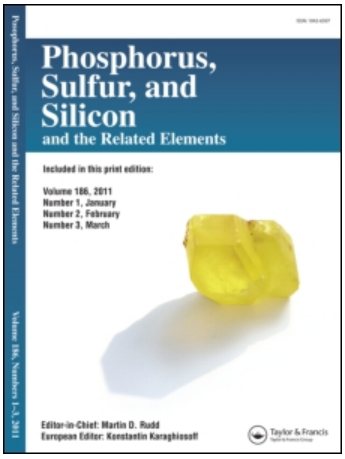

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SYNTHESIS AND NMR SPECTROSCOPIC STUDY OF NEW 5-METHYLFURYL-CONTAINING SCHIFF BASES AND RELATED BIS(AMINOPHOSPHONATES)

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The synthesis of three novel 5-methylfuryl-containing Schiff bases: N,N′*-bis(5-methylfurfurylidene)-4,4′-diaminodiphenylmethane,* N,N′*-bis(5-methylfurfurylidene)-1,4-phenylenediamine, and* N,N′*-bis(5-methylfurfurylidene)benzidine and the corresponding bis(aminophosphonates) derived from them, 4,4′-bis{*N*-methyl(diethoxyphosphonyl)-1-[(5-methyl)-2-furyl]}diaminodiphenylmethane, 1,4-bis{*N*-methyl(diethoxyphosphonyl)-1-[(5-methyl)-2-furyl]}diaminobenzene, and bis{*N*-methyl(diethoxyphosphonyl)-1-[(5-methyl)-2-furyl]}-benzidine, is reported. The compounds have been characterized by elemental analysis, TLC, IR, and NMR (^{1}H, ^{13}C, and ^{31}P) spectra. For comparison, new ^{13}C and ^{31}P NMR data of three furyl-containing analogues of the above bis(aminophosphonates) are also regarded. The NMR studies of the two series of bis(aminophosphonates) reveal the presence of one diastereomer (meso or racemic form).*

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

INTRODUCTION

The extensive studies on the biochemical properties of aminophosphonic acid derivatives revealed various possibilities for their application in agrochemistry[1–6] and medicine.[4,7,8] It has been shown that a large number of their representatives can be used as diagnostic[4,9,10] and therapeutic[11,12] agents, including antitumor drugs.[13,14] Thus, an important group among them, bis(aminophosphonate) derivatives,

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exert direct cytostatic effects on a variety of human tumor cells and are quite promising drugs in clinical practice.[13] The search for new aminophosphonate derivatives with better therapeutic characteristics has lead to the synthesis of numerous analogues.[11,15–17] The addition of dialkyl (diaryl) phosphites to azomethines is the most convenient method for the preparation of aminophosphonates.[1,18] The stereochemical aspects of this reaction attract much attention in the past years.[19–22]

Taking into account the DNA-binding properties and cytotoxic effect of some substituted furan derivatives,[23,24] bis(aminophosphonates) bearing a furan moiety appear of particular interest as potential antitumor agents combining both pharmacophoric groups.

