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# Phosphorus, Sulfur, and Silicon and the Related Elements

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## NEW DIAMINE PHOSPHONATE MONOMERS AS FLAME-RETARDANT ADDITIVES FOR POLYMERS

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**Abstract** Three new phosphonate-amine monomers were synthesized in high yields starting from commercially available aldehydes. Complete NMR and FAB-MS mass spectrometry characterization is reported for all compounds, which are useful monomers for the synthesis of phosphorus-containing flame-retardant polymers.

Keywords bis-a-Amino-phoshonate; characterization; FAB; monomers phosphonated; NMR

#### INTRODUCTION

The most commonly used approach for enhancing the fire safety performance of polymeric materials is the use of flame-retardant additives in commercial polymers. The physical incorporation of additives has several disadvantages. The additive is often required in high loadings to be effective, which may result in undesired changes of the physical and mechanical properties of the polymer. Additives can also be leached from the polymer with aging and, as a result, reduction in any flame-retardant effect.

An alternative approach is the chemical incorporation of the flame-retardant species in the polymeric chain by copolymerization or by some other type of chemical modification. In this case the flame retardant is not easily lost from the polymer; thus one of the major problem associated with the additive is eliminated.

Phosphorus-containing components have already been used in the synthesis of several flame-retardant step reaction polymers.<sup>1–4</sup> However, their use in the synthesis as monomers is much less developed; therefore, there exists a need to develop the synthesis of new monomers containing reactive selected functional groups in order to introduce phosphorus derivatives into the polymer chain.

In a previous paper<sup>5</sup> we reported the syntheses of new phosphonated derivatives of bis-phenols and used them to reduce flammability of thermosetting DGEBA epoxy resins.<sup>6-8</sup>

Moreover, N-substituted  $\alpha$ -aminophosphonic acid derivatives, as well as their cognate-bearing free amino groups, can be used as curing agents for epoxy resins and

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other polycondensates in order to impart thermal resistance and/or fire-proofing and fire-retardant proprerties.<sup>9-12</sup>

Furthermore, considering the great interest in reactive phosphorus-containing compounds as anti-flammable agents, we decided to synthesize a new bis( $\alpha$ -aminophosphonates) monomer of type **1** and the 1,4-diamino benzyl phosphonates monomer **2** (Scheme 1) in order to fully characterize them by NMR analyses and to use such compounds for the purpose described above.



#### **RESULTS AND DISCUSSION**

The adopted synthetic approach for the preparation of compounds of type **1** is sketched in Scheme 2. It is based on a three-component condensation reaction with benzylcarbamate,



aldehydes, and triphenylphosphite in the presence of acetic acid, adapted from the paper by Oleksyszyn et al.<sup>13</sup> The white solid obtained was filtered and, before its purification by crystallization from methanol, NMR spectra were measured to determine the diastereomeric ratio. We observed a complexity of the <sup>1</sup>H-NMR spectra for compounds **3a–c**, arising from the presence of the two chiral centers, due to the formation of both *racemic* and *meso* diastereomers. The presence of both diastereomers and their relative population was more easily detected by <sup>31</sup>P-NMR analyses on the crude mixture (see Table 1), although we did not assign the signals to the relative diastereomers. After crystallization, only one diastereomer

#### FLAME-RETARDANT ADDITIVES FOR POLYMERS

No.	R	<sup>1</sup> H-NMR (DMSO-d <sub>6</sub> )		$^{31}P{^{1}H}-NMR^{b}$	
		$\delta_{\text{CH-P}}$ (ppm)	δ <u>CH</u> 2-O-CO (ppm)	δ <sub>NH-CO</sub> (ppm)	$\delta_{\rm P}$ (ppm)
		$({}^{2}J_{PH}; {}^{3}J_{HH}, Hz)$	$(^{2}J_{HH}, Hz)$	$(^{3}J_{HH}, Hz)$	
3a	Н	5.63 (dd, 21; 10)	5.10 (q, 12)	8.91 (d, 10)	15.91(5%)
					15.77(95%)
3b	CH <sub>3</sub>	5.71 (dd, 21; 10)	5.08 (q, 12)	8.3 (d, 10)	16.15(50%)
			-		15.98(50%)
3c	OCH <sub>3</sub>	6.11 (dd, 20; 10)	5.10 (q, 12)	8.75 (d, 10)	14.61(50%)
					14.49(50%)

 Table 1 Diagnostic NMR signals of bis-carbamate derivatives<sup>a</sup> 3

<sup>a</sup>Full characterization of all compounds is reported in the Experimental section.

<sup>b</sup>Diastereomeric ratio is determined by <sup>31</sup>P-NMR of the crude mixture.

was recovered for compounds **3a-b**, whereas both diastereomers<sup>\*</sup> were recovered for compound **3c**.

