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New dioxytetraethyleneoxy macrocyclic cyclophosphazene derivatives

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Abstract

A series of macrocyclic cyclophosphazene containing derivatives of mono-ansa, mono-spiro, spiro-ansa and bis-ansa structure together with polymeric materials have been obtained by the reaction of hexachlorocyclotriphosphazene with tetraethylene glycol in the presence of sodium hydride. Structure determination was based on mass and ^{31}P NMR spectral analysis. The formation of macrocyclic compounds points to a template effect being operative during substitution. The structure of the mono-ansa compound has been confirmed by an X-ray diffraction study. Crystals are triclinic, $P\bar{1}$, $a=7.797(1)$, $b=10.705(1)$, $c=12.336(1)$ Å, $\alpha=88.74(1)$, $\beta=72.404(7)$, $\gamma=72.15(1)°$, $Z=2$ at 130 K. The refinement converged to $R=0.034$ for 3434 unique reflections ($I \geqslant 2.5\sigma(I)$) and 273 parameters. The basic structure consists of an N_3P_3 six-membered ring in which two different P atoms are coupled to an $O(CH_2CH_2O)_4$ chain, forming a 16-membered diphosphaza crown ether.

Keywords: Crystal structures; Cyclophosphazene; Macrocyclic ligands

1. Introduction

An interesting group of macrocyclic substituted cyclophosphazenes (ansa and spiro derivatives) has been described recently by Labarre et al. These compounds were obtained by reactions of hexachlorocyclotriphosphazene, $N_3P_3Cl_6$ (**1**) with di- and trioxodiamines [1,2]. In all cases the macrocyclic substituents were grafted onto the NP ring via exocyclic nitrogen atoms. To our knowledge, however, no data have been published with respect to the reactions of **1** or its derivatives with higher oxyethylene glycols. Only diethylene glycol derivatives have been described [3]. It therefore seemed interesting to prepare analogues of the previously described phosphazene containing macrocycles in which the oligoetheric units are linked to phosphorus atoms not via nitrogen but via oxygen atoms. Here we describe the synthesis of macrocyclic derivatives by the reaction of **1** with tetraethylene glycol in the presence of NaH, using THF as a solvent. The formation of a relatively large amount of a 16-membered ansa compound can be explained in terms of the so-called 'template' effect [4]. Due to the macrocyclic effect [4] a significant enhancement of complex forming ability might be anticipated for macrocyclic oligo-oxyethylene cyclophosphazene derivatives in comparison with their previously described acyclic analogs [5].

2. Experimental

All experiments were carried out under a dry atmosphere. $(NPCl_2)_3$ (**1**) (Aldrich Chemie, 99%) was purified by fractional crystallization from hexane. Sodium hydride, 60% dispersion in mineral oil (Aldrich Chemie), was used as received. Tetraethylene glycol (**2**) (Aldrich Chemie, 99%) was dried over molecular sieves 4 Å. Solvents were purified according to conventional methods and dried over CaH_2. Melting points were determined with use of a DuPont 1090 DSC apparatus. The ^1H and proton noise decoupled ^{31}P NMR spectra were recorded on a Varian VXR 300 spectrometer for the solutions of samples in $CDCl_3$ or C_6D_6. The mass spectra were obtained by the field desorption (FD) method at 8–11 eV using a Varian MAT 711 mass spectrometer, or on a Finnigan SSQ-

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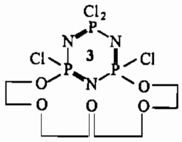
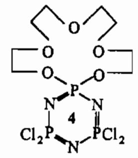
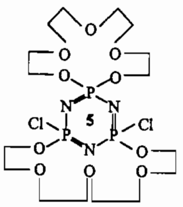
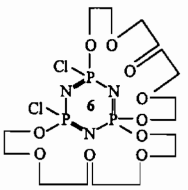
Table 1
Characterization of compounds 3–6

