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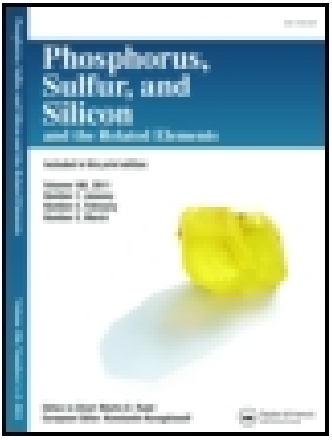

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NOVEL DIESTERS OF AMINOPHOSPHONIC ACIDS CONTAINING FURAN AND BENZIDINE RESIDUE

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NOVEL DIESTERS OF AMINOPHOSPHONIC ACIDS CONTAINING FURAN AND BENZIDINE RESIDUE

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4,4′-Bis[N-methyl(diethoxyphosphonyl)-1-(2-furyl)]benzidine and 4,4′-bis[N-methyl(diisopropoxyphosphonyl)-1-(2-furyl)]benzidine have been synthesized through addition of diethyl phosphite and diisopropyl phosphite, respectively, to the Schiff base N,N′-difurfurylidenebenzidine. The compounds have been characterized by elemental analysis, TLC and IR spectra. A comparable study of their ^{1}H-NMR spectra and ^{1}H-NMR spectra of 4,4′-bis[N-methyl(diethoxyphosphonyl)-1-phenyl]benzidine has been carried out. Some ^{1}H-NMR data of 4,4′-bis[N-methyl(dimethoxyphosphonyl)-1-phenyl]diaminodiphenylmethane, 4,4′-bis[N-methyl(diethoxyphosphonyl)-1-phenyl]diaminodiphenylmethane and 4,4′-bis[N-methyl(diisopropoxyphosphonyl)-1-phenyl]diaminodiphenylmethane in DMSO-d_6 solution are also presented.

Keywords: Schiff bases; aminophosphonic acids; furan derivatives; NMR; IR; TLC

INTRODUCTION

The preparation of novel aminophosphonic acids and their esters continues till now[1–8]. It should be mentioned that despite the large number of the compounds of this type, and the versatility of their structure, relatively few examples of aminophosphonates with the furan moiety are available[9–13]. Earlier, furyl-containing aminophosphonate diesters were prepared, and it was shown that fire retardant polymers can be obtained from them[14]. On the other hand, polymers with increased thermal stability have been prepared from the Schiff base N,N′-difurfurylidenebenzidine[15]. It seemed of interest to prepare aminophosphonates from this Schiff base and dialkyl phosphites. The compounds obtained could be used as monomers for the synthesis of polymers with enhanced fire resistance and thermostability.

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The aim of the present work is to synthesize novel furan and benzidine derived diesters of aminophosphonic acids and to study their structure by means of ^{1}H-NMR spectroscopy, as well as, to compare their spectral properties with those of similar aminophosphonates.

RESULTS AND DISCUSSION

Addition of diethyl- and diisopropyl phosphite to the Schiff base N,N′-difurfurylidenebenzidine, obtained by condensing furfural and benzidine, was performed. Two novel furan and benzidine derived aminophosphonates,
4,4′-bis[N-methyl(diethoxyphosphonyl)-1-(2-furyl)]benzidine (1) and 4,4′-bis[N-methyl(diisopropoxyphosphonyl)- 1-(2-furyl)]benzidine (2), were prepared. The reaction proceeds according to Scheme I.

The diesters **1** and **2** are yellow crystalline compounds with relatively high melting points (above 200°C). They were characterized by elemental analysis and thin layer chromatography (see Experimental).

