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Efficient synthesis of bolaform- and gemini-type alkyl-bis-[(α-amino)phosphonocarboxylic or phosphonic acid] surfactants

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Abstract—The synthesis of a new series of bolaform- and gemini-type phosphorus acid surfactants is described. The Pudovik addition reaction of P–H bond tetraoxyspirophosphoranes to symmetrical, prochiral bis-imines bearing different more or less long and rigid linkers occurs instantaneously at room temperature. This reaction is diastereoselective and quantitatively leads to the corresponding alkyl-bis-[α-aminospirophosphoranes] in good to high diastereomeric ratio. Selective and one-pot hydrolysis of these P^*–C^* bond bis-spirophosphoranes can be readily achieved either at room temperature by moist solvents giving the corresponding alkyl-bis-[α-aminophosphonocarboxylic acid] amphiphiles, or by a more drastic reaction of 20% aqueous hydrochloric acid under reflux affording free alkyl-bis-[α-aminophosphonic acid] surfactants in good yields.

1. Introduction

During the last decades much work has been done to study properties and functions of natural membranes.[1] Membrane lipids of thermophilic and acidophilic *Archaebacteria*, particular microorganisms able to survive under drastic conditions owing to the presence of very rigid membranes, are constituted by natural bolaamphiphiles.[2] Bolaamphiphiles, so-called bolaforms, refer to a class of surfactant molecules in which two hydrophilic head groups (neutral or ionic) are connected by one or more hydrophobic linkers. It has been shown that biological or synthetic bolaamphiphiles self-organize into monolayer membranes which are highly stable over time to the variation of temperature and ionic strength changes.[3] Thus, in order to understand the properties that allow the support of such extreme environmental conditions, and consequently, to prepare the stable and heat-resistant membranous materials, the synthesis of a large number of bolaamphiphiles (notably phosphorus derivates) has been described.[4,5] Their self-association studies indicate that they are able to form micellar aggregates but also vesicles, depending on the length of the hydrophobic spacer.[6,7] Moreover, it has been reported that the bolaforms had no detergent effect on cell membranes and did not tend to denature cells as the monocatenary compounds did.[8] Furthermore, synthetic amphiphiles that form vesicular aggregates in aqueous media are also attractive for their potential in various applications such as microencapsulation and formulation of hydrophobic derivatives or drug delivery,[9] ion channels,[10] catalysis,[11] synthesis of nanomaterials,[12] metal extraction,[13] and so forth. Structurally related to the bolaamphiphiles, the geminis (also called dimeric surfactants), made of two identical amphiphilic moieties connected at the level of the head groups by a (flexible or rigid) hydrophobic spacer, are known to form a great variety of supramolecular structures such as micelles, multilayers, rods, and vesicles, and appear to be superior to their monomeric counterparts.[14,15]

The aim of the present work was to find an efficient method for the preparation of bolaform- and gemini-type phosphorus acid surfactants. We have recently described the synthesis of new (α-hydroxyalkyl)- and (α-aminoalkyl)-phosphinic and phosphonic acid amphiphiles by Pudovik addition reaction of the P–H-labile phosphorus derivatives on long-chain aldehydes and imines, respectively.[16] These α-functionalized phosphonic acids are isosteres of natural aminoacids and have potential biological applications in agrochemistry and in medicine.[17] The molecular packing of these derivatives depend markedly on the length and the rigidity of the hydrophobic spacer and on the nature of the polar heads. We report here the reactivity of P–H bond spirophosphoranes towards bis-imines having various long or short and flexible or rigid linkers, and the one-pot and selective hydrolysis of the alkyl-bis-[(α-amino)-spirophosphorane] intermediates to afford bolaform- and gemini-type alkyl-bis-[(α-amino)-phosphonocarboxylic acid] oralkyl-bis [(α-amino)phosphonic acid] amphiphiles.

Keywords: phosphorus acid surfactants; alkyl-bis-[(α-amino)phosphonic acids]; alkyl-bis-[(α-amino)phosphonocarboxylic acids]; bolaform- and gemini-type amphiphiles; spirophosphorane; Pudovik reaction.

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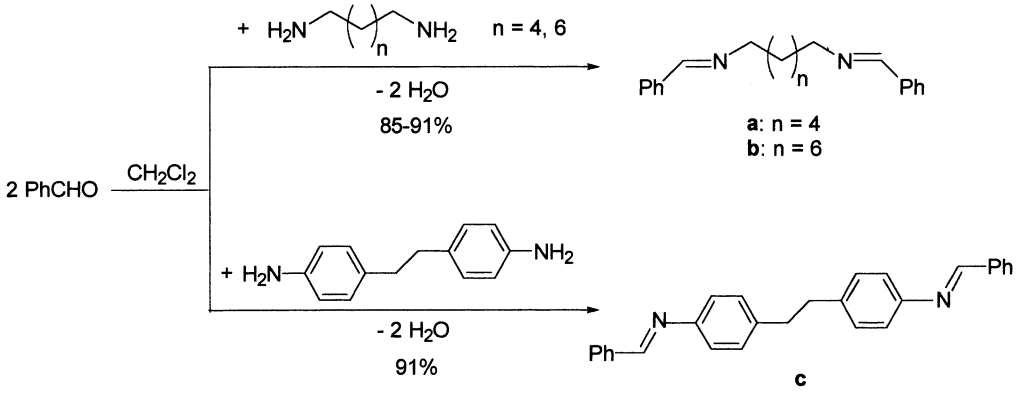


Scheme 1. Synthesis of diimines **a**–**c** from benzaldehyde and α,ω-diamines.

2. Results and discussion

The basic synthetic strategy was first to prepare the diimines **a**–**d**, then to achieve the nucleophilic addition of P-H-spirophosphorane **1** to these diimines according to the Pudovik reaction, and finally to carry out selective hydrolysis of the alkyl-bis-(P-C-spirophosphoranes) **2** affording bolaform- and gemini-type surfactants **3** and **4**.

2.1. Synthesis of diimine linkers

Diimines will be the skeleton of the hydrophobic linkers. With the aim to prepare bolaforms, three diimines have been synthetized by condensation of benzaldehyde with α,ω-diamines (flexible linkers), **a**,**b**, and 4,4′-ethylenedianiline (more rigid linker), **c** (Scheme 1).

