upsilon}$ ($cm^{-1}$): 3353 ($\upsilon_{NH}$); 1592, 1547, 1500, 1479 ($\upsilon_{C=C(Ar,Fur)}$); 1241 ($\upsilon_{P=O}$); 1049, 1015 ($\upsilon_{P-OEt,C-O-C}$). $^1H$ NMR, $\delta$(ppm), $J_{HH}$ (Hz), $J_{PH}$ (Hz). Solvent DMSO-$d_6$: 7.59 (m, 2H, FurH-5); 7.37 (d, $^3J = 8.5$, 2H, ArH-4,8); 7.23 (pseudo-t, $^3J = 8.0$, 2H, ArH-3,7); 6.79 (d, $^3J = 7.7$, 2H, ArH-2,6); 6.54 (pseudo-t, $^3J$, $^4J = 3.2$, FurH-3); 6.39 (dd, $^3J = 3.0$ and 2.0, 2H, FurH-4); 5.57 (dd, $^3J = 9.9$ and 5.2, 2H, NH); 5.32 (dd, $^2J = 23.9$, $^3J = 9.9$, 2H, CHP); 3.98 (m, 8H, $OCH_2$); 1.17 and 1.11 (2t, $^3J = 7.2$ and 7.3, 12H, $CH_3$). Solvent $CDCl_3$: 7.40 (d, $^3J = 8.5$, 2H, ArH-4,8); 7.39 (m, 2H, FurH-5); 7.28 (pseudo-t, $^3J = 8.0$, 2H, ArH-3,7); 6.63 (d, $^3J = 7.5$, 2H, ArH-2,6); 6.40 (pseudo-t, $^3J$, $^4J = 3.3$, 2H, FurH-3); 6.32 (dd, $^3J = 3.0$ and 2.0, 2H, FurH-4); 5.04 (d, $^2J = 23.5$, 2H, CHP); 4.88 (br.s., 2H, NH); 4.21, 4.09 and 3.92 (3m, 8H, $OCH_2$); 1.29 and 1.22 (2t, $^3J = 7.0$ and 7.0, 12H, $CH_3$). $^{31}P\{^1H\}$ NMR (200 MHz, $CDCl_3$), $\delta$(ppm): 20.3. $^{13}C\{^1H\}$ NMR (62.90 MHz, $CDCl_3$), $\delta$(ppm), $J_{PC}$ (Hz): 149.1 (d, $^2J = 2.4$, FurC-2); 142.5 (d, $^4J = 3.1$, FurC-5); 141.7 (d, $^3J = 13.6$, ArC-1,5); 125.5 (ArC-3,7); 124.7 (ArC-9,10); 111.1 (ArC-4,8); 110.8 (d, $^4J = 2.6$, FurC-4); 108.7 (d, $^3J = 7.2$, FurC-3); 106.9 (ArC-2,6); 63.6 and 63.4 (2d, $^2J = 6.8$ and 6.9, $OCH_2$); 50.5 (d, $^1J = 159.2$, CHP); 16.4 and 16.3 (2d, $^3J = 5.9$ and 5.9, $CH_3$).

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