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Syntheses and Structures of Precursors in the Polycondensation of Hexachlorocyclotriphosphazene and Hydroquinone

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Abstract

Under controlled reaction conditions and without using a phase-transfer catalyst the polycondensation of $(NPCl_2)_3$ and hydroquinone leads to a mixture of oligomers with formula $N_3P_3Cl_5-[(p\text{-}OC_6H_4O)-N_3P_3Cl_4]_n-(p\text{-}OC_6H_4O)-N_3P_3Cl_5$. The first compound ($n = 0$) in this series could be isolated in a pure state. In addition very small quantities of double-bridged species $N_3P_3Cl_4-(p\text{-}OC_6H_4O)_2-N_3P_3Cl_4$ have been detected.

At 130 K crystals of $N_3P_3Cl_5-(p\text{-}OC_6H_4O)-N_3P_3Cl_5$ are triclinic, space group $P\bar{1}$, $a = 7.979(4)$, $b = 12.041(6)$, $c = 13.883(4)$ Å, $\alpha = 64.87(4)$, $\beta = 81.28(3)$, $\gamma = 87.48(4)°$, $Z = 2$. The refinement converged to $R_F = 0.031$ for 4203 reflections with $F \geqslant 4.0\ \sigma(F)$. In the molecules the NP rings are in *trans* position with respect to the organic part.

The presence of the catalyst Bu_4NBr accelerates the polymerization reaction. From the reaction mixture one of the two double-bridged isomers could be isolated in a pure state.

The reaction pathway during the polymerization is discussed as well as the structure of the resulting polymers.

Introduction

Polycondensation of hexachlorocyclotriphosphazene (**1**) with hydroquinone (**2**) has received much attention due to the large variety of the polymeric products formed [1]. Generally, the polycondensation process leads to the formation of both soluble cyclolinear polymers and insoluble cross-linked polymers [1, 2]. Subsequent curing of the soluble fraction may lead to rubbery solids or tough resins [1]. In our studies on the polycondensation of cyclophosphazenes with aromatic *para*-diols we found that, when using a water-organic solvent system, the molecular weight of the products formed could be controlled by suitable reaction conditions [3, 4].

Considering the importance of dioxyarylene bridged cyclophosphazenes as intermediates in the synthesis of polymers we deemed it worthwhile to investigate the structures of these precursors. Apart from the synthetic procedures leading to mono- and double-bridged cyclophosphazenes we describe in this paper the crystal and molecular structure of $N_3P_3Cl_5-(p\text{-}OC_6H_4O)-N_3P_3Cl_5$ (**3**), together with a comparison between the structural parameters of **3** and those of $N_3P_3Cl_4-(p\text{-}OC_6H_4O)_2-N_3P_3Cl_4$ (**5a**) [5].

Experimental

All experiments were carried out under an atmosphere of nitrogen. $(NPCl_2)_3$ (**1**) (Shin Nisso Kako Co. Ltd., Japan) was recrystallized once from n-hexane. Hydroquinone (**2**) (Merck) was dried *in vacuo* over KOH pellets during 24 h. Solvents were purified according to conventional methods [6].

Purification by HPLC was carried out using a Waters system consisting of two 6000 A pumps, combined with a R401 RI detector. Separations were performed on Lichrosorb Si 60/10 column (outside diameter 22 mm, length 30 cm). Capacity factors (k') were determined under analytical conditions (Lichrosorb Si 60/7 column, outside diameter 4.6 mm, length 30 cm). Elemental analyses were performed under supervision of Mr A. F. Hamminga (Microanalytical Department, University of Groningen). Mass spectral data were recorded on an AEI M.S.9 and on a Ribermag R10/10C spectrometer (Mr A. Kiewiet, Department of Organic Chemistry, University of Groningen). ^1H NMR spectra ($CDCl_3$ solution) were recorded on a Varian XL-100 spectrometer in 5-mm tubes using $SiMe_4$ as internal standard; $^{31}P\{^1H\}$ NMR ($CDCl_3$ solution) were taken with a Nicolet NT 200 spectrometer in 10-mm tubes

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at 80.9 MHz; $(NPCl_2)_3$ in $CDCl_3$ was used as external reference (19.9 ppm); the ^2H resonance of the solvent was used for field-frequency lock.