The newly synthesized compounds **1** and **2**, and 4,4′-bis[N-methyl (diethoxyphosphonyl)-1-phenyl]benzidine,
$C_6H_5CH(P(O)(OEt)_2)NHC_6H_4C_6H_4NHCH(P(O)(OEt)_2)$ (**3**), contain common structural fragments. The synthesis of **3** has been described many years ago[16], but no spectroscopic data about it are available so far. Therefore, a comparison of the spectral properties, especially the ^{1}H-NMR parameters, of the three compounds mentioned is reasonable. The assignment of the IR spectra of **1**, **2** and **3** is in accordance with the literature data for similar compounds[2, 10, 11, 17] (see Experimental). ^{1}H-NMR parameters of compounds **1–3** are summarized in Table I. As shown in Table I, non-equivalence of the two alkyl ester groups in **1–3** takes place, similarly to other diesters of aminophosphonic acids[10–13, 18, 19]. In the DMSO-d_6 and $CDCl_3$spectra of **2**, the signals of the POCH-protons appear as two separate multiplets. More complex are the signals of the methylene protons of the ethoxy groups in **1** and **3**. For them, three separate multiplet signals are identified in the $CDCl_3$ spectra (both **1** and **3**) and in the DMSO-$d_6$spectrum (**3**) (Table I). The area of the multiplet most down-field situated is twice the area of each of the remaining two multiplets, *i. e.* the ratio of the integrals is 2:1:1. Spin-decoupling experiments showed that for the compounds **1** and **3**, the multiplet signal of the methyl-

ene protons which is most down-field situated, and the down-field triplet of the methyl protons belong to the protons of the same OCH_2CH_3 group. Thus, upon selective irradiation of the signal at 4.18 ppm in the $CDCl_3$ spectrum of **1**, only the CH_3-signal at 1.30 ppm is changed (Figure I a). The irradiation of anyone of the remaining multiplets (at 4.04 or at 3.88 ppm) in the same spectrum of **1**, caused change in the triplet at 1.21 ppm (Figure I b). these signals (at 4.04, 3.88 and 1.21 ppm) belong to the protons of the second OCH_2CH_3-group. In this case the diference in the chemical shifts of the signals of the diastereotopic geminal protons is larger, and a distinct multiplet is observed for each of the methylene protons. The elimination of the coupling with the CH_3-protons simplifies these two multiplets in the $CDCl_3$and DMSO-d_6 spectra of **1** and **3** into two quartets of AB type (AB part of an ABX system), as shown in Figure II. In the DMSO-$d_6$spectra of **1** and **3** upon decoupling, the common multiplet signal of the methylene protons of the other ethoxy group appears as down-field doublet with respect to the AB part of the ABX system (see Figure II). However, in the $CDCl_3$ spectra of **1** and **3** this signal is more complex even after eliminating the CH_3-coupling.

In the spectrum of **1** recorded in $CDCl_3$, the signal of the CH(P) protons appears as doublet of doublets as a result of the coupling with the ^{31}P nucleus and the NH proton. In the same spectrum, a triplet (at 4.54 ppm) is observed for the NH protons, like for some substituted arylmethylaminophosphonic acid monoethyl esters[8]. In the spectrum taken at higher temperature (60°C), the signal of the NH protons of 1 appears as a broad singlet at 4.45 ppm. In the $CDCl_3$ spectra of **2** and **3**, the signal of the NH proton is either not observed (**2**) or is overlapped with the signal of CH(P) protons (**3**). Only after D_2O exchange, a doublet signal of the CH(P) protons in **3** was identified (see Table I). In the DMSO-$d_6$spectra of the three compounds the signals of the CH(P) and NH protons were shifted down-field and appeared as doublet of doublets. These two signals were shifted up-field in the DMSO-d_6 spectrum of **1** recorded at 147°C. The coupling constants have similar values except the $^3J_{NHP}$ in **3** where the substituent at the carbon atom of the CH(P) fragment is a phenyl ring instead of a furyl moiety (Table I). Similar feature was observed earlier[13]. This phenomenon provoked the examination of DMSO-d_6 spectra of other diesters of aminophosphonic acids : 4,4′-bis[N-methyl(dimethoxyphosphonyl)-1-phenyl]diaminodiphenylmethane, 4,4′-bis[N-methyl(diethoxyphosphonyl)-1-phenyl]diaminodiphenylmethane and 4,4′-bis[N-methyl (diisopropoxyphosphonyl)-1-phenyl]diaminodiphenylmethane, also described earlier[20] Some unpublished ^{1}H-NMR parameters of these compounds measured in DMSO-d_6 are given in Table II. The signals of the CH(P) and NH protons of these compounds were observed as doublet of doublets in their DMSO-d_6 spectra. As seen from the data of Tables I and II, the coupling constants $^3J_{CHNH}$ measured from the DMSO-d_6 spectra of the compounds have similar values (10.00–10.30 Hz). The value of the $^3J_{CHNH}$ constant is known to depend on the nature of the substituent at the nitrogen atom[21]. In the compounds regarded here, as well as in those described earlier[12, 13], the N atom is bound to an aromatic residue (1,4-C_6H_4, 4,4′-C_6H_4-C_6H_4 or 4,4′-C_6H_4-CH_2-C_6H_4) and this explains the similarity in the values of $^3J_{CHNH}$. At the same time, a more significant difference in the $^3J_{NHP}$ values is observed with respect to the nature of the substituent at the carbon atom of the CH(P) fragment (phenyl ring or furyl moiety).