After isolation and characterization, the benzyl (1,4-phenylene)bis((diphenoxyphosp horyl)-methylene)dicarbamate derivatives were hydrolyzed to the free bis- $\alpha$ -amino-phoshonate derivative salts **1a–c** and in Table 2 the observed diasteremeric ratio is reported. Yields are good for both the first step and the second step. Analytical characterization is reported in Tables 1 and 2, as well in the Experimental section.

As far as the proton NMR characterization is concerned, we observed that for compounds 3a-c most diagnostic peaks are due to:

- the methyne hydrogen linked to the phosphonic group, which appears as a doublet of doublet because of the coupling with the phosphorus atom  $(^{2}J_{HP} \sim 21 \text{ Hz})$  and the NH group  $(^{3}J_{HH} \sim 10 \text{ Hz})$  and whose chemical shift is sensitive to the electronic environment present in the molecule ranging from 5.6 to 6.1 ppm;
- the benzyloxymethylene group, which appears as an AB quartet due to the chirality of the molecule and whose chemical shift is roughly centered at 5.10 ppm;
- the NH-CO group, very sensitive to hydrogen bond formation, appearing as a doublet in the region above 8.3–8.9 ppm.

Comparing the proton chemical shift values of compounds 1a-c (Table 2) and 3a-c (Table 2) only a small change due to the electron-withdrawing (NH<sub>3</sub><sup>+</sup>) effect on the aromatic ring is observed. On the contrary, a significant change in chemical shifts value between the amine monomer 1a-c and the cognate benzyl dicarbamate 3a-c is observed in the <sup>31</sup>P-NMR spectra. In fact, the phosphorus signal of monomers 3a-c is present at 16.15–14.49 ppm (Table 1), whereas for compounds 1a-c the <sup>31</sup>P singlet appear at 11.80–11.53 ppm (Table 2).

<sup>&</sup>lt;sup>\*</sup>We can exclude, in the room temperature spectra of our samples, the presence of conformers arising from the restricted rotation of the Cbz (carbamate) group because in previous work<sup>14</sup> dealing with mono benzyl (diphenoxyphosphoryl)(phenyl)methylcarbamate derivative we did not detect any additional complexity signals arising from the presence of this group. Moreover, in the case of bis-Cbz derivatives (**3a–c**), if restricted rotation is present, more complex NMR spectra should be noticed, due to the presence of (Z,Z), (Z,E), and (E,E) rotamers, and this is not the case for our compounds. Furthermore, the hydrolysis of **3c** yields the two expected diasteremers (*racemo* and *meso*, Table 2). Thus, all data clearly indicate that the NMR spectra are well explained by the formation of the two possible diastereomers.

No.	R	$\frac{{}^{1}\text{H-NMR (DMSO-d_{6})}}{\delta_{\text{CH-P}} \text{ (ppm)}}$	$\delta_{\rm NH3}^{+}$ (ppm)	$\frac{{}^{31}P{}^{1}H}{\delta_{P} (ppm)}$
1a	Н	5.78 (d, 18)	9.57	12.22
1b	CH <sub>3</sub>	5.68 (d, 18)	9.45	11.80
1c	OCH <sub>3</sub>	5.60 (d, 18)	9.45	11.64(50%)
				11.53(50%)

 Table 2 Diagnostic NMR signals of bis-amine derivatives<sup>a</sup> 1

<sup>a</sup>Full characterization of all compounds is reported in the Experimental section.

The aromatic diamine monomer 2 was synthesized through a three-step route as already reported by us.<sup>15</sup> In the first step the halo-benzyl derivative was quantitatively converted by the Arbuzov synthetic procedure into the phosphonate benzyl derivative, which was nitrated and subsequently the dinitro compound was converted by Pd-catalyzed H<sub>2</sub> reduction to diamine monomer 2. Using monomer 2 and adipoyl chloride, as well tereor iso-phthaloyl chloride, phosphonated polyamides were prepared by solution condensation.<sup>15</sup> All of the phosphonated polyamides were fully characterized by spectroscopic techniques. Interestingly enough, MALDI-TOF mass spectra of polyadipamides reveals that although we started from stoichiometric amounts of reagents, only amine-terminal chains are present in the polymer mixture formed by the condensation reaction along with a small amount of cyclic oligomers. Cyclic oligomers were also observed in the MALDI-TOF mass spectrum of polyamides obtained from *tere*- or *iso*-phthaloyl chloride, whereas in these cases three families of peaks corresponding to linear oligomers were detected. In particular, the most intense mass peak series corresponds to the oligomers bearing amine groups at both ends, whereas the other two series of peaks corresponds to the oligomer chains terminated with amine and carboxyl groups and to the oligomers bearing carboxyl groups at both ends.