Synthesis of $N_3P_3Cl_5$*-*$[(p\text{-}OC_6H_4O)\text{-}N_3P_3Cl_4]_n$*-*$(p\text{-}OC_6H_4O)\text{-}N_3P_3Cl_5$

A solution of 5.20 g (14.9 mmol) of **1** in 100 ml of THF was added dropwise under vigorous stirring to a solution of 3.32 g (30.2 mmol) of **2**, 2.4 g (60 mmol) of NaOH, 10.0 g (171 mmol) of NaCl and 3.1 g (30 mmol) of $NaHSO_3$ in 100 ml of water. The reaction was allowed to proceed for 5 min (including the period of addition) at room temperature. Then 6 ml of conc. hydrochloric acid were added to stop the polycondensation. The reaction mixture was placed in a separatory funnel, the organic layer was separated and poured into 1000 ml of boiling water. The precipitate was filtered off, dried *in vacuo* at room temperature during 15 h. The reaction product (3.02 g) was dissolved in 100 ml of benzene, 100 ml of n-hexane was added, and the residue formed (polymeric material) was filtered off. Evaporation of the benzene–hexane solution yielded 2.00 g of a slightly yellow, amorphous material, which was subjected to HPLC using n-hexane containing 3% tetrahydrofuran (THF) as eluant. Three fractions were obtained:

Fraction I. The bridged cyclophosphazene (**3**) was collected as the first fraction ($k' = 0.5$). Recrystallization from pentane afforded colourless crystals of **3**. Yield 1.0 g (1.37 mmol, 18%), melting point (m.p.) 115–117 °C. *Anal.* Calc. for $C_6H_4O_2N_6P_6Cl_{10}$: C, 9.84; H, 0.55; N, 11.47; Cl, 48.40; Found: C, 9.88; H, 0.53; N, 11.22; Cl, 48.48%. Mass spectrum: m/e = 729, $C_6H_4O_2N_6P_6{}^{35}Cl_{10} + H$, 12%, $m/e = 310$, $N_3P_3{}^{35}Cl_5$, 62%. NMR: ^1H, δ 7.10 [4H, s] ppm; $^{31}P\{^1H\}$, A_2B type spectrum (Fig. 1a), δ 22.5 [PCl_2], 12.6 [P(OR)Cl] ppm, ^2J(PP) 60.4 Hz.

Fraction II ($k' = 1.0$). White crystals (0.4 g, m.p. 100–110 °C) of a mixture of oligomers were obtained. Repeated crystallization did not result in a separation of compounds. *Anal.* Calc. for $N_3P_3Cl_5$–(p-OC_6H_4O)–$N_3P_3Cl_4$–(p-OC_6H_4O)–$N_3P_3Cl_5$ (**4**): Cl, 44.42; Calc. for $C_{12}H_8O_4N_6P_6Cl_8$ (**5**) [present according to the ^{31}P NMR spectrum, Fig. 1b]: Cl, 36.85. Found: Cl, 43.85%, which points to a mixture of **4**:**5** = 92:8. Mass spectrum: m/e = 1111, $C_{12}H_8O_4N_9P_9{}^{35}Cl_{14}$, 1.9%, $m/e = 766$, $C_{12}H_8O_4N_6P_6{}^{35}Cl_8$, 41%. NMR (only for **4**): $^{31}P\{^1H\}$, combination of A_2B and AB_2 spectra (Fig. 1b). A_2B part, δ 22.5 [PCl_2], 12.6, 12.5 [P(OR)Cl] ppm, ^2J(PP) 60.9 Hz; AB_2 part (2 times), δ 24.8, [PCl_2], 15.7, [P(OR)Cl] ppm, ^2J(PP) 64.2 Hz; δ 24.7, [PCl_2], 15.1, [P(OR)-Cl] ppm, ^2J(PP) 65.4 Hz.

Fraction III ($k' = 1.9$). Yield 0.1 g of a brownish, waxy material. $^{31}P\{^1H\}$ NMR spectrum resembled that of fraction II; intensity of AB_2 part increased with respect to the spectrum of fraction II (Fig. 1c).