	Analytical data			^{31}P NMR data	
		calc.	found	δ (ppm)	^2J(PP) (Hz)
	H	3.45	3.50	24.3 (PCl_2)	67.0
	C	20.50	20.55	18.0 (PClorg)	
	Cl	30.25	30.05	AB_2-type spectrum	
	M^+	467	467		
	H	3.45	3.30	22.5 (PCl_2)	62.0
	C	20.50	20.40	5.2 ($Porg_2$)	
	Cl	30.25	30.40	A_2B-type spectrum	
	M^+	467	467		
	H	5.45	5.35	23.1 (PClorg)	80.1
	C	32.55	32.45	1.6 ($Porg_2$)	
	Cl	12.00	11.90	A_2B-type spectrum	
	M^+	589	589		
	H	5.45	5.50	23.9 (PClorg)	76.6
	C	32.55	32.60	11.7 ($Porg_2$)	
	Cl	12.00	11.80	A_2B-type spectrum	
	M^+	589	589		

700 quadrupole mass spectrometer by electron ionization and/or chemical ionization (positive and negative) with isobutane matrix. Molecular mass (number average) was determined with a Knauer VP osmometer. Microanalytical data were provided by the Analytical Department of the Technical University of Gdansk (Poland). TLC experiments were performed on Merck precoated silica gel 60 plates. Flash column chromatography was performed on Kieselgel 60ASTM, 100–200 mesh (Merck) with a hexane–THF (2:1) mixture as eluant.

2.1. Synthesis of macrocyclic derivatives

To a solution of 3.48 g (0.01 mol) of **1** and 3.88 g (0.02 mol) of **2** in 300 ml of dried THF 0.04 mol of sodium hydride (60% oil dispersion) was added at 0 °C. The course of the reaction was followed by TLC. The reaction was found to be completed after 1 h. After filtration the solvent was removed in vacuo to give a yellowish oil, which was dissolved in 50 ml of dry benzene. The high-molecular weight material (2.05 g, $M_n = 5800$) was removed by the addition of 50 ml of dry hexane. The fraction soluble in benzene–hexane (3.55 g) was separated by flash column chromatography. The major product appeared to be the mono-ansa derivative $N_3P_3Cl_4[O(CH_2CH_2O)_4]$ (**3**), which could be obtained as colorless crystals after repeated recrystallization from a hexane–THF mixture (0.60 g, 0.0013 mol, 13%, m.p. 85.9 °C, $R_f = 0.29$ (in hexane–THF = 1:1)). The minor separated products were the mono-spiro-$N_3P_3Cl_4[O(CH_2CH_2O)_4]$ (**4**) (0.09 g, 0.0002 mol, 2%; $R_f = 0.42$), spiro-ansa-$N_3P_3Cl_2[O(CH_2CH_2O)_4]_2$ (**5**) (0.03 g, 0.00005 mol, 0.5%; $R_f = 0.22$) and bis-ansa-$N_3P_3Cl_2[O(CH_2CH_2O)_4]_2$ (**6**) (0.32 g, 0.0005 mol, 5%; $R_f = 0.14$) derivatives. Compounds **4**–**6** were obtained as oily products. All compounds were fully characterized by microanalysis, mass (molecular weight) and NMR spectra (Table 1). The structure of **3** was established by an X-ray structure determination.

2.2. Structure determination of 3

Suitable transparent colorless crystals in the shape of blocked plates were obtained by recrystallization from pentane. A crystal of approximate size 0.15×0.37×0.45 mm, cut from a larger single crystal, used for characterization and data collection was glued on top of a glass fiber and transferred into the nitrogen cold stream of the low temperature unit [6] mounted