The thermal properties and the thermal stability of phosphonated polyamides obtained using monomer **2** were studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) techniques. The TGA analyses show that the thermal stability of our synthesized phosphonate polyamides is strongly determined by the presence of the pendant phosphonate groups along the polymer chains.<sup>15</sup>

Now, we dispose of a variety of monomers containing phosphonate groups and reactive NH<sub>2</sub> groups that can be used in the polycondensation reaction to prepare a large variety of polyamides and can be useful as hardeners in the curing process of epoxy resins.

#### **EXPERIMENTAL**

Aldehydes, triphenyl phosphite, benzyl carbamate, acetic acid, as well as solvents used were high-purity commercial products from Aldrich. Amine monomer **2** was synthesized as already reported.<sup>15</sup>

<sup>1</sup>H- and <sup>31</sup>P-NMR spectra were recorded, in DMSO-d<sub>6</sub>, on a Varian-Inova 500 MHz instrument operating at 500 and 200 MHz, respectively, using SiMe<sub>4</sub> as internal reference and 85%  $H_3PO_4$  as external reference. Melting points were determined on a Büchi 530 melting point apparatus and are uncorrected.

#### FLAME-RETARDANT ADDITIVES FOR POLYMERS

#### General Synthetic Procedure for Compounds 3a–c

To a stirred solution of the aldehyde precursor (0.10 mol) and triphenyl phosphite (0.20 mol) in glacial acidic acid (50 mL) was added over a period of 30 min to solid benzyl carbamate (0.20 mol) in small portions. After the addition was completed, the reaction mixture was warmed to 80°C and stirred for one hour. The solvent was then evaporated in a vacuum, the oil residue was diluted with methanol (50 mL), and the solution left at room temperature for 24 h. The white solid obtained was filtered and, before its purification by crystallization from methanol, a <sup>31</sup>P-NMR spectrum was measured to determine the diastereomeric ratio. After crystallization only one diastereomer was recovered for compounds **3a–b**, whereas both diastereomers were recovered for compound **3c**.

#### General Synthetic Procedure for Compounds 1a-c

To a solution of HBr/CH<sub>3</sub>COOH 45% (w/w) was added to the corresponding solid benzyl (1,4-phenylene)bis((diphenoxyphosphoryl)-methylene)dicarbamate derivatives at room temperature and stirred overnight. For the hydrolysis of **3a** and **3b** we used one single diastereomer, whereas for **3c** the mixture of both diastereomers was employed. Then 150 mL of diethyl ether was added and a solid was formed, which was filtered off and washed several time with ether to give the diamine salts **1a–c**.

#### Spectroscopic Characteristics of Compounds Listed in Table 1

**Benzyl 1,4-phenylenebis((diphenoxyphosphoryl)methylene)dicarbamate 3a.** <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>, 27°C, ppm)  $\delta$ : 8.91 (d, <sup>3</sup>J<sub>HH</sub> = 10 Hz, 2H, NH), 7.68 (s, 4H, ArH), 7.3 (m, 18 H, ArH), 7.16 (m, 4H, ArH) 7.06 (d, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 4H, ArH), 6.94(d, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 4H, ArH), 5.63 (dd, J<sub>HP</sub> = 21.5 Hz, <sup>3</sup>J<sub>HH</sub> = 10 Hz, 2H, ArCHP), 5.10 (q, <sup>2</sup>J<sub>HH</sub> = 12 Hz, 4H, OCH<sub>2</sub>Ar). <sup>31</sup>P-NMR (DMSO-d<sub>6</sub>, ppm)  $\delta$ : 15.77. White powder, 83% yield, mp 249–250°C. Anal. Calcd. for C<sub>48</sub>H<sub>42</sub>N<sub>2</sub>O<sub>10</sub>P<sub>2</sub> (868.80): C, 66.36; H, 4.87; N, 3.22. Found: C, 66.50; H, 4.93; N, 3.20. FAB MS: m/z 869.6 [M + H]<sup>+1</sup>.

Benzyl (2,5-dimethyl-1,4-phenylene)bis((diphenoxyphosphoryl)methyle ne)dicarbamate 3b. <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>, ppm) δ: 8.83 (d, <sup>3</sup>J<sub>HH</sub> = 10 Hz, 2H, NH) 7.59 (s, 2H, ArH), 7.31 (m, 18 H, ArH), 7.17 (m, 4H, ArH), 7.06 (d, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 4H, ArH), 6.91(d, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 4H, ArH), 5.71(dd, J<sub>HP</sub> = 21.5 Hz, <sup>3</sup>J<sub>HH</sub> = 10 Hz, 2H, ArCHP), 5.07 (q, <sup>2</sup>J<sub>HH</sub> = 12 Hz, 4H, OCH<sub>2</sub>Ar), 2.32 (s, 6H, ArCH<sub>3</sub>). <sup>31</sup>P-NMR (DMSO-d<sub>6</sub>, ppm) δ: 15.98. White powder, 73% yield, mp 246–248°C. Anal. Calcd. for  $C_{50}H_{46}N_2O_{10}P_2$  (896,26): C, 66.96; H, 5.17; N, 3.12. Found: C, 67.01; H, 5.20; N, 3.15. FAB MS: m/z 897.9 [M + H]<sup>+1</sup>.

