

Synthesis, Crystal Structure and Thermal Properties of Phosphorylated Cyclotriphosphazenes

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A convergent approach for the incorporation of arylphosphonate moieties into the cyclotriphosphazene unit is described. The synthesis is based on the reaction of hexachlorocyclotriphosphazene with diethyl 4-hydroxyphenylphosphonate in the presence of anhydrous potassium carbonate. This reaction is characterised by substitution of the chloride atoms, which thus produces the hexaarylphosphono derivative in good yield. The product of this reaction is fully characterised, including a single X-ray diffraction study. The hydrolysis of the hexaphosphonate compound to its hexaphosphonic acid analogue is reported. All products were characterised by NMR and IR spectroscopy and mass spectrometry. The thermal stability and degradation behaviour of these new compounds were investigated by thermogravimetric analysis.

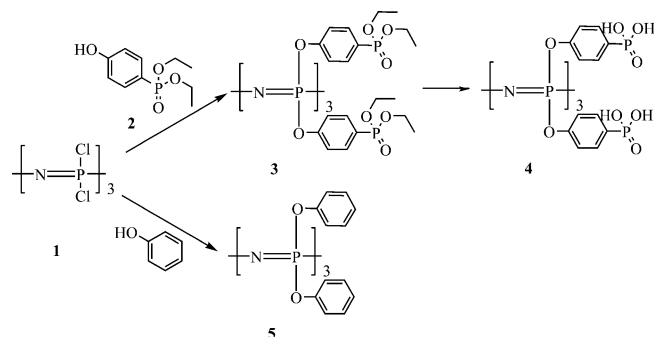
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Introduction

Despite their easy synthesis and convenient properties, hydrocarbon polymers suffer from some evident limitations in a number of applications where mechanical properties, thermal stability and light-heat or fire resistance are required. To improve the thermal properties of polymer materials, the search for fire-retardant molecules represents a major technological challenge. Traditionally, halogenated materials have been used as flame-retardant additives. However, the release of toxic materials, particularly dioxins, from incineration has led to the removal of chlorinated materials from the market and to the restriction in the use of brominated compounds.^[1] Compounds containing phosphorus have received recent attention, as they generally give off nontoxic and noncorrosive volatile products during combustion, and they generate a subsequent char residue.^[2] In some systems, flame-retardant properties can be improved drastically when phosphorus is combined with nitrogen.^[3] As an example, cyclotriphosphazene compounds characterised by the presence of an inorganic ring composed of three phosphazene units are attractive candidates for the next generation of green flame-retardant additives.^[4] Several classes of cyclotriphosphazene can be synthesised

from hexachlorocyclotriphosphazene, and each of them exhibit very different physical and chemical properties depending of the nature of the substituents.^[5] To improve the flame-retardant properties of cyclotriphosphazene-based additives, the inorganic ring could be connected to aryl- or vinylphosphonic acid moieties, which are key functionalities in polymer additives^[6] and flame retardants.^[7] Incorporation of phosphate or phosphonate groups into aryloxyphosphazenes has been reported by Allcock et al.^[8] The phosphate compounds show good thermal stability and were used as thermal additives for polystyrene.^[9]

We report here a novel and efficient method for the incorporation of arylphosphonate moieties into the cyclotriphosphazene unit according to a convergent synthesis based on the use of diethyl 4-hydroxyphenylphosphonate (2; Scheme 1). This new strategy, which is achieved in the presence of anhydrous potassium carbonate,^[10] allows the complete substitution of the chloride atoms present in



Scheme 1. Synthetic routes to 3, 4 and 5.

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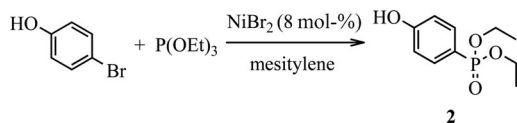
hexachlorocyclotriphosphazene (**1**) to afford **3**. The crystal structure of **3** was solved by single-crystal X-ray diffraction analysis. Furthermore, the hydrolysis of hexaphosphonate **3** to its hexaphosphonic acid analogue **4** is reported.