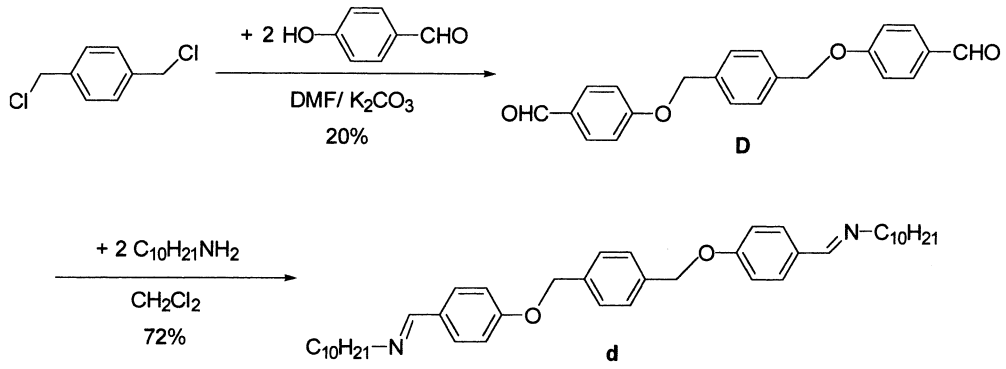
In the case of the diimine **d**, the semi-rigid and aromatic spacer for the gemini surfactant, the precursory dialdehyde **D** was prepared by *O*-alkylation of 4-hydroxybenzaldehyde with α,α′-dichloro-*p*-xylene, followed by a condensation reaction with 1-decylamine (Scheme 2).

All these diimines **a**–**d** are assumed to exist as *anti*–*anti* compounds since traces of *syn* isomers have never been observed by ^{1}H and ^{13}C NMR.

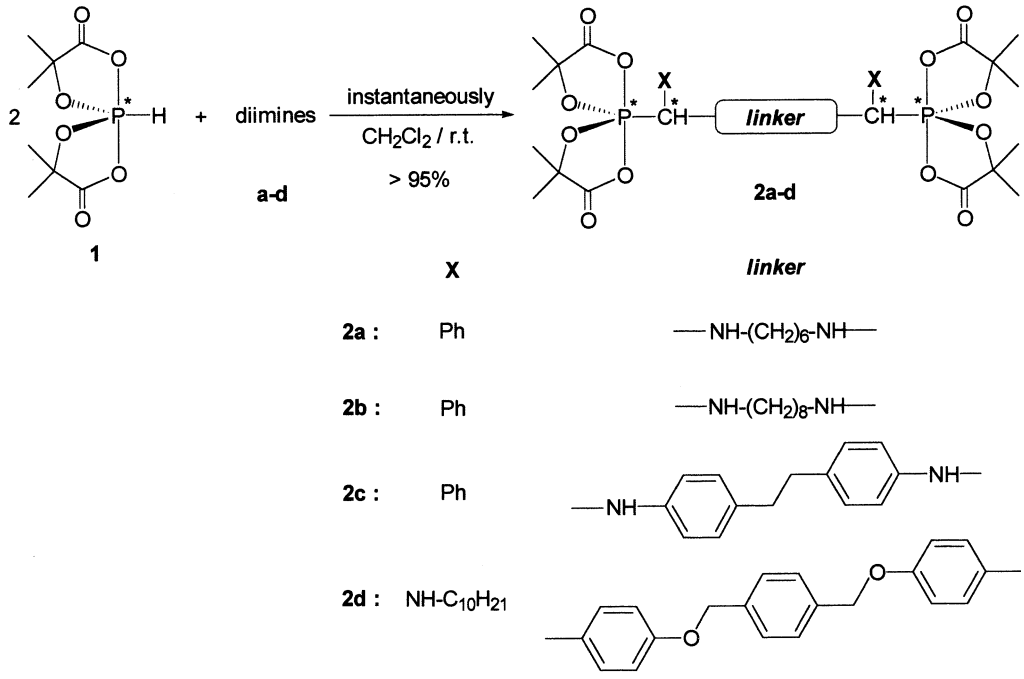
2.2. Addition reaction of P–H bond spirophosphorane with diimines

The addition reaction of two equivalents of spirophosphorane **1** with diimines **a**–**d** in anhydrous dichloromethane occurs instantaneously at room temperature and quantitatively gives the corresponding alkyl-bis-(α-aminospirophosphoranes), **2a**–**d**, bearing two P^{*}–C^{*} bonds (Scheme 3).

As observed for single chain (α-aminoalkyl)spirophosphoranes,[16c] the compounds **2a**–**d** are stable enough in solution and under argon for NMR characterization, but all attempts to their purification led to their decomposition into P^{IV} type compounds. Alkyl-bis-(α-aminospirophosphoranes) **2a**–**d** have four stereogenic centers: the two pentacoordinated phosphorus atoms, and the two carbon atoms to wich they are bonded. These compounds then exist in 16 stereoisomeric forms. However, the presence of symmetry elements in the molecule renders some structures equivalent and reduces the number of stereoisomers. Thus, we expect four racemic isomers *MRRM*/*PSSP*, *MSSM*/*PRRP*, *MRRP*/*PSSM*, and *MRSM*/*PSRP*, and two meso forms *MRSP* and *MSRP*. *M* and *P* represent, respectively, the left and right handedness of the pentacoordinated helicoidal spirophosphoranic structure, and *R*/*S* the absolute configurations of the P-linked stereogenic carbon centers. Each of these six diastereoisomers should show in ^{31}P NMR spectra (i) one signal when the two phosphorus atoms have identical helicities or they are enantiomers, and (ii) two signals when the two phosphorus nuclei are magnetically non-equivalent, leading to eight signals. However, the ^{31}P NMR spectra analysis consisted of only two high-field signals at about −30 ppm as two doublets with coupling constants $^{2}J_{PH}$ about 16–25 Hz. These two diastereomeric peaks were separated by about 1 ppm for compounds **2a**,**b**

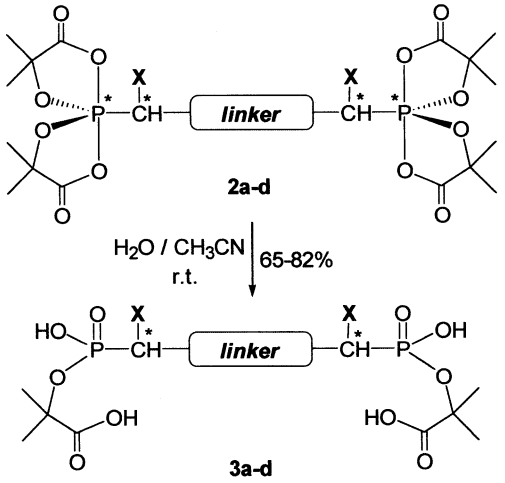


Scheme 2. Synthesis of dialdehyde **D** and diimine **d**.