EXPERIMENTAL

Starting compounds

Dialkyl phosphites (Fluka, purum) were purified by vacuum-distillation. The Schiff base N,N′-difurfurylidenebenzidine was prepared from furfural and benzidine according to Refs. 22, 23, using diethyl ether as solvent, instead of benzene, and conducting the reaction at room temperature. In this way both the yield and purity of the product were improved. Yield of crude product: 93%; recrystallized from benzene; m. p. 237–239°C (literature m. p. 232–233°C[23]). IR (KBr disk), $\tilde{\nu}$ (cm^{-1}): 1625 ($\nu_{C=N}$); 1585, 1560, 1490, 1465 ($\nu_{C=C(Ar,\ Fur)}$). ^{1}H-NMR ($CDCl_3$)δ(ppm): 8.36, s, 2H (CH=N); 7.63, m, 2H ($H_{5,\ Fur}$); 7.49, m, 8H (C_6H_4); 6.98, d, 2H ($H_{3,\ Fur}$), $^3J(H_{3,4,\ Fur})$=3.46 Hz; 6.57, dd, 2H, ($H_{4,\ Fur}$), $^3J(H_{3,4,\ Fur})$=3,46 Hz, $^3J(H_{4,5,\ Fur})$=1.77 Hz.

4,4′-Bis[N-methyl(diethoxyphosphonyl)-1-phenyl]benzidine (**3**) was prepared through addition of diethyl phosphite to the Schiff base N,N′-dibenzylidene-benzidine according to Ref.[16]; m. p. 233–234°C (literature m. p. 220–221°C[16]); R_f=0.73. IR (KBr disk), $\tilde{\nu}$ (cm-^{1}): 3215 (ν_{NH}); 1608, 1585, 1500, 1450 ($\nu_{C=C(Ar)}$); 1235 ($\nu_{P=O}$); 1055, 1025 ($\nu_{P\text{-}OEt}$). ^{1}H-NMR (in DMSO-d_6 and $CDCl_3$), see Table I.

TABLE I ^{1}H-NMR parameters of compounds **1**,**2** and **3**[a]