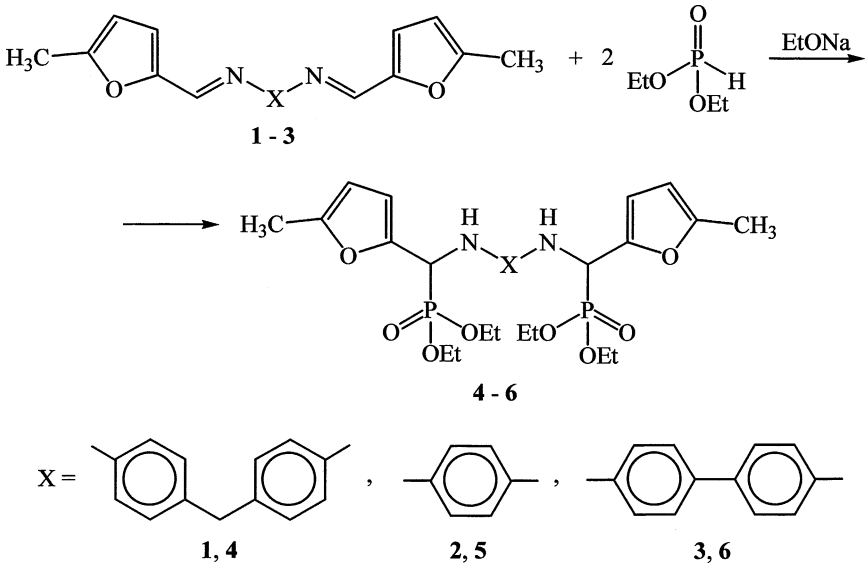
The subject of the present work is the synthesis and NMR (^{1}H, ^{13}C, and ^{31}P) spectroscopic characterization of three novel 5-methylfuryl-containing bis(imines) and bis(aminophosphonates) derived from them. For comparison, new ^{13}C and ^{31}P NMR data on several earlier described[25,26] furyl-containing bis(aminophosphonates) are also included.

RESULTS AND DISCUSSION

New Schiff bases, *N*,*N*′-bis(5-methylfurfurylidene)-4,4′-diaminodiphenylmethane (**1**), *N*,*N*′-bis(5-methylfurfurylidene)-1,4-phenylenediamine (**2**), and *N*,*N*′-bis(5-methylfurfurylidene)benzidine (**3**) were prepared in good yields by condensation of 5-methylfurfural and the corresponding aromatic diamine. The compounds are yellow crystalline solids soluble in most organic solvents. They were characterized by elemental analysis, IR, and ^{1}H NMR spectroscopy (see the Experimental section below).

Three novel bis(aminophosphonates), 4,4′-bis{*N*-methyl(diethoxyphosphonyl)-1-[(5-methyl)-2-furyl]}diaminodiphenylmethane (**4**), 1,4-bis{*N*-methyl(diethoxyphosphonyl)-1-[(5-methyl)-2-furyl]}diaminobenzene (**5**), and bis{*N*-methyl(diethoxyphosphonyl)-1-[(5-methyl)-2-furyl]}benzidine (**6**) were synthesized through addition of diethyl phosphite to the azomethine bonds of the furan-substituted bis(imines) (**1–3**). The reaction was carried out at ambient temperature in the presence of an alkaline catalyst (Scheme 1). The products obtained (**4–6**) are crystalline solids soluble in methanol, ethanol, benzene, chloroform. Thin layer chromatography (TLC) gave one spot for each of them. The expected absorption bands of the characteristic structural fragments[27–29] are observed in the IR spectra of compounds **4–6** (see the Experimental section below).

The addition of dialkyl (diaryl) phosphites to bis(imines) should lead to the formation of two diastereomeric forms, *meso* and racemic.[19–21]



SCHEME 1

Each of the compounds **4–6** exhibits only one set of signals in the ^{1}H, ^{13}C, and ^{31}P NMR spectra, suggesting that only one of the two possible diastereomers is formed in the addition reaction. In the ^{1}H NMR spectra of **4–6** registered in dimethylsulfoxide (DMSO)-d_6 solution, the signals of the CHP and NH protons appear as a doublet of doublets. One signal of the CHP proton is observed in the spectra taken in $CDCl_3$: a doublet of doublets for **4**, and a doublet for **5** and **6**. In the same solvent, the signal of the NH proton appears as a doublet of doublets in the spectrum of **4**, while in the spectra of **5** and **6** this signal is overlapped with the multiplets of the OCH_2 protons. The methyl protons of the phosphonate moiety in **4–6** give two triplets due to the nonequivalence of the two ethoxy groups.[19–21,30] The signal of the furan proton FurH-3 appears in the spectra as a pseudotriplet because of the very similar values of the coupling constants $^{3}J_{HH}$ and $^{4}J_{PH}$.[31] The signal of the furan proton FurH-4 in **4–6** is observed as a doublet (poorly resolved) or as a multiplet (see the Experimental section below). The HH COSY spectra indicated that this proton interacts with the proton FurH-3, as well as with those of the methyl substituent in the furan ring (Fur-CH_3). In the spectrum of **6** taken in $CDCl_3$, this signal is registered with the expected multiplicity—a doublet of doublets (poorly resolved)—owing to the coupling between Fur-CH_3 and the furan ring protons.