Table 2
Crystal data and details of the structure determination of 3

Chemical formula	$C_8H_{16}Cl_4N_3O_5P_3$
Molecular weight	468.96
Crystal system	triclinic, $P\bar{1}$
Cell dimensions	
a (Å)	7.797(1)
b (Å)	10.705(1)
c (Å)	12.336(1)
α (°)	88.74(1)
β (°)	72.404(7)
γ (°)	72.15(1)
V (Å^3)	931.4(2)
Z	2
D_{calc} (g cm^{-3})	1.672
$F(000)$, electrons; μ(Mo Kα) (cm^{-1})	476; 9.1
Approx. crystal dimensions (mm)	$0.15 \times 0.37 \times 0.45$
Radiation, wavelength (Å)	Mo K$\bar{\alpha}$, 0.71073
Monochromator	graphite
Temperature (K)	130
θ Range: min., max. (°)	1.74, 26.0
$\omega/2\theta$ Scan (°)	$\Delta\omega = 0.75 + 0.34$ tg θ
Data set	h: $-1 \rightarrow 9$; k: $-12 \rightarrow 13$; l: $-14 \rightarrow 15$
Reference reflections (measured every 3 h)	130, $\bar{1}0\bar{3}$, $\bar{1}0\bar{1}$
Total data	4498
Unique data	3654
Observed data ($I \geqslant 2.5\sigma(I)$)	3434
No. refined parameters	273
$R_F = \Sigma(\|\|F_o\| - \|F_c\|\|)/\Sigma\|F_o\|$	0.034
$wR = [\Sigma(w(\|F_o\| - \|F_c\|)^2)/\Sigma w\|F_o\|^2]^{1/2}$	0.049
Weighting scheme	1
Residual electron density in final difference Fourier map (e Å^{-3})	-0.52, 0.60
Max. (shift/σ) final cycle	0.3773
Average (shift/σ) final cycle	0.0253

on an Enraf-Nonius CAD-4F diffractometer, interfaced to a VAX-11/730 computer. Unit cell parameters were determined from a least-squares treatment of the angular settings of 22 reflections with $12.86 < \theta < 16.88°$. Unit cell parameters were checked for the presence of higher lattice symmetry [7]. The unit cell was identified as triclinic, space group $P\bar{1}$; the E-statistics showed a centrosymmetric space group [8]. Examination of the final atomic coordinates of the structure did not yield extra metric symmetry elements [9,10]. Intensity data were corrected for Lorentz and polarization effects and scale variation, but not for absorption. The structure was solved by Patterson methods and extension of the model was accomplished by direct methods applied to difference structure factors using the program DIRDIF [11]. The positional and anisotropic thermal displacement parameters for the non-hydrogen atoms were refined with block-diagonal least-squares procedures. A subsequent difference Fourier map showed all the hydrogen positions, which were included in the next refinements. Final refinement on F_o was carried out by full-matrix least-squares techniques with anisotropic thermal displacement parameters for the non-hydrogen atoms and isotropic thermal displacement parameters for the hydrogen atoms. Convergence was reached at $R_F = 0.034$ ($wR = 0.049$). Unit weights were used. An overview of the structure determination and refinement is given in Table 2.

Scattering factors were taken from Cromer and Mann [12]; anomalous dispersion factors from Cromer and Liberman [13]. The final fractional atomic coordinates and the equivalent isotropic thermal parameters are given in Table 3. All calculations were carried out on the CDC-Cyber 962-31 computer of the University of Groningen with the program packages XTAL [14], PLATON [15] (calculation of geometric data) and a locally modified version of the program PLUTO [16,17] (preparation of illustrations).