Compd. No	*Solvent*	*Chemical shifts, δ (ppm)*					*Coupling constants, J (Hz)*						
		CH_3	*OCH*	*CHP*	*NH*	*C_6H_4*	^3J *($CHCH_3$)*	^3J *(POCH)*	^2J *(HCH)*	^2J *(CHP)*	^3J *(CHNH)*	^3J *(NHCH)*	^3J *(NHP)*
1	DMSO-d_6	1.13, t	3.91, m	5.11, dd	5.97, dd	6.99, m	7.06	8 20	–	24.12	10.30	10.32	4.57
		1.07, t		4.93, d[b]	5.20, s,br.[b]		7.04	7.67	10.44	23.24[b]			
								8.49	10.32				
	$CDCl_3$	1.30, t	4.18, m	4.90, dd	4.54, t	7.00, m	7.07	–	–	23 71	9.09	–	–
		1.21, t	4.04, m	4.88, dd[c]	4.45, s, br.[c]		7.06	7.25	10.51	23.57[c]	6.85[c]		
			3.88, m					8 25	10.51				
2	DMSO-d_6	1.25, d	4.66, m	5.02, dd	5.90, dd	7.04, m	6.18	6.53	–	24.42	10.22	10.17	4.90
		1.21, d	4.46, m				6.17	6.36					
		1.16, d					6.18						
		1.03, d					6.17						
	$CDCl_3$	1.34, d	4.78, m	4.84, d	–	6.98, m	6.18	6.98	–	23.92	–	–	–
		1.30, d	4.58, m				6.17	7.01					
		1.26, d					6.18						
		1.07, d					6.20						
3	DMSO-d_6	1.18, t	4.04, m	5.02, dd	6.32, dd	6.96, m	7.05	8.15	–	24.84	10.13	9.92	6.34
		1.03, t	3.87, m				7.05	7.57	10.14				
			3.69, m					8.55	10.00				
	$CDCl_3$	1.27, t	4.10, m	4.80–4.71	4.80–4.71	6.90, m	7.07	–	–	–	–	–	–
		1.10, t	3.93, m	4.75,d[d]			7.07	7.17	9.99	24.17[d]			
			3.67, m					8.57	9.90				

[a] ^{1}H-NMR in DMSO-d_6 and in $CDCl_3$, δ(ppm): **1** – 6.38 and 6.36, respectively (m, $H_{3,4,\,Fur}$), 7.55 and 7.39, respectively (m, $H_{5,\,Fur}$); **2** – 6.42 and 6.35, respectively (m, $H_{3,4,\,Fur}$), 7.59 and 7.37, respectively (m, $H_{5,\,Fur}$); **3** – 7.37 in both solvents (m, C_6H_5).

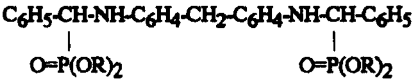
[b] These data were obtained at 147°C.

[c] These data were obtained at 60°C.

[d] These parameters were determined after D_2O-exchange

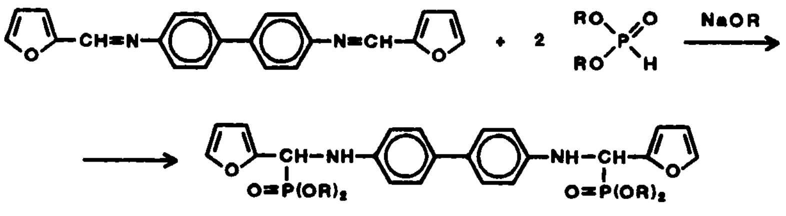
4,4′-Bis[N-methyl(dimethoxyphosphonyl)-1-phenyl]diaminodiphenylmethane, 4,4′-Bis[N-methyl(diethoxyphosphonyl)-1-phenyl]diaminodiphenylmethane and 4,4′-Bis[N-methyl(diisopropoxyphosphonyl)-1-phenyl]diaminodiphenylmethane were prepared as described in[20]. ^{1}H-NMR (in DMSO-d_6), see Table II.