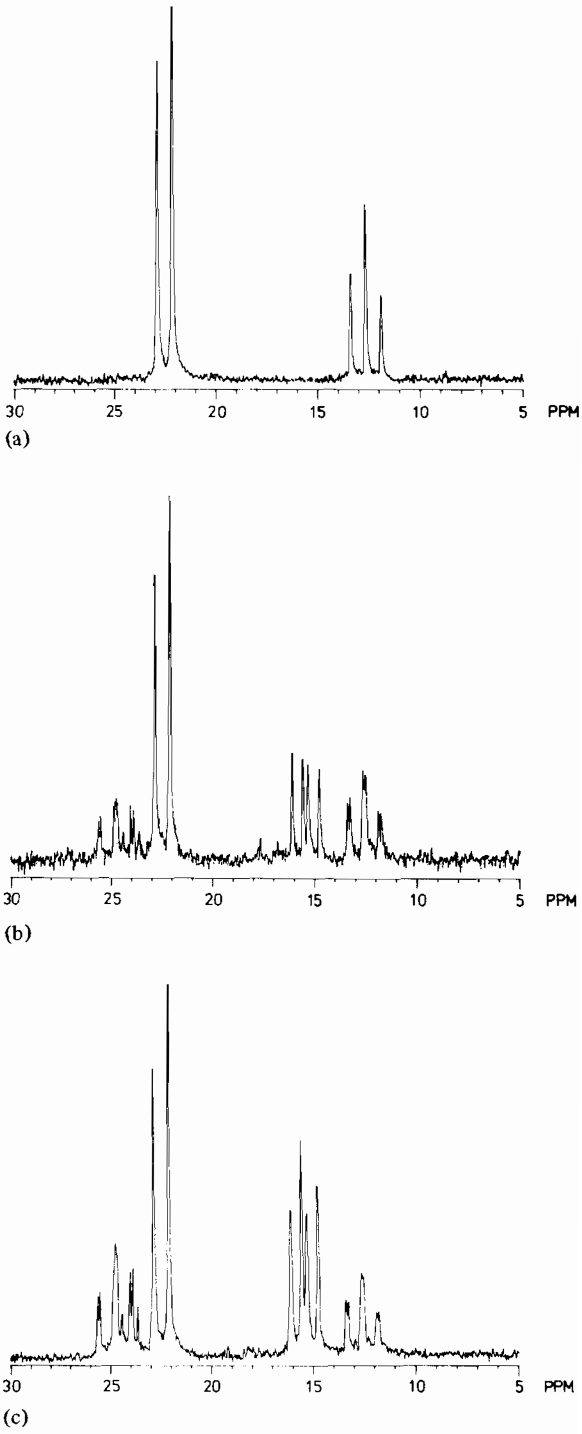


Fig. 1. $^{31}P\{^1H\}$ NMR spectra: (a) $N_3P_3Cl_5$–(p-OC_6H_4O)–$N_3P_3Cl_5$ (**3**); (b) $N_3P_3Cl_5$–(p-OC_6H_4O)–$N_3P_3Cl_4$–(p-OC_6H_4O)–$N_3P_3Cl_5$ (**4a, b**) and traces of $N_3P_3Cl_4$–(p-$OC_6H_4O)_2$–$N_3P_3Cl_4$ (**5b**); (c) fraction III of the reaction of **1** and **2** without the use of a phase-transfer catalyst.

Synthesis of $N_3P_3Cl_4$–(p-$OC_6H_4O)_2$–$N_3P_3Cl_4$ (5a, b)

A solution of 7.80 g (22.4 mmol) of **1** in 150 ml of THF was added dropwise under vigorous stirring to a solution of 4.93 g (44.8 mmol) of **2**, 3.6 g (90 mmol) of NaOH, 15.0 g (256 mmol) of NaCl, 4.5 g (43 mmol) of $NaHSO_3$ and 1.5 g (4.7 mmol) of the phase-transfer catalyst Bu_4NBr in 150 ml of water. The reaction was allowed to proceed for 3 min (including the time of addition) after which 9 ml of conc. hydrochloric acid were added. According to the procedure described above (using 1500 ml of boiling water, 150 ml of hexane, 150 ml of benzene) 2.6 of a light yellow reaction product was obtained, which was freed from higher oligomers by HPLC. Preparative HPLC (n-hexane containing 3% THF as eluant) afforded three fractions.

Fraction I ($k' = 0.2$). Yield 0.2 g of a brownish, waxy material. The $^{31}P\{^1H\}$ NMR spectrum resembled that of fraction II of the previous experiment.

Fraction II ($k' = 0.7$). Yield 0.3 g of a brownish, waxy material, which was subjected to flash chromatography (silica gel, Merck, 230–400 mesh, hexane–benzene 2:1 as eluant). A fraction could be obtained, consisting of two isomers of compound **5**. By recrystallization from pentane one of the isomers could be obtained in a pure state. Isomer **5a**: yield 0.06 g (0.08 mmol, 0.7%) of white crystals, m.p. 244–245 °C. *Anal.* Calc. for $C_{12}H_8O_4N_6P_6Cl_8$: C, 18.72; H, 1.05; N, 10.92; Cl, 36.85. Found: C, 18.46; H, 1.12; N, 10.75; Cl, 35.92%. Mass spectrum: m/e = 766, $C_{12}H_8O_4N_6P_6{}^{35}Cl_8$, 35%. NMR: ^1H, δ 7.16 [4H, s], 7.08 [4H, s] ppm; $^{31}P\{^1H\}$, AB_2 type spectrum, δ 26.6 [PCl_2], 18.8 [P(OR)Cl] ppm, ^2J(PP) 64.2 Hz. Isomer **5b**: $^{31}P\{^1H\}$ NMR (from a mixture of **5a** and **5b**): AB_2 spectrum, δ 25.7 [PCl_2], 17.2 [P(OR)Cl] ppm, ^2J(PP) 67.8 Hz.

Fraction III ($k' = 1.6$). Yield 0.3 g of a waxy, brown material. The ^{31}P NMR spectrum pointed to polymeric material.