The thermal properties of the phosphorylated cyclotriphosphazenes were studied by ATG and compared to those of nonphosphorylated cyclotriphosphazene **5**.

Results and Discussion

Synthesis and Characterisation

Phosphonic acid **4** was obtained by the hydrolysis of **3**, which was synthesised by reaction of diethyl 4-hydroxyphenylphosphonate (**2**) with hexachlorocyclotriphosphazene (**1**). Compound **1** was commercially available and **2** could be obtained either in several steps or in one step by a palladium-catalysed cross-coupling reaction.^[11] These approaches, however, have some disadvantages due to the presence of the phenol functionality, which can affect the reactivity.^[12] In this work, we adapted a cheaper and straightforward method based on the catalytic Arbusov reaction involving an iodoarene or a bromoarene and triethylphosphite in presence of a nickel salt.^[13,14] We found that this method, which needs high thermal activation, was more reproducible when nickel bromide was used as the catalyst (Scheme 2). According to this methodology, diethyl 4-hydroxyphenylphosphonate (**2**) was obtained in a one-step reaction without protection of the phenol group. It is worth noting that this reaction was successful (76% yield) on a relatively large scale (production of 10 g of compound **2** in one batch).



Scheme 2. Synthesis of phosphonate **2**.

The substitution reaction of **1** with phenolate derivative **2** proceeded in the presence of potassium carbonate, which is a common base used for substitution reactions of hexachlorocyclotriphosphazene by phenolate nucleophiles.^[10] Under these conditions, arylphosphonated cyclotriphosphazene **3** was obtained after 2 h in an excellent yield (82%). No byproduct was detected. The structure of **3** was established by ³¹P NMR spectroscopy, and the peaks at 7.5 ppm (intensity of 1) and at 17.7 ppm (intensity of 2) can be attributed to the phosphazene ring and the arylphosphonate groups, respectively. The ¹³C and ¹H NMR spectra match the structure of **3**. The structure of **3** was unambiguously established by its single-crystal structure. It should be noted that in the presence of potassium phosphate as the base, the reaction produces only an unidentifiable mixture of products.^[15]

Finally, the conversion of the phosphonate groups to phosphonic acid groups was performed under mild conditions in a two-step process involving treatment of **3** with bromotrimethylsilane followed by methanolysis.^[16] Phosphonic acid **4** was isolated in quantitative yield, and its formation was evident from the disappearance of the signals corresponding to the ethyl groups in the ¹H and ¹³C NMR spectra and by the appearance in the IR spectrum of the characteristic bands between 2500 and 3500 cm⁻¹ that can be attributed to the OH and POH stretching vibrations. Its structure was also confirmed by HRMS spectrometry.

Crystal Structure of **3**

Single-crystal X-ray structure determination of arylphosphonated cyclotriphosphazene **3**, which was crystallized from a solution of pentane and ethyl acetate as colourless crystals, was carried out. Details of the data collections are given in Table 1. Figure 1 shows a view of the asymmetric unit of **3**, which consists of one molecule. The phosphazene ring is not rigorously planar in the crystal structure; it is somewhat puckered. Maximum deviation from the mean least-squares plane was detected at the P2 atom [0.1084(15) Å]. This deviation has the same magnitude as that observed by us in a previously solved structure of monochloropentaphenoxycyclotriphosphazene.^[17] In that crystal structure, we detected asymmetry in the P–N–P and N–P–N bond angles of the phosphazene ring, and in the crystal of **3** the same asymmetry exists: the mean of the N–P–N and P–N–P angles is 117.5(5)° and 121.6(5)°, respectively (Figure 2, Table 1). The values of the P–N, P–O and O–C_{aromatic} bond lengths are similar to the values observed in other structures with phosphazene ring as deposited in the CSD (Table 1). The phenyl rings lying in the periphery of the phosphazene unit were assigned the numbers 1 to 6. In the crystal, a disordered position was detected and refined for the phosphonate group attached to phenyl ring 2.