Scheme 3. Diastereoselective synthesis of the P–C bond alkyl-bis-[(α-aminoalkyl)-spirophosphoranes] **2a–d**.

and **2d**, and by about 3 ppm in the case of **2c**. In each case, the major isomer corresponded to the more deshielded signal. This observation may be attributed to the presence of a long linker, leading to two completly independant P atoms sufficiently far from each other so that the molecule behaves like the monocatenary derivatives. The chemical shifts of the carbon atoms adjacent to the phosphorus ones (δ ^{13}C ~67) and the corresponding coupling constants ($^{1}J_{CP}$=190 Hz) clearly demonstrate the replacement of P–H bonds by new P–C ones and so the presence of (α-amino)spirophosphorane moieties. The methine proton resonance appears in most cases as a doublet at approximately δ=4–5 and $^{2}J_{HP}$ about 20–25 Hz. The addition reaction is diastereoselective (75/25≤diastereomeric ratio≤95/5) due to the rigid structure of the spirophosphoranide intermediate formed by deprotonation of hydrido-spirophosphorane **1** by the prochiral imines, during the P–C bond formation. It is of importance to state that the introduction of the semi-rigid aromatic linker to the molecule of bis-imine **c** decreased the stereoselectivity of the spirophosphorane addition. This phenomenon can be attributed to the presence of phenyl groups on nitrogen atoms of the bis-imine **c**, decreasing the basicity of the nitrogen lone pairs and so reducing the rate of formation of the phosphoranide intermediate and consequently the addition reaction. The high diastereoselectivity observed for the other bis-imines (**a**,**b**,**d**) is similar to that of the monocatenary ones,[16c] and we can consider that the spacer is long enough so that the two stereogenic centers were created independently from each other.

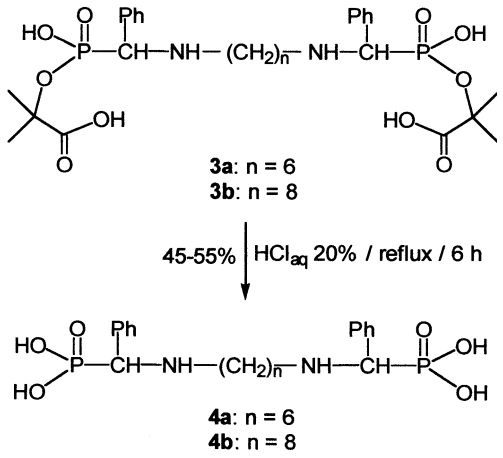


Scheme 4. Synthesis of bolaform- and gemini-type alkyl-bis-[(α-aminoalkyl)-phosphono-carboxylic acid] surfactants **3a–d**.

2.3. Selective hydrolysis of alkyl-bis-(α-aminospirophosphoranes)

We have already described the selective hydrolysis of the P-C-spirophosphorane derivatives in the case of single-chain surfactants.[16c] The reaction with water led to the corresponding α-aminophosphonocarboxylic acid monoesters, whereas more drastic acid conditions were required to obtain free α-aminophosphonic acids. Of course, the direct conversion of P-C-spirophosphoranes to free phosphonic acids was also possible. Thus, bolaform-type **2a–c** and gemini-type **2d** bis-spirophosphoranes were hydrolyzed in situ by water in acetonitrile (1:1 mixture) (Scheme 4).

The reaction occurs instantaneously at room temperature for compounds **2a**,**b** and **2d**, in contrast to **2c** which seems to be more stable. Indeed, its hydrolysis was achieved after 10 h at room temperature, as monitored by ^{31}P NMR. This can be due to the presence of aromatic groups as substituent on amine functions of the molecule, **2c** being the only compound possessing such structure. This stabilization seems to be very significant because it reduces the rate of the P=O phosphoryl moiety formation, the main driving



Scheme 5. Synthesis of bolaform alkyl-bis-[(α-aminobenzyl)phosphonic acid] surfactants **4a**,**b**.

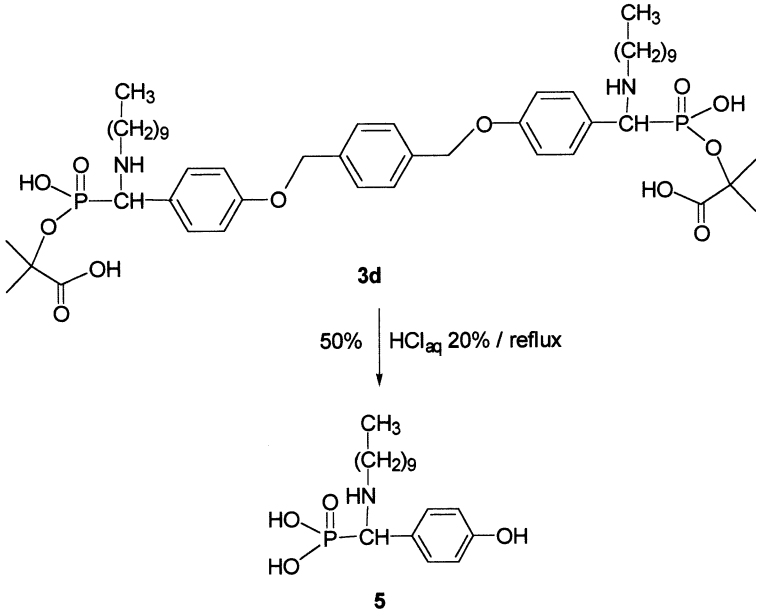
force in organophosphorus conversions. The alkyl-bis-[phosphonocarboxylic acid monoesters] **3a**–**d** have only two stereogenic centers (the two α-carbon atoms) and they exist as two diastereomeric products (meso and racemic forms) giving two distinguishable signals in ^{31}P NMR spectra. However, the presence of only one signal as a sharp doublet (with a $^{2}J_{PH}$ coupling constant around 16 Hz) in ^{31}P NMR could indicate that the magnetic non-equivalence of the two phosphorus atoms in the molecule is too week due to their long hydrophobic spacer: the bipolar molecule behaves like a single-chain surfactant. The conversion of the pentacoordinated phosphorus atoms into tetracoordinated ones was confirmed by the deshielding of chemical shifts around δ=8–17 (i.e. $\Delta\delta\sim+40$ ppm with respect to chemical shifts of the corresponding P–C bond spirophosphoranes **2**). The chemical shift of α-carbon atoms did not change significantly (δ ^{13}C$\sim$61) while the $^{1}J_{CP}$ coupling constant decreased by about 45 Hz. As in the case of single-chain derivatives, the ^{1}H NMR spectra of **3a**–**d** show two distinguishable singlets for the methyl groups of the monoesters's lateral chain, this non-equivalency being attributed to the proximity of stereogenic centers.

Obtention of polyfunctional bipolar surfactants **3** bearing phosphonic acid monoester, α-amino and β-carboxylic acid groups opens up various application fields owing to their synthetic, chelating and biological properties. Their usefulness in hydrometallurgy as metal-extractants and corrosion inhibitors has been described.[18] Their metal-ion-coordinating properties were used in diagnostic medicine as radioligands for screening experiences, in therapeutic area as anticancer or anti-viral agents.[19] Furthermore, their good crosslinking ability for cellulose has been shown.[20]

Treatment of alkyl-bis-[(α-amino)phosphonocarboxylic acids] **3a**,**b** by 20% aqueous solution of hydrochloric acid at reflux for several hours afforded in nearly quantitative yields the alkyl-bis-[(α-amino)phosphonic acids] **4a**,**b** by acidic cleavage of the P–O–C ester moieties (Scheme 5).