Likewise, in the ^{1}H NMR spectra one set of signals is observed in the $^{31}P\{^{1}H\}$ and $^{13}C\{^{1}H\}$ NMR spectra of compounds **4–6** registered in $CDCl_3$, thus confirming the stereoselectivity of the reaction (see the Experimental section below). For comparison, analogous addition products (**7–9**) of diethyl phosphite to difuryl-containing Schiff bases described earlier[25,26] were also studied now by means of ^{31}P and ^{13}C NMR spectroscopy (Table I). The NMR studies showed that the bis(aminophoshonates) **7–9** also consist in only one diastereomer (*meso* or *racemic* form). The $^{31}P\{^{1}H\}$ NMR spectra of the two series of bis(aminophosphonates) (**4–9**) consist of one singlet at 20–21 ppm.

The assignment of the carbon atom signals in compounds **4–9** was achieved by joint use of 1D ($^{13}C\{^{1}H\}$) and 2D (CH COSY and CH COLOC) NMR spectra and is in accordance with the literature data for similar compounds.[32] In the $^{13}C\{^{1}H\}$ spectra of **4–9**, the carbon atoms of the CHP, furane, and PhC-NH fragments give doublet signals due to the carbon–phosphorus interaction. The nonequivalence of the ethoxy groups gives rise to the appearance of pairs of signals for their methyl and methylene carbons. Each of these signals is split into a doublet because of the coupling with ^{31}P. Long-range coupling between ^{31}P and the aromatic carbon atoms PhC-*o*,*m* and PhC-1,1′ in **4–9** was not detected. There are no substantial differences in the ^{13}C-chemical shifts of the corresponding atoms of the phosphonate residues and of the phenylene rings in the two series of bis(aminophosphonates). The spectra of compounds **4–6** reveal a minimal shielding at the two carbon atoms FurC-2 and FurC-4, whereas the FurC-5 carbon is deshielded (*ca*. 10 ppm) relative to the analogous atom in **7–9**.

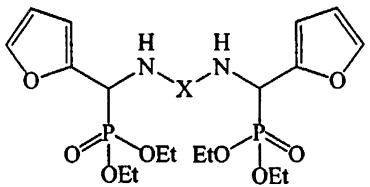
All compounds **4–9** exhibit a weak two-bond coupling (up to 2 Hz) to ^{31}P for FurC-2, while the three-bond interaction is stronger—^{3}J(P-FurC-3) is in the range of 7.00–7.38 Hz. The long-range coupling constants ^{4}J(P-FurC-4) and ^{4}J(P-FurC-5) are in the intervals of 2.25–2.63 and 2.28–3.25 Hz, respectively. The P—C coupling constants for carbon atoms adjacent to nitrogen (CHP and PhC—NH), and of the ethoxy groups in **4–9** are in agreement with the values reported for other aminophosphonate derivatives.[32]

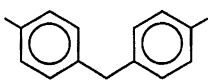
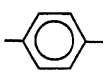
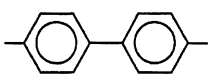
EXPERIMENTAL

Starting Compounds

Diethyl phosphite (Fluka Chemie AG, Switzerland) was purified by vacuum distillation, 5-methylfyrfural, 4,4′-diaminodiphenylmethane, 1,4-phenylenediamine (Fluka, *pract*.), and benzidine (Fluka, *purum*) were used as received. All solvents were freshly distilled prior to use.