TABLE II ^{1}H-NMR parameters for DMSO-d_6 solutions of compounds of the type:



$$\underset{\displaystyle O{=}P(OR)_2}{C_6H_5\text{-}CH}\text{-}NH\text{-}C_6H_4\text{-}CH_2\text{-}C_6H_4\text{-}NH\text{-}\underset{\displaystyle O{=}P(OR)_2}{CH\text{-}C_6H_5}$$

R	*Chemical shifts, δ (ppm)*		*Coupling constants, J (Hz)*			
	CH(P)	*NH*	*^2J(CHP)*	*^3J(CHNH)*	*^3J(NHCH)*	*^3J(NHP)*
CH_3	5.02, dd	6.15, dd	24.95	10.15	10.12	6.43
C_2H_5	4.93, dd	6.09, dd	24.81	10.07	10.05	6.60
i-C_3H_7	4.80, dd	5.99, dd	24.99	10.07	10.08	6.68



R = C_2H_5 (1), *i*-C_3H_7 (2)

SCHEME 1

Apparatus and Conditions

The melting points were measured on a Kofler microscope and are uncorrected. The IR spectra were taken on a UR-20 spectrophotometer as KBr disks. 1H-NMR spectra were recorded on a Bruker DRX-250 spectrometer (250 MHz) at room temperature and at 60°C or 147°C; DMSO-d_6 and

$CDCl_3$ were used as solvents and TMS – as internal standard. The thin layer chromatograms were performed on Kieselgel-60 F_{254} plastic sheets (Merck). The samples were applied as methanolic solutions and the chromatograms were developed ascendingly using the ethyl acetate – tetrahydrofuran - methanol (12:3:1) solvent system. The spots were detected under UV light and in iodine vapour atmosphere.

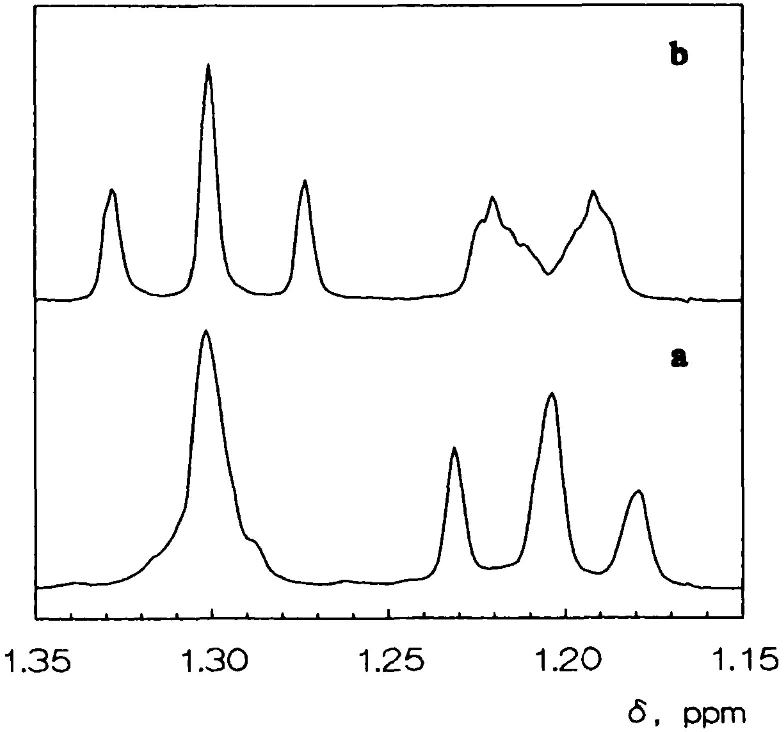


FIGURE 1 ^1H-NMR spectrum ($CDCl_3$) of CH_3 proton region of compound **1**: a) decoupling at 4.18 ppm; b) decoupling at 4.04 or 3.88 ppm.

4,4′-Bis[N-methyl(diethoxyphosphonyl)-1-(2-furyl)]benzidine (1)

N,N′-difurfurylidenebenzidine (3.04 g, 0.0089 mol) and diethyl phosphite (3.21 g, 0.0232 mol) were mixed in a flask and a saturated solution of C_2H_5ONa was added dropwise with stirring until exothermicity ceased. The mixture was stirred for two hours at room temperature, then – for

3 hours at 70–75 °C. The reaction mixture was washed with water and filtered to obtain a crude product in a good yield (4.81 g, 87%). The precipitate was purified by recrystallization from ethanol. The yellow crystalline powder obtained was dried *in vacuo* to constant weight.