Structure Determination of $N_3P_3Cl_5$–(p-OC_6H_4O)–$N_3P_3Cl_5$

A suitable colourless block shaped crystal of **3** was glued on the top of a glass fiber and transferred into the cold nitrogen stream of the low temperature unit mounted on an Enraf-Nonius CAD-4F diffractometer interfaced to a PDP-11/23 computer. Unit cell parameters and their standard deviations were derived from the angular settings of 23 reflections in the range $9.11 < \theta < 14.20°$. Reduced cell calculations did not indicate any higher lattice symmetry [7]. The intensities of two standard reflections were measured every 200 min of X-ray exposure time to trace crystal decomposition and/or movement. Crystal decomposition was not observed. The net intensities of the data were corrected for the scale variation, Lorentz and polarization effects. Variance $\sigma^2(I)$ was calculated based on counting statistics and the term (P^2I^2) where P (=0.034) is the instability constant as derived from the excess variance in the reference reflections [8]. Crystal data and the experimental details of the structure determination are compiled in Table 1. The structure was solved by direct methods (GENTAN) [9]. After the isotropic refinement correction for absorption was applied by means of the program DIFABS [10]. Final refinement was carried out on F by block-diagonal least-squares techniques with anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were located on a difference Fourier map and included in the final refinement with isotropic temperature factors. The final values of the positional parameters are presented in Table 2. Neutral atom scattering factors [11] were used with anomalous dispersion corrections [12] being applied to the non-hydrogen atoms. All calculations were carried out on the CDC-Cyber 170/760 computer of the University of Groningen with the program XTAL [10], the EUCLID package [13] and an extended version of the program PLUTO [14].

Results and Discussion

Polycondensation Process

Our studies on the reactivity of **1** and **2** in a THF–aqueous NaOH solvent mixture showed that the initial stages of the uncatalyzed polycondensation can result in a reasonable yield of the low-molecular weight compounds **3** and **4** when applying a reaction period of 5 min. However, when using a catalyst (Bu_4NBr), high-molecular weight polymers are formed in addition to very low yields of **3**, **4** and the double-bridged derivatives **5a**, **b**.

It is clear, that the presence of a phase-transfer catalyst accelerates the substitution of **1** by **2**, resulting in a high initial concentration of $N_3P_3Cl_5$-OC_6H_4OH (**6**). Owing to its heterofunctionality (Cl and OH functions), compound **6** can undergo homocondensation in two ways: (a) Elimination of one molecule of HCl per two molecules of **6** as predominant process, leading ultimately to the formation of linear polymers. (b) Elimination of two molecules of HCl per two molecules of **6**, offering isomers **5**. Without a phase-transfer catalyst the formation of **6** is supposed to be relatively slow and therefore a subsequent reaction with **1** is obvious, resulting in a formation of compounds **3**, **4** and higher homologues. The presence of only a trace of **5** fits this reasoning.

Previously described methods of polycondensation of the trimer **1** with aromatic *para*-diols render high yields of insoluble cross-linked cyclomatrix-type

TABLE 1. Crystal Data and Details of the Structure Determination, Data Collection and Refinement

Chemical formula	$C_6H_4Cl_{10}N_6O_2P_6$
Molecular weight	732.51
Crystal system	triclinic
Space group, no.	$P\bar{1}$, 2
a (Å)	7.979(4)
b (Å)	12.041(6)
c (Å)	13.883(4)
α (°)	64.87(4)
β (°)	81.28(3)
γ (°)	87.48(4)
V (Å^3)	1193 (1)
Z	2
D_{calc} (g cm^{-3})	2.039
F(000), electrons	716
μ(Mo Kα) (cm^{-1})	16.0
Approx. crystal dimension (mm)	0.30 × 0.25 × 0.04
Diffractometer	Enraf-Nonius CAD-4F
Radiation (Å)	Mo K$\bar{\alpha}$, 0.71073
Monochromator	graphite
Temperature (K)	130
θ range; min. max. (°)	1.64, 27.0
$\omega/2\theta$ scan (°)	$\omega = 1.05 + 0.35 \text{ tg } \theta$
Data set	h: $-10 \rightarrow 10$; k: $-13 \rightarrow 15$; l: $0 \rightarrow 17$
Crystal to receiving aperture distance (mm)	173
Horizontal, vertical aperture (mm)	$3.2 + 1.0 \text{ tg } \theta$, 4.0
Reference reflections	$4\bar{1}\bar{2}$, 1.8
r.m.s. deviation in %	357, 2.2
Instability constant P	0.034
Drift correction	0.98–1.02
Min. and max. absorption correction factor	0.89–1.17
X-ray exposure time (h)	166.3
Total data	5367
Total unique	5150
Observed $F \geqslant 4.0\ \sigma(F)$	4203
No. reflections	4203
No. refined parameters	288
Final $R = \Sigma(\|\|F_o\| - \|F_c\|\|)/\Sigma\|F_o\|$	0.031
Final $R_w = [\Sigma(w(\|F_o\| - \|F_c\|)^2)/\Sigma\|wF_o^2\|]^{1/2}$	0.037
Weighting scheme	1
R.m.s. deviation of reflections on unit weight $(\Sigma w(\|F_o\| - \|F_c\|)^2/(m - n))^{1/2}$ (m = number of observations, n = number of variables)	1.404
Min. and max. residual densities in final Fourier map (e/Å^{-3})	−0.57, 0.65
Max. (shift/sigma) final cycle	0.156
Average (shift/sigma) final cycle	0.0133

polymers (arising from the substitution of more than two chlorine atoms per PN ring system), whereas the soluble polymers possess rather low molecular weights [1, 2]. The advantage of performing the polycondensation process in the THF–aqueous NaOH solvent system is the possibility to replace not more than two (or at the highest three) chlorine atoms per phosphazene ring. This has also been demonstrated by the model reaction of **1** with phenol (molar ratio 1:6; reaction period 30 min), in which the diphenoxy derivative appeared to be the main reaction product in addition to small amounts of the mono- and trisubstituted derivatives.