^{31}P NMR spectra of the free acids **4a**,**b** exhibit a single signal ($\delta\sim$10–12) slightly deshielded with respect to the corresponding monoesters **3**. $^{2}J_{HP}$ and $^{1}J_{CP}$ coupling constants, determined from ^{1}H and ^{13}C NMR spectra, indicate the conservation of P–C bonds under acid conditions. Direct synthesis of bolaforms **4a**,**b** can be achieved by one-pot hydrolysis of the corresponding bis-spiro-phosphoranes **2a**,**b** in the presence of 20% hydrochloric acid under reflux for 6 h. On the contrary, when the gemini-type monoester **3d** was treated under the same conditions, benzylic ether functions of the spacer were hydrolyzed in addition to carboxyisobutyl moieties, affording the single-chain (4-hydroxybenzyl)(α-amino-decyl)-phosphonic acid **5** (Scheme 6).

This degradation could be surprising because ether cleavage usually requires more drastic conditions and the use of concentrated solutions of HI or HBr. However, hydrolysis



Scheme 6. Acid hydrolysis of gemini amphiphile **3d** into monocatenary (α-aminoalkyl)-phosphonic acid **5**.

of alkylarylethers with HBr in phase transfer catalysis (PTC) conditions or more recently by concentrated aqueous HCl in the presence of cationic surfactants (micellar catalysis) has been described.[21] In our case, self-assembly of gemini-type surfactant **3d** leading to supramolecular aggregates (micelles, vesicles, etc) could promote the hydrolysis of ether moieties.

3. Conclusion

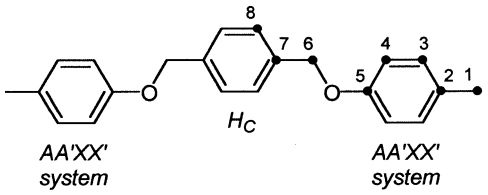
Synthesis of variously substituted bolaform- and gemini-type alkyl-bis(α-amino-phosphonic acid) surfactants and their monoesters can be readily performed by diastereoselective addition of P–H bond spirophosphoranes to the corresponding bis-imine precursors, followed by selective one-pot hydrolysis of the bis-spirophosphorane intermediates containing two P^*–C^* bonds. This procedure, thanks to its simplicity, should find general application in the synthesis of various polyfunctional bolaform- and gemini-type phosphorus amphiphiles. Investigation of the aggregation behavior of these new surfactants is in progress and some practical applications including their use as models of biological membranes, drug transport systems, extractants or precursors of highly functionalized materials can be considered.

4. Experimental

4.1. General

NMR spectra were obtained with Brucker AC200 or 250WM spectrometers. IR spectra were recorded on a Perkin–Elmer FT/IR-1600. Mass spectra were recorded on a Nermag R10-10H by chemical ionization (DCI/NH_3) or by FAB (positive or negative) modes. Melting points were measured in open glass capillaries with a Leitz Biomed apparatus and are uncorrected. Elemental analysis were performed by the Microanalytical Service Laboratory of the 'Laboratoire de Chimie de Coordination' of Toulouse.

Benzaldehyde, α,α′-*p*-dichloroxylene, 1,6-hexanediamine, 1,8-octanediamine, 4,4′-ethylene-dianiline, decylamine, propylene oxide, 2-hydroxyisobutyric acid, phosphorus trichloride (Aldrich) and 4-hydroxy-benzaldehyde (Acros) were used as received without further purification. DMF (Normapur, Prolabo), $CHCl_3$ and CH_2Cl_2 (Analytical reagent, SDS), reagent grade products, were maintained over 4 Å molecular sieves and stored in dark bottles protected from moisture. For column chromatography, silica gel (0.063–0.200 mm, Merck) was used. Spirophosphorane **1** was prepared according to the procedure already described.[22]



Scheme 7. Notation used for ^1H and ^{13}C NMR assignments of the carbon and hydrogen atoms in compounds **D**, **d**, **2d** and **3d**.

In order to readily interpret the ^1H and ^{13}C NMR spectroscopical data, the carbon and hydrogen atoms in compounds **D**, **d**, **2d** and **3d**, bearing a polyaromatic semi-rigid linker, were numbered as shown below (Scheme 7).

4.2. Synthesis

4.2.1. 1,4-Benzyloxy-bis-(4-benzaldehyde) (D). Dry potassium carbonate (1.45 g, 10.5 mmol) was added to a solution of 4-hydroxybenzaldehyde (1.22 g, 10 mmol) in anhydrous DMF (35 mL) and the heterogeneous mixture was stirred 1 h at 25°C. A solution of α-α′-dichloro-*p*-xylene (0.88 g, 5 mmol) in anhydrous DMF (17 mL) was added dropwise and the stirring continued for 6 h at 25°C. The solid was separated by centrifugation and the surnageant was evaporated under reduce pressure at 40°C. The yellow solid was dissolved in CH_2Cl_2 and this organic solution was washed with water, dried over $MgSO_4$ then evaporated in vacuo to give a pale yellow solid which was purified by chromatography (silica gel column, eluent: CH_2Cl_2/EtOH), (0.69 g, 20%). Mp 160–162°C.[23] ^1H NMR ($CDCl_3$): δ= 9.86 (s, 2H, CHO), 7.82 (m, 4H, $H_{AA'}$), 7.45 (s, 4H, H_C), 7.05 (m, 4H, $H_{XX'}$), 5.14 (s, 4H, CH_2–O). ^{13}C NMR ($CDCl_3$): δ=190.91 (s, CHO), 163.64 (s, C_5), 136.18 (s, C_7), 132.11 (s, C_3), 130.22 (s, C_2), 127.92 (s, C_8), 115.18 (s, C_4), 69.92 (CH_2–O). IR (KBr, cm^{-1}): ν=1724.6 (C=O). MS (DCI/NH_3): *m/z* 347 $(M+1)^+$, 364 $(M+NH_4)^+$.

4.3. Diimines derived from benzaldehyde

Benzaldehyde (2.12 g, 20 mmol) was added to a solution of diamine (10 mmol) in dry chloroform (30 mL). The mixture was stirred at 40°C for 6 h in the presence of 3 Å molecular sieves. The heterogeneous mixture was centrifuged, the organic phase was separated, then evaporated to dryness, and dried under vacuum.