3. Results and discussion

In addition to a large quantity of oligomeric material the reaction of **1** and **2** in the presence of sodium hydride was found to yield both mono-spiro and mono-ansa cyclophosphazenes, the ansa derivative being formed preferentially. The respective bis-cyclo substituted derivatives were also isolated (Table 1). Optimum

Table 3
Final fractional atomic coordinates and equivalent isotropic thermal displacement parameters for non-H atoms with e.s.d.s in parentheses

	x	y	z	U_{eq} [a] (Å^2)
Cl(1)	0.25553(13)	0.33413(9)	0.18273(8)	0.0247(3)
Cl(2)	-0.32496(14)	0.38945(9)	0.39494(8)	0.0279(3)
Cl(3)	-0.16424(17)	0.14458(10)	-0.05313(9)	0.0349(3)
Cl(4)	-0.19644(14)	0.42927(9)	0.01012(8)	0.0248(3)
P(1)	0.16169(12)	0.18316(8)	0.16120(7)	0.0133(2)
P(2)	-0.20653(12)	0.21991(9)	0.29292(7)	0.0149(2)
P(3)	-0.12285(13)	0.24755(9)	0.06284(7)	0.0163(3)
O(1)	0.3440(3)	0.0623(2)	0.1330(2)	0.0173(7)
O(2)	0.3931(3)	-0.1690(2)	0.2546(2)	0.0185(7)
O(3)	0.1535(3)	-0.3074(2)	0.3717(2)	0.0195(7)
O(4)	-0.2534(3)	-0.1419(2)	0.4454(2)	0.0207(8)
O(5)	-0.3078(3)	0.1250(2)	0.3612(2)	0.176(7)
N(1)	0.0121(4)	0.1727(3)	0.2781(2)	0.0161(8)
N(2)	-0.2708(4)	0.2449(3)	0.1824(3)	0.0226(9)
N(3)	0.0946(4)	0.2030(3)	0.0508(2)	0.0202(9)
C(1)	0.4567(5)	0.0318(4)	0.2118(3)	0.0189(10)
C(2)	0.5409(5)	-0.1129(4)	0.2092(3)	0.0199(10)
C(3)	0.4648(5)	-0.3046(3)	0.2694(3)	0.0199(10)
C(4)	0.3145(5)	-0.3687(4)	0.2767(3)	0.0214(11)
C(5)	-0.0025(5)	-0.3527(4)	0.3763(3)	0.0242(11)
C(6)	-0.1734(5)	-0.2731(4)	0.4710(3)	0.0229(11)
C(7)	-0.1552(5)	-0.0537(3)	0.4605(3)	0.0168(10)
C(8)	-0.2832(5)	0.0844(4)	0.4722(3)	0.0154(10)

[a] $U_{eq}=\frac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$.

(no unreacted **1** present) were obtained when the reaction was carried out as described. Reaction mixtures of **1** and **2** in the presence of pyridine (HCl acceptor) still showed, even after prolonged reaction periods, the presence of large quantities of the starting material **1** and only a minor quantity of **3** (^{31}P NMR evidence).

The driving force which induces the formation of macrocyclic products probably results from the operation of the 'template effect', characteristic for the synthesis of macrocycles [4]. This effect arises from the ability of metal cations to coordinate with poly(oxyethylene) units in a specific manner, leading to high regio- and stereospecificity in the succeeding reactions. In the present case the conformation induced due to the 'template effect' in the intermediate formed by the attachment of one end of **2** to **1** via a P–O bond must favor the interaction of the remained hydroxyl function with the second P atom of the same N_3P_3 cycle. The reaction products were separated by column chromatography on Kieselgel 60, a mixture of hexane–THF being used as an eluant. Great losses were observed during the chromatographic procedures, probably due to decomposition reactions. Changing of the column material did not cause significant improvements.

It may be anticipated that these new compounds can serve as novel cyclophosphazene containing macrocycles of crown ether type. Studies on their complex forming ability with respect to various metal and ammonium cations are under way.