As already mentioned above, high yields of high-molecular weight polymers can be obtained by using a phase-transfer catalyst. As a typical example: the

TABLE 2. Final Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for Non-H Atoms[a]

	x	y	z	U_{eq} (Å^2)[b]
Molecule I				
Cl(1)	0.6194(1)	0.64287(8)	0.06919(7)	0.0211(3)
Cl(2)	0.6014(1)	1.05274(8)	0.07967(8)	0.0261(3)
Cl(3)	0.4695(1)	0.9237(1)	0.32226(8)	0.0282(3)
Cl(4)	0.9361(1)	0.67592(9)	0.40770(7)	0.0237(3)
Cl(5)	1.1373(1)	0.79069(9)	0.18011(8)	0.0230(3)
P(1)	0.6296(1)	0.66749(8)	0.20011(7)	0.0134(2)
P(2)	0.6179(1)	0.89463(8)	0.20613(7)	0.0145(2)
P(3)	0.8999(1)	0.75467(8)	0.25277(7)	0.0139(2)
O(1)	0.5207(3)	0.5506(2)	0.2842(2)	0.0165(6)
N(1)	0.5345(4)	0.7897(3)	0.1895(2)	0.0165(8)
N(2)	0.8064(4)	0.8795(3)	0.2319(3)	0.0183(8)
N(3)	0.8191(4)	0.6574(3)	0.2248(2)	0.0152(6)
C(1)	0.5120(4)	0.5266(3)	0.3938(3)	0.014(1)
C(2)	0.3814(4)	0.5758(3)	0.4395(3)	0.018(1)
C(3)	0.6317(4)	0.4515(3)	0.4521(3)	0.018(1)
Molecule II				
Cl(6)	0.0759(1)	0.12280(8)	0.07205(7)	0.0210(2)
Cl(7)	−0.4714(1)	0.32218(9)	0.16116(8)	0.0267(3)
Cl(8)	−0.4033(1)	0.19973(9)	0.39560(8)	0.0269(3)
Cl(9)	0.1230(1)	0.40168(9)	0.32283(7)	0.0237(3)
Cl(10)	0.1151(1)	0.54036(8)	0.08054(7)	0.0240(3)
P(4)	0.0121(1)	0.15721(8)	0.19979(7)	0.0139(2)
P(5)	−0.2794(1)	0.26879(8)	0.24482(7)	0.0152(2)
P(6)	0.0291(1)	0.38455(8)	0.20363(7)	0.0145(2)
O(2)	0.0795(3)	0.0363(2)	0.2875(2)	0.0177(6)
N(4)	−0.1880(4)	0.1611(3)	0.2241(2)	0.0157(6)
N(5)	−0.1713(4)	0.3843(3)	0.2267(2)	0.0190(8)
N(6)	0.1164(4)	0.2735(3)	0.1855(2)	0.0181(8)
C(4)	0.0384(4)	0.0187(3)	0.3952(3)	0.016(1)
C(5)	0.1453(4)	0.0676(3)	0.4377(3)	0.019(1)
C(6)	−0.1071(4)	−0.0482(3)	0.4554(3)	0.019(1)

[a] e.s.d.s given in parentheses. [b] $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

polycondensation of **1** and **2** (molar ratio 1:2, THF–aqueous NaOH solvent system) in the presence of Et_4NBr (2% based on the amount of **1**) yields after a reaction period of 10 min a polymer with a MW equal to 20000, which is still soluble in common organic solvents [3].

It is worth noting that the solubility of this polymer, combined with the presence of reactive Cl atoms, offers the possibility to introduce other reactive functionalities.

$^{31}P\{^1H\}$ *NMR Spectra*

As stated above the reaction of **1** and **2** without the use of a catalyst leads to the formation of oligomers with general formula $N_3P_3Cl_5-[(p\text{-}OC_6H_4O)-N_3P_3Cl_4]_n-(p\text{-}OC_6H_4O)-N_3P_3Cl_5$. In Fig. 1 the $^{31}P\{^1H\}$ NMR spectra of these compounds, obtained as fractions I, II and III, are given. On going from Fig. 1b to 1c the intensity of the AB_2 part (around 24.8 and 15.4 ppm) increases in comparison with the intensity of the A_2B part (around 22.5 and 12.5 ppm). This is in line with a chain elongation by units $-N_3P_3Cl_4-(p\text{-}OC_6H_4O)-$. Apart from the PCl_2 resonances in the A_2B part all other resonance lines of **4** appear as doublets (Fig. 1b). The occurrence of *cis-* and *trans*-isomers may explain this doubling. The low-intensity resonance lines at 16.8 and 17.7 ppm in spectrum Ib reflect the presence of isomer **5b**. A rough estimate based on intensities shows the relative amount of **5b** about equal to that derived from the elemental analysis (see 'Experimental').