4.3.1. *N,N′*-Dibenzylidene-hexane-1,6-diamine (a). Yellow oil (2.66 g, 91%).[24] ^1H NMR ($CDCl_3$): δ=8.26 (s, 2H, CH=N), 7.77–7.61 (m, 4H, CH_{Ph}), 7.42–7.34 (m, 6H, CH_{Ph}), 3.61 (t, $^3J_{HH}$=6.5 Hz, 4H, CH_2–N=), 1.73 (m, 4H, CH_2–C–N), 1.43 (m, 4H, CH_2). ^{13}C NMR ($CDCl_3$): δ= 160.85 (s, CH=N), 136.39 (s, C_{ipso}), 130.53 (s, CH_{Ph}), 128.65 (s, CH_{Ph}), 128.10 (s, CH_{Ph}), 61.77 (s, CH_2–N), 30.94 (s, CH_2–C–N), 27.24 (s, CH_2). IR (KBr, cm^{-1}): ν=1644.4 (C=N), 1578.6 (C=C). MS (DCI/NH_3): *m/z* 293 $(M+1)^+$.

4.3.2. *N,N′*-Dibenzylidene-octane-1,8-diamine (b). Yellow solid (2.72 g, 85%). Mp 35–36°C.[24] ^1H NMR ($CDCl_3$): δ=8.24 (s, 2H, CH=N), 7.75–7.71 (m, 4H, CH_{Ph}), 7.39–7.36 (m, 6H, CH_{Ph}), 3.60 (t, $^3J_{HH}$=7.0 Hz, 4H, CH_2–N=), 1.72 (m, 4H, CH_2–C–N), 1.38 (m, 8H, CH_2). ^{13}C NMR ($CDCl_3$): δ=160.65 (s, CH=N), 136.45 (s, C_{ipso}), 130.45 (s, CH_{Ph}), 128.59 (s, CH_{Ph}), 128.08 (s, CH_{Ph}), 61.80 (CH_2–N=), 30.99 (s, CH_2), 29.47 (s, CH_2), 27.39 (s, CH_2). IR (KBr, cm^{-1}): ν=1640.9 (C=N), 1570.0 (C=C). MS (DCI/NH_3): *m/z* 321 $(M+1)^+$.

4.3.3. *N*,*N*′-Dibenzylidene-4,4′-ethylenedianiline (c). Yellow solid (3.53 g, 91%). Mp 167–169°C.[25] ^{1}H NMR ($CDCl_3$): δ=8.48 (s, 2H, CH=N), 7.93–7.48 (m, 10H, CH_{Ph}), 7.22–7.18 (m, 8H, CH_{C6H4}), 2.96 (s, 4H, CH_2). ^{13}C NMR ($CDCl_3$): δ=159.88 (s, CH=N), 149.96 (s, C_q–N), 139.63 (s, C_q–CH), 136.36 (s, C_q–CH_2), 131.33 (s, CH_{Ph}), 129.34 (s, CH_{Ph}), 128.82 (s, CH_{Ph}), 120.97 (s, CH_{Ph}), 37.57 (CH_2). IR (KBr, cm^{-1}): ν=1619.9 (C=N), 1567.3 (C=C). MS (DCI/NH_3): *m*/*z* 389 $(M+1)^+$.

4.4. Diimine (d) derived from dialdehyde D

The same protocol that for the diimines (**a**–**c**) was followed, using dialdehyde **D** (1.38 g, 4 mmol) and decylamine (1.26 g, 8 mmol) in dry chloroform (12 mL).

4.4.1. 1,4-Benzyloxy-bis-*N*-(4-benzylidene)-bis-(decylimine) (d). White solid (1.90 g, 72%). Mp 107–109°C. ^{1}H NMR ($CDCl_3$): δ=8.19 (s, 2H, CH=N), 7.69–7.64 (m, 4H, $H_{AA'}$), 7.45 (s, 4H, H_C), 7.01–6.97 (m, 4H, $H_{XX'}$), 5.11 (s, 4H, CH_2–O), 3.57 (t, $^3J_{HH}$=7.0 Hz, 4H, CH_2–N=), 1.67 (m, 4H, CH_2–C–N), 1.26 (m, 28H, CH_2), 0.88 (t, $^3J_{HH}$=6.7 Hz, 6H, CH_3). ^{13}C NMR ($CDCl_3$): δ=160.54 (s, C_5), 160.00 (s, CH=N), 136.57 (s, C_7), 129.68 (s, C_2), 129.60 (s, C_3), 127.78 (s, C_8), 114.89 (s, C_4), 69.74 (s, CH_2–O), 61.83 (s, CH_2–N=), 31.97–22.76 (m, CH_2), 14.21 (s, CH_3). IR (KBr, cm^{-1}): ν=1646.8 (C=N), 1607.2 (C=C). MS (DCI/NH_3): *m*/*z* 625 $(M+1)^+$, 483 $(M-C_{10}H_{21}+1)^+$.

4.5. General procedure for the synthesis of alkyl-bis-[α-aminospirophosphoranes] (2a–d)

Diimine **a**–**d** (5 mmol) in dry CH_2Cl_2 (15 mL) was added dropwise to a stirred solution of spirophosphorane **1** (2.36 g, 10 mmol) in anhydrous CH_2Cl_2 (15 mL) at room temperature under argon. The progress of the reaction was followed by ^{31}P NMR analysis. The addition reaction occured instantaneously and afforded alkyl-bis-[α-aminospirophosphoranes] **2a**–**d** in quantitative yields. In spite of their stability in solution under argon during several days, all attempts to their purification failed due to their decomposition into tetracoordinated phosphorus compounds. In order to characterize these alkyl-bis-[α-aminospirophosphoranes], the addition reaction was then carried out directly in a NMR tube (5 mm diameter) in deuterated solvent under argon, using diimine **a**–**d** (0.2 mmol) in $CDCl_3$ (0.5 mL) and spirophosphorane **1** (94.4 mg, 0.4 mmol) in $CDCl_3$ (0.5 mL) at room temperature. The P^V–C-bond bis-spirophosphoranes **2a**–**d** were instantaneously and quantitatively formed, then characterized by ^{31}P, ^{1}H and ^{13}C NMR analysis.