Table 1. Selected bond lengths and angles in **3**.

Bond lengths [Å]			
P1–N2	1.579(3)	P2–O50	1.586(2)
P1–N3	1.580(3)	P11–O13	1.459(3)
P3–N2	1.574(3)	P11–O11	1.573(3)
P3–N1	1.582(3)	P11–O12	1.582(3)
P2–N1	1.580(3)	C10–O10	1.411(4)
P2–N3	1.581(3)	C20–O20	1.400(4)
P1–O10	1.582(3)	C30–O30	1.404(4)
P1–O40	1.587(3)	C40–O40	1.409(4)
P3–O30	1.581(3)	C50–O50	1.404(4)
P3–O60	1.584(2)	C60–O60	1.397(4)
P2–O20	1.582(2)		
Bond angles [°]			
N2–P1–N3	116.96(15)	P2–N1–P3	121.01(18)
N2–P3–N1	118.07(15)	P1–N3–P2	121.72(18)
N1–P2–N3	117.34(15)	P3–N2–P1	122.10(18)

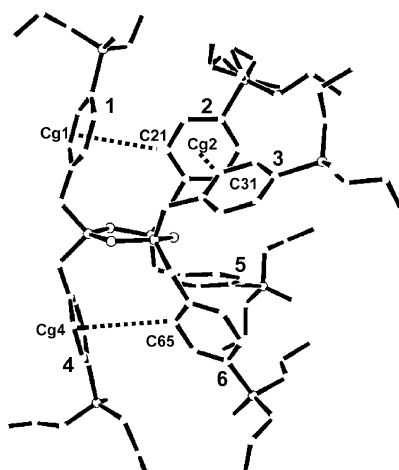


Figure 1. Ball-and-stick representation of **3**. The hydrogen atoms were omitted for the clarity and π -stacking interactions are indicated by the lines. Cg*i* denotes the centre of gravity of the *i*th ring.

Important thermal agitations were also observed for the ethyl groups of the arylphosphonate moieties in the 1, 2, 3 and 4 rings. The refinement of the disordered positions for the ethyl groups was tested, but only one position remained stable during the refinement.

The π -stacking interactions occur between the phenyl rings, but they are perturbed in comparison, for example, to the monochloropentaphenoxycyclotriphosphazene. However, the supplementary weak interactions of H-bond type are introduced in the crystal packing by the presence of the P=O motifs of the phosphonate group. Three phenyl rings (rings 1, 2 and 3) are situated above the cyclic phosphazene, and the other three phenyl rings are situated below the phosphazene ring (rings 4, 5 and 6). The position of the phenyl rings on each side is such that stacking interactions occur between them. Above the plane, phenyl rings 1, 2 and 3 are oriented perpendicularly with respect to each other such that T-shaped π -stacking occurs between the rings. The H31 hydrogen atom attached to C31 of ring 3 is directed into the centre of phenyl ring 2. The distance between C31 and the centre of gravity of phenyl ring 2 (Cg2) is about ca. 3.566 Å, and the angle between these two rings is about 72.21(13)°. T-shaped π -stacking also exists between rings 2 and 1. The H21 hydrogen atom of C21 from ring 2 is oriented into the centre of ring 1 ($d_{\text{C21-Cg1}}$ ca. 3.832 Å). The angle between the planes of phenyl rings 2 and 1 is about 77.16(12)°. The π -stacking interaction between rings 2 and 3 seems to be stronger than that between rings 2 and 1. There are no stacking interactions between rings 1 and 3.