Structure of 3

Relevant data on the geometry are given in Tables 3 and 4. The molecular structure is depicted in Fig. 2, which also explains the atom-numbering scheme. The triclinic unit cell contains two molecules. Each asymmetric unit contains half molecules with no atom setting at a special position; each molecule has a crystallographic imposed center of inversion. The

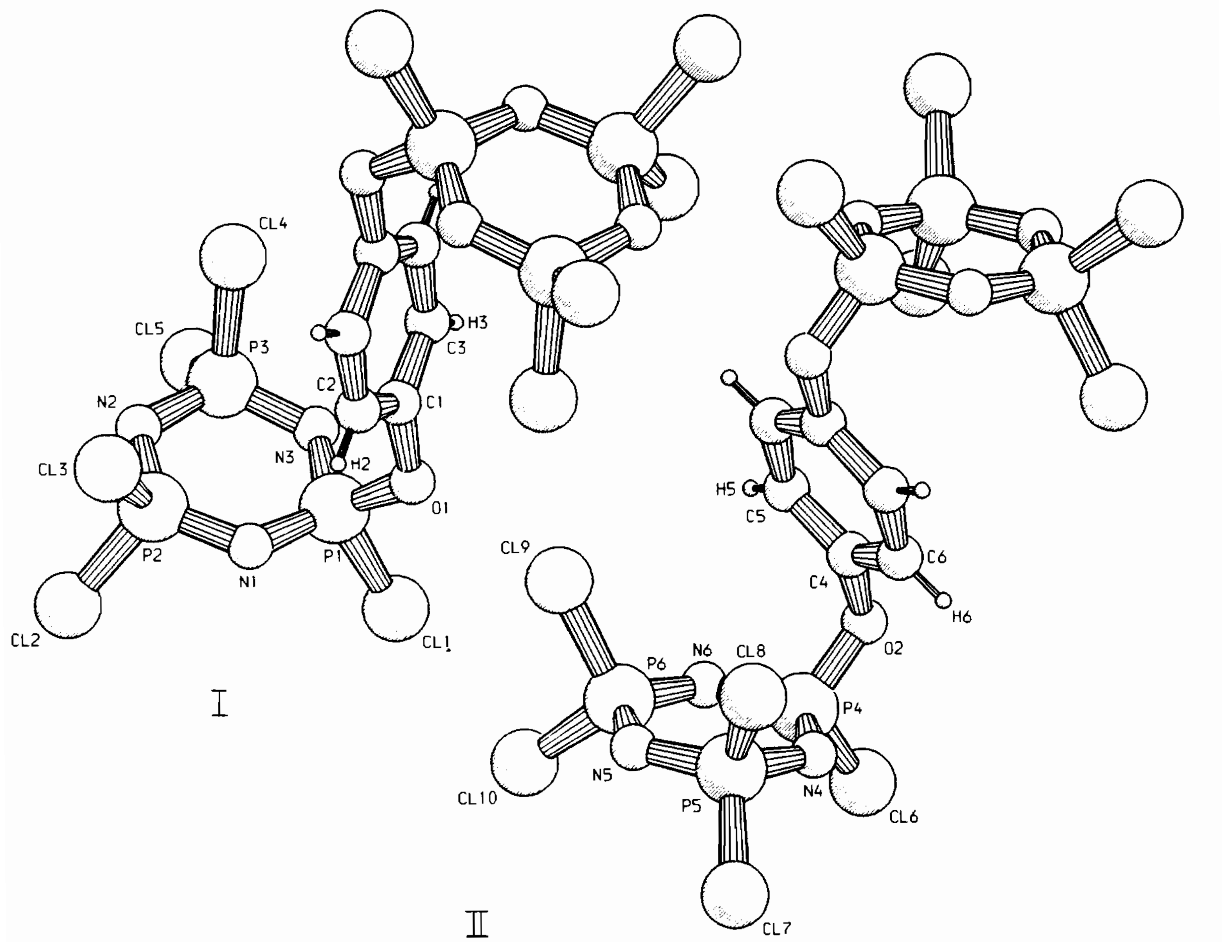


Fig. 2. PLUTO drawing of the independent molecules (I and II) of $N_3P_3Cl_5$–(p-OC_6H_4O)–$N_3P_3Cl_5$.