4.5.1. Hexyl-1,6-bis-[(α-aminobenzyl)spirophosphorane] (2a). ^{31}P NMR ($CDCl_3$): δ=−31.5 (d, $^2J_{PH}$=24.7 Hz, 90%), −32.9 (d, $^2J_{PH}$=18.5 Hz, 10%). ^{1}H NMR ($CDCl_3$): δ=7.26 (m, 10H, CH_{Ph}), 4.55 and 4.36 (2d, $^2J_{HP}$=21.4 Hz, 8% and $^2J_{HH}$=24.7 Hz, 9%, 2H, CH–P), 2.30 (m, 4H, CH_2–N), 1.44–1.18 (m, 20H, CH_2 and $CH_{3\ endo}$), 0.96 (s, 12H, $CH_{3\ exo}$). ^{13}C NMR ($CDCl_3$): δ=172.28 (d, $^2J_{CP}$=7.2 Hz, C=O), 135.15 (s, C_{ipso}), 129.20–128.51 (m, CH_{Ph}), 80.82 (d, $^2J_{CP}$=5.7 Hz $C_q(Me)_2$), 67.26 (d, $^1J_{CP}$=191.4 Hz, CH–P), 47.32 (d, $^3J_{CP}$=24.7 Hz, CH_2–N), 29.68 (s, CH_2), 26.60 (s, CH_2), 26.25 (s, CH_3), 23.31 (d, $^3J_{CP}$=8.1 Hz, CH_3).

4.5.2. Octyl-1,8-bis-[(α-aminobenzyl)spirophosphorane] (2b). ^{31}P NMR ($CDCl_3$): δ=−31.4 (d, $^2J_{PH}$=24.7 Hz, 90%), −32.9 (d, $^2J_{PH}$=21.2 Hz, 10%). ^{1}H NMR ($CDCl_3$): δ=7.35 (m, 10H, CH_{Ph}), 4.48 and 4.36 (2d, $^2J_{HP}$=24.2 Hz, 12% and $^2J_{HP}$=24.9 Hz, 88%, 2H, CH–P), 2.43–2.31 (m, 4H, CH_2–N), 1.46 (m, 12H, $CH_{3\ endo}$), 1.41–1.10 (m, 12H, CH_2), 1.05 (m, 12H, $CH_{3\ exo}$). ^{13}C NMR ($CDCl_3$): δ=172.50 (d, $^2J_{CP}$=7.1 Hz, C=O), 135.24 (d, $^2J_{CP}$=2.6 Hz, C_{ipso}), 129.30–127.93 (m, CH_{Ph}), 80.95 (d, $^2J_{CP}$=6.2 Hz, $C_q(Me)_2$), 67.42 (d, $^1J_{CP}$=190.9 Hz, CH–P), 47.57 (d, $^3J_{CP}$=24.3 Hz, CH_2–N), 29.89–26.95 (m, CH_2), 26.34 (s, CH_3), 23.47 (d, $^3J_{CP}$=8.1 Hz, CH_3).

4.5.3. Bibenzyl-4,4′-bis-[(α-aminobenzyl)spirophosphorane] (2c). ^{31}P NMR ($CDCl_3$): δ=−31.6 (d, $^2J_{PH}$=15.7 Hz, 75%), −34.5 (d, $^2J_{PH}$=22.3 Hz, 25%). ^{1}H NMR ($CDCl_3$): δ=7.53–7.39 (m, 10H, CH_{Ph}), 6.90–6.61 (m, 8H, CH_{C6H4}), 5.40 and 5.36 (2d, $^2J_{HP}$=22.7 Hz, 25% and $^2J_{HP}$=16.1 Hz, 75%, 2H, CH–P), 2.66 (s, 4H, CH_2), 1.48 (s, 12H, $CH_{3\ endo}$), 0.85 (s, 12H, $CH_{3\ exo}$). ^{13}C NMR ($CDCl_3$): δ=172.48 (d, $^2J_{CP}$=5.9 Hz, C=O, main product), 171.75 (d, $^2J_{CP}$=7.0 Hz, C=O, minor product), 143.68 (d, $^3J_{CP}$=10.5 Hz, C_q–N, minor product), 143.26 (d, $^3J_{CP}$=10.8 Hz, C_q–N, main product), 134.28–133.04 (m, $C_{q\ arom}$), 129.82–114.71 (m, CH_{arom}), 81.48 (d, $^2J_{CP}$=6.6 Hz, $C_q(Me)_2$, minor product), 81.27 (d, $^2J_{CP}$=6.5 Hz, $C_q(Me)_2$, main product), 64.91 (d, $^1J_{CP}$=175.8 Hz, CH–P, minor product), 63.71 (d, $^1J_{CP}$=178.8 Hz, CH–P, main product), 37.18 (s, CH_2), 27.22–23.11 (m, CH_3).

4.5.4. 1,4-Benzyloxy-bis-[(4-benzyl-α-aminodecyl)spirophosphorane] (2d). ^{31}P NMR ($CDCl_3$): δ=−31.1 (d, $^2J_{PH}$=24.6 Hz, 95%), −32.5 (d, $^2J_{PH}$=20.3 Hz, 5%). ^{1}H NMR ($CDCl_3$): δ=7.39 (s, 4H, H_C), 7.31–7.25 (m, 4H, $H_{AA'}$), 6.98–6.93 (m, 4H, $H_{XX'}$), 5.04 (s, 4H, CH_2–O), 4.50 and 4.32 (2d, $^2J_{HP}$=20.7 Hz, 8% and $^2J_{HP}$=24.1 Hz, 92%, 2H, CH–P), 2.39 (m, 4H, CH_2–N), 1.46 (s, 12H, $CH_{3\ endo}$), 1.20 (m, 32H, CH_2), 1.09 (s, 12H, $CH_{3\ exo}$), 0.85 (t, $^3J_{HH}$=5.1 Hz, CH_3). ^{13}C NMR ($CDCl_3$): δ=172.61 (d, $^2J_{CP}$=6.9 Hz, C=O), 159.03 (s, C_5), 136.48 (s, C_7), 129.95 (d, $^3J_{CP}$=8.9 Hz, C_3), 127.39 (s, C_8), 127.34 (s, C_2), 115.62 (s, C_4), 80.98 (d, $^2J_{CP}$=6.2 Hz, $Cq(Me)_2$), 69.67 (s, C_6), 66.75 (d, $^1J_{CP}$=192.1 Hz, CH–P), 47.55 (d, $^3J_{CP}$=23.8 Hz, CH_2–N), 31.91–22.71 (m, CH_2), 26.39 (s, CH_3), 23.58 (d, $^3J_{CP}$=7.9 Hz, CH_3), 14.19 (s, CH_3).

4.6. General procedure for the synthesis of alkyl-bis-[carboxyisobutyl(α-aminoalkyl) phosphonic acid monoesters] (3a–d)

Diimine **a**–**d** (5 mmol) in anhydrous CH_2Cl_2 (15 mL) was added dropwise to a solution of spirophosphorane **1** (2.36 g, 10 mmol) in anhydrous CH_2Cl_2 (15 mL) under argon at room temperature. The mixture was stirred for 5–10 min at room temperature and then concentrated to dryness. Concerning the compounds **3a**,**b** and **3d**, the residue was treated by CH_3CN/H_2O 1:1 (50 mL) at room temperature. The hydrolysis occurred instantaneously and the bolaform surfactant precipitated. For **3c**, the hydrolysis required longer time (10 h at room temperature) and the use of acetic acid instead of CH_3CN. In all cases, the precipitates were collected by filtration, washed several times with CH_3CN,

recrystallized from ethanol and then dried under vacuum to give more or less colored powders.