However, weak electrostatic interactions were observed between cycle 1 and the P=O group of symmetrically related molecules (Figure 2). Firstly, C12–H12 bonds to P11=O13 from symmetrical ring 1 ($d_{\text{H12-O13}}$ ca. 2.484 Å, Table 2), and secondly, C14–H14 bonds to P41=O43 from ring 4 ($d_{\text{H14-O43}}$ ca. 2.436 Å, Table 2). On the bottom side, T-shaped π -stacking is also observed between rings 6 and 4. The H65 atom of C65 is directed into the ring centre of

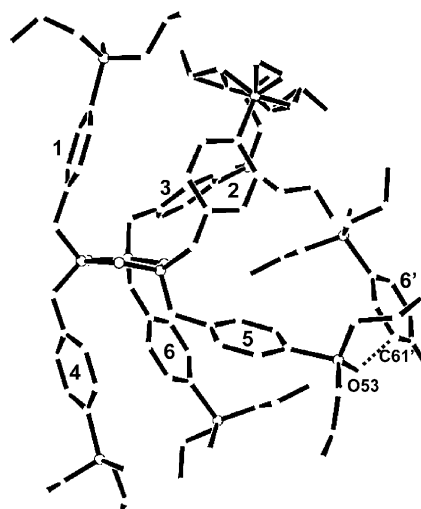
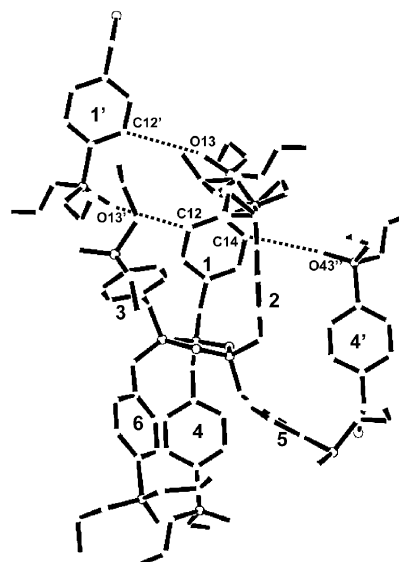


Figure 2. Ball-and-stick representation for two detailed views of the crystal packing in **3**. H-bonding interactions are presented as dashed lines; hydrogen atoms were omitted for the clarity.

ring 4 and is situated at a distance of 3.950 Å with respect to the centre of ring 4. The angle between the rings is about 55.28(11)°. Ring 5 leans out and so it is situated outside of the aromatic cluster. However, in the crystal packing, some close contacts of a H-bonding nature occur between O53 of ring 5 and C61–H61 from symmetrically related ring 6, and the distance O53–H61 is ca. 2.390 Å.

Table 2. Hydrogen bonds in **3**.

D–H...A	$d(\text{D–H})$ [Å]	$d(\text{H...A})$ [Å]	$d(\text{D...A})$ [Å]	DHA [°]
C14–H14...O43 ^[a]	0.93	2.44	3.144(5)	132.9
C12–H12...O13 ^[b]	0.93	2.48	3.267(5)	141.9
C61–H61...O53 ^[c]	0.93	2.39	3.095(4)	132.5

[a] Symmetry transformations used to generate equivalent atoms: $-x + 1, -y + 1, -z + 1$. [b] $-x + 1, -y + 1, -z$. [c] $-x, -y + 2, -z + 1$.

TGA Analyses

Although not necessarily direct, the thermal stability of a molecule has a significant influence on the fire resistance of a polymer in which it could be incorporated. The thermal stabilities of compounds **3** and **4** were estimated by TGA techniques under a nitrogen atmosphere with a heating rate of $20\text{ }^{\circ}\text{C min}^{-1}$; the obtained values were compared to those of nonphosphorylated hexaphenoxycyclotriphosphazene **5**. One of the main questions of interest is the temperature at which the compound has lost 5% of its original weight ($T_{5\%}$). Another important factor is the weight of the ceramic-like residue or “char” that remains at a given temperature (defined in terms of the percentage of the original weight). Although decomposition temperatures and residues yields as determined by TGA cannot be used directly to predict flammability, an increase in $T_{5\%}$, or in the char yield can often decrease the flammability of a material by reducing the supply of fuel to the flame.^[18] Thermogravimetric analyses on phosphate-functionalised cyclotriphosphazenes, $\text{N}_3\text{P}_3[\text{OC}_6\text{H}_4\text{OP}(\text{O})\text{OEt}_2]_3$, were carried out under atmospheric conditions by Allcock et al., and a $T_{5\%}$ value of $240\text{ }^{\circ}\text{C}$ and a residual char yield of 32% at $650\text{ }^{\circ}\text{C}$ were obtained.^[9] Until now, no thermal analysis has been carried out on phosphonate cyclotriphosphazene, which should have a good thermal stability.