TABLE I ^{13}C and ^{31}P NMR Parameters of Compounds of the Type:



No.	x	^{13}C NMR: δ, ppm (J_{PC}, Hz)									^{31}P NMR δ, ppm
		CH_3, 2d (^3J)	OCH_2, 2d (^2J)	CHP, d (^1J)	FurC-2, d (^2J)	FurC-3, d (^3J)	FurC-4, d (^4J)	FurC-5, d (^4J)	PhC-NH, d (^3J)	PhC- $o+m$	
7[a]		16.21 (5.50) 16.37 (5.50)	63.18 (7.00) 63.41 (7.13)	50.40 (158.38)	149.47 (1.50)	108.64 (7.13)	110.69 (2.63)	142.35 (3.00)	144.12 (13.25)	113.99 129.43	20.57
8		16.20 (5.63) 16.35 (5.88)	63.10 (7.00) 63.37 (7.00)	51.29 (158.75)	149.66 (1.50)	108.60 (7.00)	110.64 (2.63)	142.29 (3.00)	139.18 (14.38)	115.66	20.72
9[a]		16.22 (5.50) 16.38 (5.88)	63.25 (7.00) 63.45 (7.00)	50.30 (158.50)	149.38 (1.38)	108.72 (7.00)	110.73 (2.25)	142.42 (2.88)	144.68 (13.25)	114.18 127.08	20.47

[a] $^{13}C\{^1H\}$ NMR: δ, ppm: **7**, 132.13 (PhC-1,1′), 40.03 (CH_2Ph); **9**, 131.81 (PhC-1,1′).

4,4′-Bis[*N*-methyl(diethoxyphosphonyl)-1-(2-furyl)]diaminodiphenylmethane (**7**) and 1,4-bis[*N*-methyl(diethoxyphosphonyl)-1-(2-furyl)]-diaminobenzene (**8**) were prepared as described in Kraicheva et al.[25] and bis[*N*-methyl(diethoxyphosphonyl)-1-(2-furyl)]benzidine (**9**) was prepared according to Kraicheva.[26]

Apparatus and Conditions

The melting points of the products were determined on a Kofler microscope and are uncorrected. The IR spectra were recorded on a Bruker IFS 1113 spectrophotometer in KBr disks.

All $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ (solvent $CDCl_3$) NMR spectra of compounds **6–9** were registered on a Varian_Inova 500 MHz spectrometer at room temperature using 85% H_3PO_4 as external reference, and tetramethylsilane (TMS) as internal standard. The ramaining NMR spectra—^1H (solvents dimethylsulfoxide (DMSO)-d_6 and $CDCl_3$), $^{13}C\{^1H\}$, DEPT, HH COSY, CH COSY, and CH COLOC (solvent $CDCl_3$)–were recorded on a Bruker DRX-250 250 MHz spectrometer at room temperatute and TMS as internal standard.

The thin layer chromatography (TLC) was performed on Kieselgel-60 F254 plastic sheets (Merck Sigma Chemical Co., Germany) at room temperature. The samples were applied as $CHCl_3$ solutions. The chromatograms were developed ascendingly using the benzene: methanol (10:1) solvent system. The spots were detected under UV light and in I_2 vapor atmosphere.

Schiff Bases 1–3

The Schiff bases **1–3** were prepared from 5-methylfurfural and aromatic diamines according to the example given for **1**.

N,N′-*Bis(5-methylfurfurylidene)-4,4′-diaminodiphenylmethane (1)*

4,4′-Diaminodiphenylmethane (5.64 g, 28.48 mmol) was dissolved in diethyl ether (150 ml) and 5-methylfurfural (6.89 g, 62.67 mmol) was added. The solution was stirred at room temperature under nitrogen for 4 h. The yellow precipitate obtained was filtered and recrystallized from cyclohexane.

Yield: 9.14 g (84%); m.p. 110–111°C. Anal. Calc. (%) for $C_{25}H_{22}N_2O_2$: C, 78.53; H, 5.76; N, 7.33. Found: C, 78.27; H, 5.58; N, 7.12. IR (KBr disk), $\tilde{\nu}$ (cm^{-1}): 1629 ($\nu_{C=N}$); 1600, 1579, 1531, 1431 ($\nu_{C=C(Ar,Fur)}$); 1026 (ν_{C-O-C}). ^1H NMR ($CDCl_3$), δ(ppm), J_{HH} (Hz): 8.17 (s, 2H, CH=N); 7.19 (m, 8H, PhH); 6.81 (d, ^3J = 3.22, 2H, FurH-3; 6.16 (m, 2H, FurH-4); 3.99 (s, 2H, CH_2Ph); 2.42 (s, 6H, Fur-CH_3).