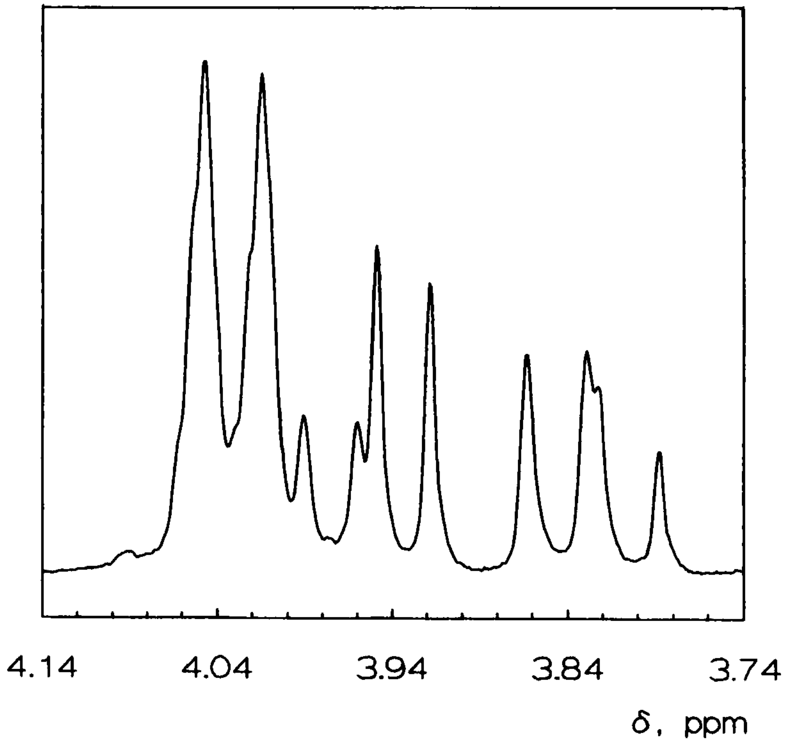


FIGURE 2 ^{1}H-NMR spectrum (DMSO-d_6) of OCH_2 proton region of compound 1 after CH_3 proton decoupling

Yield: 3.81 g (69%); m. p. 232–233°C; R_f=0.71.

Analysis: calcd. for $C_{30}H_{38}N_2O_8P_2$: N, 4.55%; P, 10.06%; found: N, 4.45%; P, 10.11%.

IR (KBr disk), $\tilde{\nu}$ (cm^{-1}): 3285 (ν_{NH}); 1580, 1510, 1495, 1450 ($\nu_{C=C(Ar, Fur)}$); 1240 ($\nu_{P=O}$); 1060, 1030 ($\nu_{P\text{-}OEt}$).

^{1}H-NMR (in DMSO-d_6 and in $CDCl_3$), see Table I.

4,4′-Bis[N-methyl(diisopropoxyphosphonyl)-1-(2-furyl)]benzidine (2)

N,N′-difurfurylidene-benzidine (2.78 g, 0.0082 mol) and diisopropyl phosphite (3.53 g, 0.0213 mol) were mixed together and i-C_3H_7ONa was added as catalyst. After stirring at room temperature for an hour and heating at 70–80°C for two hours, a yellow reaction product was obtained. The crude product was recrystallized from methanol.

Yield: 3.90 g (71%); m. p. 223–224°C; R_f=0.76.

Analysis: calcd. for $C_{34}H_{46}N_2O_8P_2$: N, 4.17%; P, 9.23%; found: N, 4.38%; P, 9.08%

IR (KBr disk), $\tilde{\nu}$ (cm^{-1}): 3290 (ν_{NH}); 1580, 1555, 1515, 1465 ($\nu_{C=C(Ar, Fur)}$); 1238 ($\nu_{P=O}$); 1010, 1000 ($\nu_{P\text{-}OPr\text{-}i}$).

^{1}H-NMR (in DMSO-d_6 and in $CDCl_3$), see Table I.

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