The TGA curves of compounds **3** and **4** have two weight-loss regions (Figure 3). For **3**, the first weight-loss region concerns the simultaneous release of 12 ethylene molecules and 6 water molecules, which result from cleavage of the ester linkages at high temperature to give the corresponding acidic functionalities that were instantaneously condensed. The second degradation step concerns the formation of the polyphosphate resin. For **4**, the first step of decomposition is related to the release of six water molecules obtained by the condensation of the hydrogen phosphonate groups. This method of degradation is beneficial to fire-retardant additives as no toxic vapour is released, no fuel is supplied to the flame and the transformation of liquid water to gas occurs as an endothermic process. The second step is similar to the degradation process of **3** and corresponds to the formation of the polyphosphate resin.

In comparison, hexaphenoxycyclotriphosphazene **5** underwent single-step decomposition, which left less than 4% of the original material as a nonvolatile residue at $450\text{ }^{\circ}\text{C}$ (Table 3). Phosphonate cyclotriphosphazenes **3** and **4** did not show an improvement in the value of $T_{5\%}$ relative to that of **5**; however, for both **3** and **4**, the amount of nonvolatile residue formed at high temperature was important and the compounds retained 45 and 58% of the original weight, respectively. It is worth noting that the thermal analysis of **4** was carried out in air and showed a $T_{5\%}$ of $172\text{ }^{\circ}\text{C}$ and 68% char at $650\text{ }^{\circ}\text{C}$. In terms of TGA behaviour, the best additive examined here was phosphonic acid cyclic trimer **4**, which released nontoxic vapour below $400\text{ }^{\circ}\text{C}$ and formed a high char yield in air or under an atmosphere of N_2 .

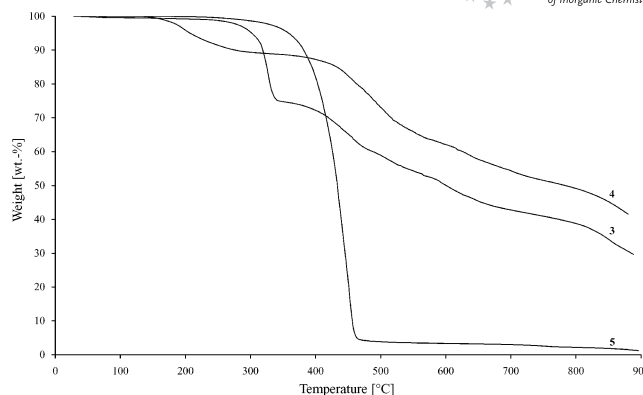


Figure 3. Thermogravimetric analyses of **3**, **4** and **5** at a heating rate of $20\text{ }^{\circ}\text{C min}^{-1}$ under a N_2 atmosphere.

Table 3. Thermal properties of cyclotriphosphazene derivatives.

Compound	$T_{5\%}$ [$^{\circ}\text{C}$]	Char at $650\text{ }^{\circ}\text{C}$ [wt.-%]
3	301	45
4	207	58
5	359	3

Conclusions

A convergent scheme for the synthesis of two original cyclotriphosphazenes functionalised by phosphonate-aryl-oxy and phosphonic acid-aryl-oxy groups was developed. The synthetic strategy involved the use of anhydrous potassium carbonate as the base, and complete substitution of the chloride atoms present in the hexachlorocyclotriphosphazene by arylphosphonate moieties was observed. The structure of **3** was unambiguously established by single-crystal X-ray diffraction analysis. Furthermore, the hydrolysis of hexaphosphonate **3** into hexaphosphonic acid analogue **4** was reported. Finally, the thermal properties of these new compounds were evaluated, and the analyses showed that phosphonic acid **4** has a very interesting thermal behaviour. This compound might be useful as a fire-resistant additive in polymers.