N,N′-*Bis(5-methylfurfurylidene)-1,4-phenylenediamine (2)*

Yield: 7.10 g (85%), m.p. 139–140°C (from toluene). Anal. Calc. (%) for $C_{18}H_{16}N_2O_2$: C, 73.97; H, 5.48; N, 9.59. Found: C, 73.72; H, 5.32; N, 9.43. IR (KBr disk), $\tilde{\nu}$ (cm^{-1}): 1613 ($\nu_{C=N}$); 1576, 1528, 1484, 1453 ($\nu_{C=C(Ar,Fur)}$); 1027 (ν_{C-O-C}). ^1H NMR ($CDCl_3$), δ(ppm), J_{HH} (Hz): 8.22 (s, 2H, CH=N); 7.27 (s, 4H, PhH); 6.83 (d, $^3J = 3.29$, 2H, FurH-3); 6.18 (m, 2H, FurH-4); 2.44 (s, 6H, Fur-CH_3).

N,N′-*Bis(5-methylfurfurylidene)benzidine (3)*

Yield: 8.28 g (79%); m.p. 180–182°C (from toluene). Anal. Calcd. (%) for $C_{24}H_{20}N_2O_2$: C, 78.26; H, 5.43; N, 7.61. Found: C, 78.32; H, 5.33; N, 7.54. IR (KBr disk), $\tilde{\nu}$ (cm^{-1}): 1628 ($\nu_{C=N}$); 1594, 1578, 1529, 1480 ($\nu_{C=C(Ar,Fur)}$); 1023 (ν_{C-O-C}). ^1H NMR ($CDCl_3$), δ(ppm), J_{HH} (Hz): 8.24 (s, 2H, CH=N); 7.48 (m, 8H, PhH); 6.85 (d, $^3J = 3.32$, 2H, FurH-3); 6.19 (m, 2H, FurH-4); 2.45 (s, 6H, Fur-CH_3).

Bis(aminophosphonates) 4–6

Compounds **4–6** were synthesized from diethyl phosphite and the corresponding Schiff bases **1–3** following the procedure given for **4**.

*4,4′-Bis{*N*-methyl(diethoxyphosphonyl)-1-[(5-methyl)-2-furyl]}diaminodiphenylmethane (4)*

N,*N*′-Bis(5-methylfurfurylidene)-4,4′-diaminodiphenylmethane (6.86 g, 17.96 mmol) and diethyl phosphite (6.44 g, 46.69 mmol) were mixed, and a saturated solution of C_2H_5ONa was added dropwise with stirring until the exothermicity ceased. The mixture was then stirred for 4 h at room temperature. The crude product was purified by recrystallization from ethanol. The colorless crystalline powder obtained was dried in vacuo to constant weight.