Benzyl (2,5-dimethoxy-1,4-phenylene)bis((diphenoxyphosphoryl)methy lene)dicarbamate 3c. <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>, ppm) δ: 8.75 (d, <sup>3</sup>J<sub>HH</sub> = 10 Hz, 2H, NH), 7.48 (s, 2H, ArH), 7.32 (m, 18H, ArH), 7.18 (m, 4H, ArH), 6.96 (d, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 4H, ArH) 6.89 (d, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 4H, ArH), 6.1(q, J<sub>HP</sub> = 21.5 Hz, <sup>3</sup>J<sub>HH</sub> = 10 Hz, 2H, ArCHP), 5.1 (dd, <sup>2</sup>J<sub>HH</sub> = 12 Hz, 4H, OCH<sub>2</sub>Ar), 3.71 (s, 6H, OCH<sub>3</sub>). <sup>31</sup>P-NMR (DMSO-d<sub>6</sub>, ppm). δ: 14.61 (50%), 14,49 (50%). White powder, 75% yield, mp 220–240°C. Anal. Calcd. for  $C_{50}H_{46}N_2O_{12}P_2$  (928,85): C, 64.65; H, 4.99; N, 3.02. Found C, 64.71; H, 5.06; N, 3.06. FAB MS: m/z 929.8 [M + H]<sup>+1</sup>.

#### **Spectroscopic Characteristics of Compounds Listed in Table 2**

**Tetraphenyl 1,4-phenylenebis(aminomethylene)diphosphonate 1a.** <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>, ppm) δ: 9.57 (bs, 6H, NH<sub>3</sub><sup>+</sup>), 7.86 (s, 4H, ArH), 7.38 (m, 18H, ArH), 7.20 (m, 4H, ArH), 7.12 (m, 4H, ArH), 6.98 (m, 4H, ArH), 5.78 (d, J<sub>HP</sub> = 18 Hz, 2H, ArCHP). <sup>31</sup>P-NMR (DMSO-d<sub>6</sub>, ppm). δ: 12.22. White powder, 85% yield, mp > 250°C. Anal. Calcd. for  $C_{32}H_{32}Br_2N_2O_6P_2$  (762,36): C, 50.41; H, 4.23; N, 3.67. Found C, 50.49; H, 5.27; N, 3.61. FAB MS: m/z 601.5 [M - 2HBr + H]<sup>+1</sup>.

**Tetraphenyl (2,5-dimethyl-1,4-phenylene)bis(aminomethylene)diphosp honate 1b.** <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>, ppm) δ: 9.45 (bs, 6H, NH<sub>3</sub><sup>+</sup>), 7.81 (s, 2H, ArH), 7.39 (m, 18H, ArH), 7.24 (m, 4H, ArH), 7.11 (m, 8H, ArH), 5.68 (d, J<sub>HP</sub> = 18 Hz, 2H, ArCHP), 2.44 (s, 6H, ArCH<sub>3</sub>). <sup>31</sup>P-NMR (DMSO-d<sub>6</sub>, ppm). δ: 11.80. White powder, 83% yield, mp > 250°C. Anal. Calcd. for C<sub>34</sub>H<sub>36</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>6</sub>P<sub>2</sub> (790,41): C, 51.66; H, 4.59; N, 3.54. Found C, 51.71; H, 4.63; N, 3.51. FAB MS: m/z 629.4 [M – 2HBr + H]<sup>+1</sup>.

**Tetraphenyl (2,5-dimethoxy-1,4-phenylene)bis(aminomethylene)diphos phonate 1c.** <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>, ppm) δ: 9.43 (bs, 6H, NH<sub>3</sub><sup>+</sup>), 7.66 (s, 2H, ArH), 7.37 (m, 18H, ArH), 7.23 (m, 4H, ArH), 7.05 (m, 4H, ArH), 6.98 (m, 4H, ArH), 5.60 (d, J<sub>HP</sub> = 18 Hz, 2H, ArCHP), 3.74 (s, 6H, ArOCH<sub>3</sub>). <sup>31</sup>P-NMR (DMSO-d<sub>6</sub>, ppm). δ: 11.64 (50%), 11,53 (50%). White powder, 83% yield, mp > 250°C. Anal. Calcd. for  $C_{34}H_{36}Br_2N_2O_8P_2$  (822,41): C, 49.65; H, 4.41; N, 3.41. Found C, 49.70; H, 4.47; N, 3.40. FAB MS: m/z 661.6 [M - 2HBr + H]<sup>+1</sup>.

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