TABLE 3. Selected Data on the Geometry of 3[a]

Bond distances (Å)			
Molecule I			
Cl(1)–P(1)	1.976(2)	P(2)–N(1)	1.569(4)
Cl(2)–P(2)	1.983(2)	P(2)–N(2)	1.583(3)
Cl(3)–P(2)	1.997(2)	P(3)–N(2)	1.580(4)
Cl(4)–P(3)	2.010(2)	P(3)–N(3)	1.571(4)
Cl(5)–P(3)	1.979(2)	O(1)–C(1)	1.414(5)
P(1)–O(1)	1.582(3)	C(1)–C(2)	1.380(5)
P(1)–N(1)	1.586(4)	C(1)–C(3)	1.386(5)
P(1)–N(3)	1.589(3)	C(2)–C(3B)	1.385(5)
Molecule II			
Cl(6)–P(4)	1.977(2)	P(5)–N(4)	1.570(4)
Cl(7)–P(5)	1.982(2)	P(5)–N(5)	1.576(4)
Cl(8)–P(5)	2.004(2)	P(6)–N(5)	1.582(3)
Cl(9)–P(6)	2.005(2)	P(6)–N(6)	1.577(4)
Cl(10)–P(6)	1.986(2)	O(2)–C(4)	1.406(5)
P(4)–O(2)	1.586(3)	C(4)–C(5)	1.384(5)
P(4)–N(4)	1.584(3)	C(4)–C(6)	1.383(5)
P(4)–N(6)	1.584(4)	C(5)–C(6A)	1.387(5)

(continued)

TABLE 3. *(continued)*

Bond angles (°)	
Molecule I	
Cl(1)–P(1)–O(1)	98.3(1)
Cl(2)–P(2)–Cl(3)	101.42(7)
Cl(4)–P(3)–Cl(5)	100.60(7)
N(1)–P(1)–N(3)	116.6(2)
N(1)–P(2)–N(2)	118.7(2)
N(2)–P(3)–N(3)	119.0(2)
P(1)–N(1)–P(2)	122.7(2)
P(2)–N(2)–P(3)	120.0(2)
P(1)–N(3)–P(3)	121.7(2)
P(1)–O(1)–C(1)	116.4(2)
C(2)–C(1)–C(3)	122.5(3)
C(1)–C(2)–C(3B)	118.9(3)
C(1)–C(3)–C(2B)	118.6(3)
Molecule II	
Cl(6)–P(4)–O(2)	99.1(1)
Cl(7)–P(5)–Cl(8)	100.94(7)
Cl(9)–P(6)–Cl(10)	100.30(7)

(continued)

TABLE 3. *(continued)*

Molecule II	
N(4)–P(4)–N(6)	117.0(2)
N(4)–P(5)–N(5)	119.1(2)
N(5)–P(6)–N(6)	118.3(2)
P(4)–N(4)–P(5)	121.9(2)
P(5)–N(5)–P(6)	120.6(2)
P(4)–N(6)–P(6)	122.4(2)
P(4)–O(2)–C(4)	116.5(2)
C(5)–C(4)–C(6)	122.2(3)
C(4)–C(5)–C(6A)	119.3(3)
C(4)–C(6)–C(5A)	118.5(3)

[a] e.s.d.s given in parentheses. (A) indicates symmetry operation: $-x$, $-y$, $1-z$; (B) indicates symmetry operation: $1-x$, $1-y$, $1-z$.

TABLE 4. Mean Geometric Data [a]

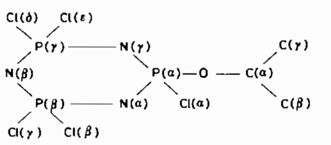
Bond distances (Å)

Cl(α)–P(α)	1.977(1)	P(β)–N(α)	1.570(3)
Cl(β)–P(β)	1.983(1)	P(β)–N(β)	1.580(3)
Cl(γ)–P(β)	2.001(4)	P(γ)–N(β)	1.581(2)
Cl(δ)–P(γ)	2.008(3)	P(γ)–N(γ)	1.574(3)
Cl(ε)–P(γ)	1.983(4)	O–C(α)	1.410(4)
P(α)–N(α)	1.585(2)		
P(α)–N(γ)	1.587(2)	C–C	1.384(2)

Bond angles (°)

Cl(α)–P(α)–O	98.7(4)
Cl(β)–P(β)–Cl(γ)	101.2(2)
Cl(δ)–P(γ)–Cl(ε)	100.5(1)
N(α)–P(α)–N(γ)	116.8(2)
N(α)–P(β)–N(β)	118.9(2)
N(β)–P(γ)–N(γ)	118.7(4)
P(α)–N(α)–P(β)	122.3(4)
P(β)–N(β)–P(γ)	120.3(3)
P(α)–N(γ)–P(γ)	122.1(4)
P(α)–O–C(α)	116.5(1)
C(β)–C(α)–C(γ)	122.4(1)
Remaining C–C–C	118.8(2)

[a] Atom labelling:



observed conformations of the nearly flat, heterocyclic rings approach that of an envelope [15] for [P(1)–N(3)] with torsion angles ranging from –13.3(3) to 12.3(3)°, lowest asymmetry parameter value C_s[P(3)] = 1.1(2)° [16]; a chair for [P(4)–N(6)] with torsion angles ranging from –6.0(2) to 7.8(3)°, lowest asymmetry parameter value C_s[P(5)] = 0.9(2)°. Puckering parameters [17] are $Q = 0.104(3)$ Å, $\theta = 46.5(2)°$, $\phi = 246(2)°$ and $Q = 0.068(2)$, $\theta = 18(3)$, $\phi = 142(7)$, respectively (e.s.d.s following Norrestam [18]).