4.6.1. Hexyl-1,6-bis-[carboxyisobutyl(α-aminobenzyl)-phosphonic acid monoester] (3a). White solid (2.55 g, 81%). Mp 201–203°C (from ethanol). ^{31}P NMR (D_2O+KOH): δ=12.9 (d, $^2J_{PH}$=17.5 Hz). ^{1}H NMR (D_2O+KOH): δ=7.39–7.28 (m, 10H, CH_{Ph}), 3.76 (d, $^2J_{HP}$=18.9 Hz, 2H, CH–P), 2.24 (t, $^3J_{HH}$=7.4 Hz, 4H, CH_2–N), 1.53 (s, 6H, CH_3), 1.42 (s, 6H, CH_3), 1.29 (m, 4H, CH_2–C–N), 1.05 (m, 4H, CH_2). ^{13}C NMR (D_2O+KOH): δ=184.90 (d, $^3J_{CP}$=5.3 Hz, C=O), 136.71 (s, C_{ipso}), 131.70–130.97 (m, CH_{Ph}), 84.30 (d, $^2J_{CP}$=9.1 Hz, $C_q(CH_3)_2$), 64.30 (d, $^1J_{CP}$=146.4 Hz, CH–P), 49.43 (d, $^3J_{CP}$=10.6 Hz, CH_2–N), 29.73 (d, $^3J_{CP}$=3.7 Hz, CH_3), 29.35 (d, $^3J_{CP}$=2.3 Hz, CH_3), 28.94 (s, CH_2), 28.12 (s, CH_2). IR (KBr, cm^{-1}): ν=3428.9 (OH, NH), 2531.4 (PO–H), 1724.5 (C=O), 1631.3 (C=C), 1170.1 (P=O), 1067.2 (P–O). MS (Glycerol, FAB>0): *m/z* 629 $(M+1)^+$. Anal. calcd for $C_{28}H_{42}N_2O_{10}P_2$: C, 53.50; H, 6.74; N, 4.46. Found: C, 53.11; H, 6.86; N, 4.41.

4.6.2. Octyl-1,8-bis-[carboxyisobutyl(α-aminobenzyl)-phosphonic acid monoester] (3b). Pale yellow solid (2.95 g, 90%). Mp 176–178°C (from ethanol). ^{31}P NMR (CD_3COOD): δ=8.6 (d, $^2J_{PH}$=14.7 Hz). ^{1}H NMR (CD_3COOD): δ=7.59–7.43 (m, 10H, CH_{Ph}), 4.64 (d, $^2J_{HP}$=17.8 Hz, 2H, CH–P), 2.97 (m, 4H, CH_2–N), 1.75 (m, 4H, CH_2–C–N), 1.63 (s, 6H, CH_3), 1.52 (s, 6H, CH_3), 1.27 (m, 8H, CH_2). ^{13}C NMR (CD_3COOD): δ=184.06 (s, C=O), 131.12 (s, C_{ipso}), 130.27–129.63 (m, CH_{Ph}), 81.46 (s, $C_q(Me)_2$), 61.53 (d, $^1J_{CP}$=147.1 Hz, CH–P), 47.69 (s, CH_2–N), 29.18 (s, CH_2), 27.74 (s, CH_3), 26.90 (s, CH_3), 26.65 (s, CH_2), 26.10 (s, CH_2). IR (KBr, cm^{-1}): ν=3428.0 (OH, NH), 2545.0 (PO–H), 1726.4 (C=O), 1635.4 (C=C), 1167.9 (P=O), 1067.9 (P–O). MS (Glycerol, FAB>0): *m/z* 657 $(M+1)^+$. Anal. calcd for $C_{30}H_{46}N_2O_{10}P_2$: C, 54.87; H, 7.06; N, 4.27. Found: C, 54.20; H, 6.72; N, 4.16.

4.6.3. Bibenzyl-4,4′-bis-[carboxyisobutyl(α-aminobenzyl)-phosphonic acid monoester] (3c). Beige solid (2.35 g, 65%). Mp 170–172°C (from ethanol). ^{31}P NMR (D_2O+KOH): δ=16.2 (d, $^2J_{PH}$=22.9 Hz). ^{1}H NMR (D_2O+KOH): δ=7.40–7.20 (m, 10H, CH_{Ph}), 6.77–6.48 (m, 8H, CH_{C6H4}), 4.52 (d, $^2J_{HP}$=22.9 Hz, 2H, CH–P), 2.42 (s, 4H, CH_2), 1.50 (s, 6H, CH_3), 1.47 (s, 6H, CH_3). ^{13}C NMR (D_2O+KOH): δ=175.42 (s, C=O), 148.04 (s, C_q–N), 141.40 (s, C_{ipso}), 135.84 (s, C_q–CH_2), 131.87–117.03 (CH_{arom}), 83.84 (d, $^2J_{CP}$=9.2 Hz, $C_q(Me)_2$), 60.88 (d, $^1J_{CP}$=141.5 Hz, CH–P), 38.75 (s, CH_2), 29.41 (d, $^3J_{CP}$=3.1 Hz, CH_3), 29.11 (s, CH_3). IR (KBr, cm^{-1}): ν=3407.4 (OH, NH), 2589.9 (PO–H), 1685.6 (C=O), 1616.2 (C=C), 1188.1 (P=O), 1017.6 (P–O). MS (Glycerol, FAB<0): *m/z* 724 $(M-1)^-$.

4.6.4. 1,4-benzyloxy-4,4′-bis-[carboxyisobutyl(α-amino-benzyl)phosphonic acid monoester] (3d). Pale yellow solid (3.94 g, 82%). Mp 172–175°C (from ethanol). ^{31}P NMR ($CDCl_3$+CD_3COOD): δ=9.0 (d, $^2J_{PH}$=17.2 Hz). ^{1}H ($CDCl_3$+CD_3COOD): δ=7.38 (m, 8H, $H_{AA'}$ and H_C), 6.94 (m, 4H, $H_{XX'}$), 5.07 (s, 4H, CH_2–O), 4.52 (d, $^2J_{HP}$=17.9 Hz, 2H, CH–P), 2.83 (m, 4H, CH_2–N), 1.64 (m, 4H, CH_2–C–N), 1.59 (s, 6H, CH_3), 1.45 (s, 6H, CH_3), 1.17 (m, 28H, CH_2), 0.78 (t, $^3J_{HH}$=6.1 Hz, 6H, CH_3). ^{13}C NMR ($CDCl_3$+CD_3COOD): δ=179.01 (s, C=O), 159.21 (s, C_5), 136.52 (s, C_7), 130.70 (s, C_3), 127.57 (s, C_8), 122.04 (s, C_2), 115.05 (s, C_4), 80.14 (d, $^2J_{CP}$=7.8 Hz, $C_q(Me)_2$), 69.44 (CH_2–O), 60.31 (d, $^1J_{CP}$=148.5 Hz, CH–P), 46.81 (s, CH_2–N), 31.65–22.41 (m, CH_2), 27.09 (s, CH_3), 25.92 (s, CH_3), 13.63 (CH_3). IR (KBr, cm^{-1}): ν=3428.6 (OH, NH), 2522.1 (PO–H), 1723.2 (C=O), 1609.9 (C=C), 1178.0 (P=O), 1070.8 (P–O). MS (Glycerol, FAB>0): *m/z* 961 $(M+1)^+$, 793 $(M-P(O)(OH)OC(CH_3)_2$-$COOH+1)^+$. Anal. calcd for $C_{50}H_{78}N_2O_{12}P_2$: C, 62.48; H, 8.18; N, 2.91. Found: C, 62.31; H, 7.87; N, 2.75.