Experimental Section

High-field ^1H (400 MHz), ^{13}C (100.6 MHz), and ^{31}P (162 MHz) NMR spectra were obtained with a Bruker AC-400 spectrometer. The ^{31}P and ^{13}C spectra were proton decoupled. ^{31}P NMR spectra were referenced to external 85% H_3PO_4 with positive shifts recorded downfield from the reference. ^1H and ^{13}C were referenced to external tetramethylsilane. NMR spectra were obtained in CDCl_3 for **2** and **3** and in CD_3OD for **4** with chemical shifts recorded in ppm and coupling constants recorded in Hertz. TGA measurements were carried out with a Perkin–Elmer-7 thermal analysis system equipped with a PC computer at $20\text{ }^{\circ}\text{C min}^{-1}$ under an atmosphere of nitrogen. Infrared (IR) spectra were recorded with a Perkin–Elmer Spectrum One with an ATR accessory. Mass spectra (MS) and high-resolution mass spectra (HRMS) were obtained with a Waters Q-TOF Micro instruments in electrospray

ionisation positive mode (ES+) and lockspray with phosphoric acid, with an infusion introduction of $5 \mu\text{L min}^{-1}$, a source temperature of 80°C , a desolvation temperature of 120°C and external calibration with NaI. X-ray data were collected at 150 K with graphite-monochromated Mo- K_α radiation with a Bruker-Nonius Kappa II diffractometer equipped with a CCD area detector. The crystal structure was solved by direct methods with the SHELX97 package.^[19] All non-hydrogen atoms were refined anisotropically. All H atoms were calculated and fixed on the heavy atoms in the ideal geometry. Hexaphenoxycyclotriphosphazene **5** was prepared according to the method reported by Liu.^[15]

Diethyl 4-Hydroxyphenylphosphonate (2): A mixture of 4-bromophenol (10 g, 58 mmol, 1 equiv.), nickel(II) bromide (1 g, 4.6 mmol, 0.08 equiv.) in mesitylene (10 mL) was heated at 160 – 180°C under an atmosphere of nitrogen. Triethylphosphite (14.4 g, 87 mmol, 1.5 equiv.) was added dropwise. The mixture was heated at the same temperature and stirred under an atmosphere of nitrogen for the next 2 h. After cooling to room temperature, the mixture was filtered through Celite, dissolved in ether and extracted twice with a 10% solution of sodium hydroxide. The aqueous phase was washed twice with ether, acidified by concentrated hydrochloric acid and extracted with diethyl ether three times. The organic phase was dried with anhydrous magnesium sulfate. Then solvent was removed under reduced pressure to yield a colourless liquid that crystallised at room temperature to yield a white powder (10.13 g, 76% yield). M.p. 98°C . ^1H NMR (400 MHz, CDCl_3): $\delta = 1.31$ (t, $^3J_{\text{H,H}} = 7.0$ Hz, 6 H, CH_3), 4.00–4.17 (m, 4 H, $-\text{CH}_2-$), 6.96–7.01 (m, 2 H, Ar-H), 7.59–7.68 (m, 2 H, Ar-H) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): $\delta = 20.9$ (s) ppm. ^{13}C NMR (100.6 MHz, CDCl_3): $\delta = 16.6$ (d, $^3J_{\text{C,P}} = 6.6$ Hz, CH_3), 62.7 (d, $^2J_{\text{C,P}} = 5.3$ Hz, $-\text{CH}_2-$), 116.4 (d, $^3J_{\text{C,P}} = 16.5$ Hz, $\text{C}=\text{C}-\text{OH}$), 117.1 (d, $^1J_{\text{C,P}} = 197$ Hz, $\text{C}=\text{C}-\text{P}$), 134.2 (d, $^2J_{\text{C,P}} = 11.6$ Hz, $\text{C}=\text{C}-\text{P}$), 161.9 (d, $^4J_{\text{C,P}} = 3.2$ Hz, $\text{C}=\text{C}-\text{OH}$) ppm. IR (ATR): $\tilde{\nu} = 3300$ – 3600 (O–H), 1595 and 1494 ($\text{C}=\text{C}$), 1245 ($\text{P}=\text{O}$), 1160 ($\text{C}-\text{O}$), 1014 ($\text{P}-\text{O}$) cm^{-1} . MS: m/z (%) = 231.1 (100) [$\text{M} + \text{H}$] $^+$, 203.0 (35), 175.0 (20). HRMS: calcd. for $\text{C}_9\text{H}_{10}\text{NO}_2$ [$\text{M} + \text{H}$] $^+$ 231.0786; found 231.0796.