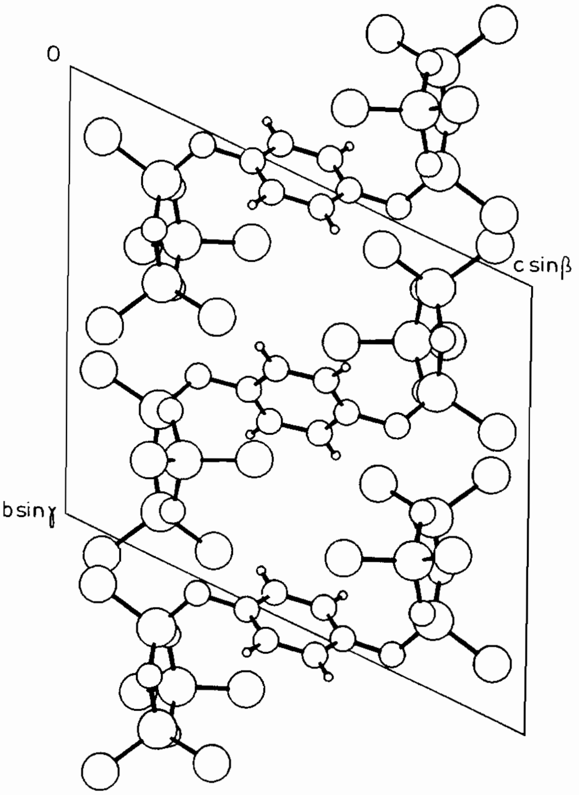


Fig. 3. Molecular packing viewed down [100].

The PLUTO drawing of the molecules (Fig. 2) clearly indicates the inorganic and organic rings almost being perpendicular to each other in one molecule with angles 68.0(2) (molecule I) and 80.7(2)° (molecule II). With respect to the organic moiety the inorganic rings are in *trans*-position. This is also reflected by the projection of the structure along the a-axis (Fig. 3). Moreover, this projection shows that the crystal packing can be described in terms of a regular pattern of inorganic and organic 'layers', almost parallel to [100]. No significant differences are observed between the geometric data of the two residues I and II (Table 3); mean values of the asymmetric units are given in Table 4.* As found for the double-bridged compound **5a** [5] the difference between the P–N bond lengths in a P(OR)Cl–N–PCl_2 segment is small. This can be explained from the small difference in electronegativity between the P(OR)Cl and PCl_2 centres [20, 21]. The P–Cl bonds can be divided into two sets, those having a mean bond length of 2.006(2) Å and pointing to the aryl moiety and the others having a mean bond length of

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*Throughout this paper the mean values and their standard errors have been calculated using the formulae given by Dominicano *et al.* [19].

1.983(4) Å. Lattice effects may be responsible for the difference observed, the more as in the double-bridged compound **5a** the P–Cl bonds within a PCl_2 group are equal but differ when going from one inorganic part to the other.

Structures of the Polymers Formed in the Polycondensation

Compound **3** offers, in principle, five chlorine atoms per N_3P_3 unit for the third reaction step ('step' means formation of a P–O–C linkage). However, the chlorine atom geminally positioned to the aryloxy group already present can be excluded, as the introduction of a second aryloxy group preferentially proceeds via a non-geminal S_N2 type process [1]. Substitution of one of the four remaining atoms can lead to a *cis*- or a *trans*-disubstituted phosphazene ring. As indicated by the ^{31}P NMR spectrum (Fig. 1b) both isomers are formed in about equal yields. With respect to the formation of the fourth P–O–C linkage it is clear that disubstitution at the other N_3P_3 part of the molecule is more favourable than trisubstitution at the former one.

From the above it can be concluded that the polycondensation of **1** and **2** without the use of a phase-transfer catalyst leads to a linear polymer with repeating unit $-[-N_3P_3Cl_4-(-p\text{-}OC_6H_4O)-]-$.

For the condensation in the presence of a catalyst the picture is less clear, as a high-yield isolation of precursors failed by the enhanced reactivity. We assume, however, the same polymeric structure to be formed as in the uncatalysed process, as from steric reasons chain-propagation may expect to proceed more faster than the formation of double-bridged compounds.

Supplementary Material

Lists of structure factors, anisotropic thermal parameters, H atom parameters and bond lengths and angles involving H atoms and an ORTEP plot [22] are available from the authors on request.

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