4.7. General procedure for the synthesis of alkyl-bis-[α-aminophosphonic acids] (4a–b)

Their synthesis can be achieved either by acid hydrolysis of alkyl-bis-[carboxyisobutyl-(α-amino) phosphonic acid monoesters] **3a**,**b** (Method A), or by *one-pot* acid hydrolysis of the reaction mixture (Method B).

Method A. Alkyl-bis-[(α-amino)phosphonocarboxylic acids] **3a**,**b** (2 mmol) in 20% aqueous hydrochloric acid (20 mL) were refluxed for 6 h and the progress of the reaction was followed by ^{31}P NMR analysis. The mixture was allowed to cool to room temperature then concentrated to dryness under vacuum. The crude residue was dissolved in a minimum of absolute ethanol then treated under argon by an excess of propylene oxide. The precipitate was collected by filtration and purified by H_2O/EtOH precipitation, then dried under vacuum to give a white powder.

Method B. The reaction mixture obtained from the addition reaction of spirophosphorane **1** (0.94 g, 4 mmol) with diimines **a**,**b** (2 mmol) in dry CH_2Cl_2 (10 mL) under argon at room temperature was concentrated to dryness under vacuum after 5–10 min stirring. The crude residue was treated by 20% aqueous hydrochloric acid (20 mL) under reflux for 6 h. The mixture was then worked up as described in method A.

When this procedure was applied to compound **3d**, the benzylic ether moieties of the spacer were hydrolyzed in addition to the ester functions affording the single-chain derivative **5**.

4.7.1. Hexyl-1,6-bis-[(α-aminobenzyl)phosphonic acid] (4a). White solid (0.41 g, 45%). Mp 238–241°C. ^{31}P NMR (D_2O): δ=10.6 (d, $^2J_{PH}$=15.0 Hz). ^{1}H NMR (D_2O): δ=7.32 (m, 10H, CH_{Ph}), 4.22 (d, $^2J_{HP}$=16.0 Hz, 2H, CH–P), 2.73 (m, 4H, CH_2–N), 1.43 (m, 4H, CH_2–C–N), 1.03 (m, 4H, CH_2). ^{13}C NMR (D_2O): δ=133.05 (d, $^2J_{CP}$=4.3 Hz, C_{ipso}), 131.93–131.30 (m, CH_{Ph}), 62.50 (d, $^1J_{CP}$=138.3 Hz, CH–P), 49.28 (d, $^3J_{CP}$=5.3 Hz, CH_2–N), 27.50 (s, CH_2), 27.16 (s, CH_2). IR (KBr, cm^{-1}): ν=3377.8 (OH, NH), 1607.4 (C=C), 1175.5 (P=O), 1059.2 (P–O). MS (Glycerol, FAB>0): *m/z* 457 $(M+1)^+$, 375 $(M-P(O)(OH)_2+1)^+$, 293 $(M-2[P(O)(OH)_2]+1)$. Anal. calcd for $C_{20}H_{30}N_2O_6P_2\cdot H_2O$: C, 50.63; H, 6.80; N, 5.90. Found: C, 50.61; H, 6.82; N, 5.68.

4.7.2. Octyl-1,8-bis-[(α-aminobenzyl)phosphonic acid] (4b). White solid (0.53 g, 55%). Mp 224–227°C (from ethanol). ^{31}P NMR (CD_3COOD): δ=12.4 (d, $^2J_{PH}$=15.8 Hz). ^{1}H

NMR (CD_3COOD): δ=7.74–7.42 (m, 10H, CH_{Ph}), 4.64 (d, $^2J_{HP}$=17.2 Hz, 2H, CH–P), 2.94 (m, 4H, CH_2–N), 1.79 (m, 4H, CH_2–C–N), 1.25 (m, 8H, CH_2). ^{13}C NMR (CD_3COOD): δ=130.64 (d, $^2J_{CP}$=4.8 Hz, C_{ipso}), 129.99–129.69 (m, CH_{Ph}), 61.60 (d, $^1J_{CP}$=137.9 Hz, CH–P), 47.97 (d, $^3J_{CP}$=7.2 Hz, CH_2–N), 29.13 (s, CH_2), 26.66 (s, CH_2), 26.05 (s, CH_2). IR (KBr, cm^{-1}): ν=3748.5 (OH, NH), 1612.8 (C=C), 1175.5 (P=O), 1084.5 (P–O). MS (Glycerol, FAB>0): *m/z* 485 $(M+1)^+$. Anal. calcd for $C_{22}H_{34}N_2O_6P_2{\cdot}0.5H_2O{\cdot}0.5HCl$: C, 51.64; H, 6.99; N, 5.47. Found: C, 52.61; H, 7.25; N, 5.57.

4.7.3. Decyl-[α-amino(*p*-hydroxybenzyl)]phosphonic acid (5). Beige solid (0.68 g, 50%). Mp 214–216°C (from ethanol). ^{31}P NMR (CD_3COOD): δ=13.0 (d, $^2J_{PH}$=16.2 Hz). ^{1}H NMR (CD_3COOD): δ=7.40–6.90 (m, 4H, CH_{arom}), 4.49 (d, $^2J_{HP}$=17.6 Hz, 1H, CH–P), 2.91 (m, 2H, CH_2–N), 1.74 (m, 2H, CH_2–C–N), 1.29 (m, 14H, CH_2), 0.90 (t, $^3J_{HH}$=5.7 Hz, 3H, CH_3). IR (KBr, cm^{-1}): ν=3351.2 (OH, NH), 1615.2 (C=C), 1164.2 (P=O), 1043.7 (P–O). MS (Glycerol, FAB>0): *m/z* 344 $(M+1)^+$.

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