Hexa(4-diethoxyphosphorylphenoxy)cyclotriphosphazene (3): A mixture of hexachlorocyclotriphosphazene (1 g, 2.87 mmol, 1 equiv.), diethyl 4-hydroxyphenylphosphonate (**2**; 4.10 g, 17.86 mmol, 6 equiv.) and anhydrous potassium carbonate (5.72 g, 41.5 mmol, 14.4 equiv.) in acetone (80 mL) was heated at reflux for 2 h and then cooled to room temperature. The solid was filtered and washed twice with dichloromethane. The filtrate and the washings were combined, and the solvent was removed under reduced pressure. The residue was dissolved in ethyl acetate and washed with a 10% solution of sodium hydroxide two times and then once with water and dried with anhydrous magnesium sulfate. The solvent was removed under reduced pressure to obtain a colourless liquid that crystallised at room temperature to yield a white powder (3.51 g, 82% yield). The product was dissolved in ethyl acetate and recrystallised by diffusion of pentane to yield colourless crystals. M.p. 50°C . ^1H NMR (400 MHz, CDCl_3): $\delta = 1.28$ (t, $^3J_{\text{H,H}} = 7.0$ Hz, 6 H, CH_3), 4.00–4.15 (m, 4 H, $-\text{CH}_2-$), 7.00–7.02 (m, 2 H, Ar-H), 7.67–7.73 (m, 2 H, Ar-H) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): $\delta = 7.5$ (s, 1 P, N_3P_3), 17.7 [s, 2 P, $\text{PO}(\text{OEt})_2$] ppm. ^{13}C NMR (100.6 MHz, CDCl_3): $\delta = 16.75$ (d, $^3J_{\text{C,P}} = 6.2$ Hz, CH_3), 62.70 (d, $^2J_{\text{C,P}} = 5.6$ Hz, $-\text{CH}_2-$), 121.27 (d, $^3J_{\text{C,P}} = 14.8$ Hz, $\text{C}=\text{C}-\text{OH}$), 126.30 (d, $^1J_{\text{C,P}} = 191.1$ Hz, $\text{C}=\text{C}-\text{P}$), 134.07 (d, $^2J_{\text{C,P}} = 10.9$ Hz, $\text{C}=\text{C}-\text{P}$), 153.70–153.71 (m, $\text{C}=\text{C}-\text{O}$) ppm. IR (ATR): $\tilde{\nu} = 1605$ and 1510 ($\text{C}=\text{C}$), 1290 ($\text{P}=\text{O}$), 1195 ($\text{P}=\text{N}$), 1140 ($\text{C}-\text{O}$), 1007 ($\text{P}-\text{O}$), 956 ($\text{NP}-\text{O}$) cm^{-1} . MS: m/z (%) = 1532.3 (20) [$\text{M} + \text{Na}$] $^+$, 1509.9 (2) [$\text{M} + \text{H}$] $^+$, 755.6 (100), 766.6 (97), 777.6 (75).