Yield: 7.92 g (67%); m.p. 154–155°C; $R_f = 0.66$. Anal. Calc. (%) for $C_{33}H_{44}N_2O_8P_2$: C, 60.18; H, 6.69; N, 4.26. Found: C, 60.03; H, 6.58; N, 4.36. IR (KBr disk), $\tilde{\nu}$ (cm^{-1}): 3294 (ν_{NH}); 1614, 1557, 1518, 1441 ($\nu_{C=C(Ar,Fur)}$); 1240 ($\nu_{P=O}$); 1057, 1026 ($\nu_{P-OEt,C-O-C}$). ^1H NMR, δ(ppm), J_{HH} (Hz),J_{HP} (Hz). Solvent DMSO-d_6: 6.77 (m, 8H, PhH); 6.29 (pseudo-t, ^3J, $^4J = 3.15$, 2H, FurH-3); 5.97 (d, $^3J = 2.98$, 2H, FurH-4); 5.73 (dd, $^3J = 10.31$ and 4.57, 2H, NH); 4.97 (dd, $^2J = 23.98$, $^3J = 10.28$, 2H, CHP); 3.95 (m, 8H, OCH_2); 3.57 (s, 2H, CH_2Ph); 2.20 (s, 6H, Fur-CH_3); 1.17 and 1.12 (2t, $^3J = 6.87$ and 6.82, 12H, CH_3). Solvent $CDCl_3$: 6.75 (m, 8H, PhH); 6.22 (pseudo-t, ^3J, $^4J = 3.30$, 2H, FurH-3); 5.88 (m, 2H, FurH-4); 4.77 (dd, $^2J = 23.63$, $^3J = 9.36$, 2H, CHP); 4.37 (dd, $^3J = 9.31$ and 6.70, 2H, NH); 4.11 and 3.87 (2m, 8H, OCH_2); 3.71 (s, 2H, CH_2Ph); 2.25 (m, 6H, Fur-CH_3); 1.28 and 1.20 (2t, $^3J = 7.09$ and 7.08, 12H, CH_3).

$^{31}P\{^{1}H\}$ NMR (200 MHz, $CDCl_3$), δ(ppm): 20.79. $^{13}C\{^{1}H\}$ NMR (62.90 MHz, $CDCl_3$), δ(ppm), J_{CP} (Hz): 152.09 (d, $^{4}J = 3.16$, FurC-5); 147.29 (d, $^{2}J = 1.98$, FurC-2); 144.23 (d, $^{3}J = 13.34$, PhC-NH); 132.03 (PhC-1,1′); 129.42 and 114.00 (PhC-*ortho* and *meta*); 109.51 (d, $^{3}J = 7.36$, FurC-3); 106.70 (d, $^{4}J = 2.30$, FurC-4); 63.35 and 63.19 (2d, $^{2}J = 6.89$ and 6.89, OCH_2); 50.39 (d, $^{1}J = 160.01$, CHP); 40.08 (CH_2Ph); 16.41 and 16.22 (2d, $^{3}J = 5.67$ and 5.90, CH_3); 13.60 (CH_3-Fur).

*1,4-Bis{*N*-methyl(diethoxyphosphonyl)-1-[(5-methyl)-2-furyl]}diaminobenzene (5)*

Yield: 5.20 g (51%), m.p. 182–184°C; $R_f = 0.59$. Anal. Calc. (%) for $C_{26}H_{38}N_2O_8P_2$: C, 54.93; H, 6.69; N, 4.93. Found: C, 54.82; H, 6.57; N, 5.00. IR (KBr disk), $\tilde{\nu}$ (cm^{-1}): 3335 (ν_{NH}); 1610, 1551, 1521, 1473, 1443 ($\nu_{C=C(Ar,Fur)}$); 1226 ($\nu_{P=O}$); 1056, 1022 ($\nu_{P-OEt,C-O-C}$). ^{1}H NMR, δ(ppm), J_{HH} (Hz), J_{HP} (Hz). Solvent DMSO-d_6: 6.60 (s, 4H, PhH); 6.26 (pseudo-t, $^{3}J,^{4}J = 3.19$, 2H, FurH-3); 5.96 (d, $^{3}J = 2.94$, 2H, FurH-4); 5.15 (dd, $^{3}J = 10.76$ and 4.53, 2H, NH); 4.85 (dd, $^{2}J = 23.99$, $^{3}J = 10.74$, 2H, CHP); 3.93 (m, 8H, OCH_2); 2.19 (s, 6H, Fur-CH_3); 1.17 and 1.10 (2t, $^{3}J = 7.05$ and 7.05, 12H, CH_3). Solvent $CDCl_3$: 6.53 (s, 4H, PhH); 6.19 (pseudo-t, $^{3}J,^{4}J = 3.27$, 2H, FurH-3); 5.87 (d, $^{3}J = 2.98$, 2H, FurH-4); 4.67 (d, $^{2}J = 23.51$, 2H, CHP); 4.09 and 3.86 (2m, 10H, OCH_2, NH); 2.24 (m, 6H, Fur-CH_3); 1.27 and 1.19 (2t, $^{3}J = 7.07$ and 7.08, 12H, CH_3). $^{31}P\{^{1}H\}$ NMR (200 MHz, $CDCl_3$), δ(ppm): 20.96. $^{13}C\{^{1}H$NMR (62.90 MHz, $CDCl_3$), δ(ppm), J_{CP} (Hz): 152.00 (d, $^{4}J = 3.13$, FurC-5); 147.51 (FurC-2); 139.19 (d, $^{3}J = 14.05$, PhC-NH); 115.63 (PhC-*ortho*); 109.44 (d, $^{3}J = 7.38$, FurC-3); 106.64 (d, $^{4}J = 2.26$, FurC-4); 63.29 and 63.08 (2d, $^{2}J = 6.76$ and 6.96, OCH_2); 51.26 (d, $^{1}J = 160.05$, CHP); 16.38 and 16.21 (2d, $^{3}J = 5.87$ and 5.96, CH_3); 13.58 (CH_3-Fur).

*Bis{*N*-methyl(diethoxyphosphonyl)-1-[(5-methyl)-2-furyl]}benzidine (6)*

Yield: 6.82 g (59%), m.p. 201–203°C; $R_f = 0.63$. Anal. Calc. (%) for $C_{32}H_{42}N_2O_8P_2$: C, 59.63; H, 6.52; N, 4.35. Found: C, 59.63; H, 6.27; N, 4.45. IR (KBr disk), $\tilde{\nu}$ (cm^{-1}): 3299 (ν_{NH}); 1612, 1557, 1507, 1442 ($\nu_{C=C(Ar,Fur)}$); 1236 ($\nu_{P=O}$); 1057, 1026 ($\nu_{P-OEt,C-O-C}$). ^{1}H NMR, δ(ppm), J_{HH} (Hz), J_{HP} (Hz). Solvent DMSO-d_6: 7.05 (m, 8H, PhH); 6.33 (pseudo-t, $^{3}J,^{4}J = 3.14$, 2H, FurH-3); 6.00 (m, 2H, FurH-4); 5.95 (dd, $^{3}J = 10.27$ and 4.53, 2H, NH); 5.07 (dd, $^{2}J = 23.91$, $^{3}J = 10.19$, 2H, CHP); 3.96 (m, 8H, OCH_2); 2.22 (s, 6H, Fur-CH_3); 1.19 and 1.14 (2t, $^{3}J = 6.91$ and 6.81, 12H, CH_3). Solvent $CDCl_3$: 7.01 (m, 8H, PhH); 6.27 (pseudo-t, $^{3}J,^{4}J = 3.27$, 2H, FurH-3); 5.90 (m, 2H, FurH-4); 4.84 (d, $^{2}J = 23.50$, 2H, CHP); 4.12 and 3.89 (2m, 10H, OCH_2, NH); 2.26 (dd, $^{4}J = 1.81$, $^{5}J = 0.98$, 6H, Fur-CH_3); 1.30 and 1.21 (2t, $^{3}J = 7.09$ and 7.09, 12H, CH_3). $^{31}P\{^{1}H\}$ NMR

(200 MHz, $CDCl_3$), δ(ppm): 20.68. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$), δ(ppm), J_{CP} (Hz): 152.14 (d, $^4J = 3.25$, FurC-5); 147.24 (d, $^2J = 1.88$, FurC-2); 144.78 (d, $^3J = 12.63$, PhC-NH); 131.71 (PhC-1,1′); 127.04 and 114.18 (PhC-*ortho* and *meta*); 109.56 (d, $^3J = 7.00$, FurC-3); 106.71 (d, $^4J = 2.13$, FurC-4); 63.33 and 63.20 (2d, $^2J = 6.63$ and 7.00, OCH_2); 50.32 (d, $^1J = 159.13$, CHP); 16.38 and 16.20 (2d, $^3J = 6.00$ and 5.63, CH_3); 13.56 (CH_3-Fur).

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