HRMS: calcd. for $\text{C}_{60}\text{H}_{85}\text{N}_3\text{O}_{24}\text{P}_9$ [$\text{M} + \text{H}$] $^+$ 1510.3162; found 1510.3099.

Hexa(4-phosphonophenoxy)cyclotriphosphazene (4): Hexa(4-diethoxyphosphorylphenoxy)cyclotriphosphazene (**3**; 0.25 g, 0.16 mmol, 1 equiv.) was dissolved under an atmosphere of nitrogen in dichloromethane (2 mL). Bromotrimethylsilane (0.52 mL, 3.97 mmol, 24 equiv.) was added, and the solution was stirred at room temperature for 24 h. Methanol (2 mL) was added, and the solution was stirred at room temperature for 3 h. Solvents were removed under reduced pressure to produce a white powder (0.19 g, 100% yield). ^1H NMR (400 MHz, MeOD): $\delta = 7.03$ – 7.06 (m, 2 H, Ar-H), 7.67–7.72 (m, 2 H, Ar-H) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, MeOD): $\delta = 8.8$ (s, 1 P, N_3P_3), 15.3 [s, 2 P, $\text{PO}(\text{OH})_2$] ppm. ^{13}C NMR (100.62 MHz, MeOD): $\delta = 121.0$ (d, $^3J_{\text{C,P}} = 15.1$ Hz, $\text{C}=\text{C}-\text{OH}$), 129.3 (d, $^1J_{\text{C,P}} = 187.0$ Hz, $\text{C}=\text{C}-\text{P}$), 133.0 (d, $^2J_{\text{C,P}} = 11.4$ Hz, $\text{C}=\text{C}-\text{P}$), 153.0 (s, $\text{C}=\text{C}-\text{O}$) ppm. IR (ATR): $\tilde{\nu} = 2500$ – 2800 and 2200 – 2450 ($\text{PO}-\text{H}$), 1593 and 1494 ($\text{C}=\text{C}$), 1182 ($\text{P}=\text{N}$), 1163 ($\text{P}=\text{O}$), 1128 ($\text{C}-\text{O}$), 970 ($\text{NP}-\text{O}$), 922 ($\text{P}-\text{OH}$). MS: m/z (%) = 1196.4 (25) [$\text{M} + \text{Na}$] $^+$, 1174.4 (20) [$\text{M} + \text{H}$] $^+$, 620.7 (30), 609.7 (75), 598.7 (100), 587.7 (70). HRMS: calcd. for $\text{C}_{36}\text{H}_{37}\text{N}_3\text{O}_{24}\text{P}_9$ [$\text{M} + \text{H}$] $^+$ 1173.9406; found 1173.9401.

Crystal Data for 3: $\text{C}_{60}\text{H}_{84}\text{N}_3\text{O}_{24}\text{P}_9$, $M = 1510.03$ g mol $^{-1}$, triclinic, space group $P\bar{1}$, $a = 13.7651(7)$ Å, $b = 15.0141(8)$ Å, $c = 19.3629(11)$ Å, $\alpha = 85.735(2)^\circ$, $\beta = 74.334(2)^\circ$, $\gamma = 68.019(2)^\circ$, $V = 3571.4(3)$ Å 3 , $Z = 2$, $F(000) = 1584$, $\mu = 0.295$ mm $^{-1}$, $D_{\text{calcd.}} = 1.404$ Mg m $^{-3}$. The 85674 reflections were collected of which 15177 were unique [$R_{\text{int}} = 0.0426$]; 10323 reflections were observed [$I > 2\sigma(I)$]. The final refinement gave $R_1 = 0.1058$ and $wR_2 = 0.1599$ for all reflections. Goodness of fit = 1.023, residual electron density in the final Fourier map was 1.640 and -1.818 e Å $^{-3}$. CCDC-654369 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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