3.1. NMR spectroscopic studies

Comparative studies on proton coupled and decoupled ^{31}P NMR spectra, combined with the mass spectral

Table 4
Selected data on the geometry. Standard deviations in the last decimal place are given in parentheses

Interatomic distances (Å)			
Cl(1)–P(1)	2.020(1)	P(1)–N(1)	1.584(3)
Cl(2)–P(2)	2.025(1)	P(1)–N(3)	1.589(3)
Cl(3)–P(3)	1.983(2)	P(2)–N(1)	1.575(3)
Cl(4)–P(3)	2.006(1)	P(2)–N(2)	1.580(4)
P(1)–O(1)	1.552(2)	P(3)–N(2)	1.580(4)
P(2)–O(5)	1.555(2)	P(3)–N(3)	1.575(4)
O(1)–C(1)	1.466(5)	C–C	1.498(7) (mean value)
O(5)–C(8)	1.477(4)		
O–C (remaining)	1.423(2) (mean value)		
Bond angles (°)			
N(1)–P(1)–N(3)	117.8(2)	Cl(1)–P(1)–O(1)	103.1(1)
N(1)–P(2)–N(2)	118.4(2)	Cl(2)–P(2)–O(5)	103.5(1)
N(2)–P(3)–N(3)	119.2(2)	Cl(3)–P(3)–Cl(4)	101.0(2)
P(1)–N(1)–P(2)	120.9(2)		
P(2)–N(2)–P(3)	120.6(2)		
P(1)–N(3)–P(3)	120.3(2)		
P(1)–O(1)–C(1)	120.1(2)	O(3)–C(4)–C(3)	108.7(3)
P(2)–O(5)–C(8)	120.7(2)	O(3)–C(5)–C(6)	108.7(3)
C(2)–O(2)–C(3)	111.9(3)	O(4)–C(6)–C(5)	113.6(3)
C(4)–O(3)–C(5)	111.8(3)	O(4)–C(7)–C(8)	109.2(3)
C(6)–O(4)–C(7)	114.0(3)	O(5)–C(8)–C(7)	110.7(3)
O(1)–C(1)–C(2)	109.3(3)		
O(2)–C(2)–C(1)	109.0(3)		
O(2)–C(3)–C(4)	109.3(3)		

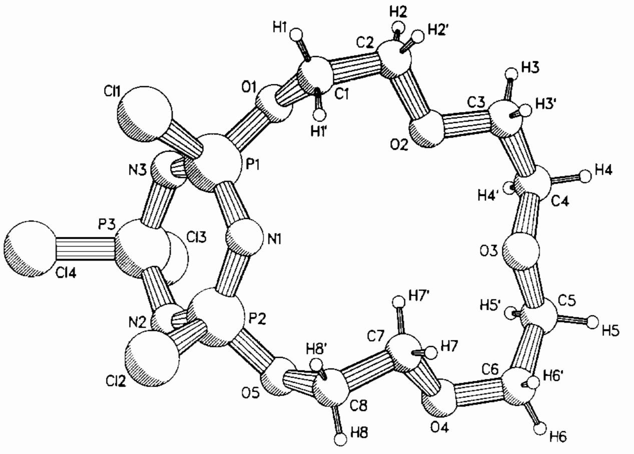


Fig. 1. PLUTO drawing of the molecule of **3** illustrating the puckering and the adopted numbering scheme.

molecular mass determination, appeared to be powerful tools for distinguishing between the spiro and ansa structures of isomers formed via reactions of **1** with various diols and diamines [3,18,19]. In line with its X-ray structure (ansa, see Fig. 1) compound **3** with molecular weight equal to 469 mass units exhibits an AB_2-type $^{31}P\{^1H\}$ spectrum (Table 1). Proton coupling affects only the B_2 part. The spectrum of the other isomer **4** is of the A_2B-type, of which the B part gives further splitting on proton coupling. This clearly points to a spiro structure for **4**, with two PCl_2 groups (A_2) and one $P[O(CH_2CH_2)_4]O$ group (B). From their molecular weights compounds **5** and **6** are disubstituted derivatives, obeying the composition $N_3P_3Cl_2\{[(OCH_2CH_2)_4O]\}_2$. Their ^{31}P NMR spectra are very similar and belong to the A_2B type, in which both the A_2 and B parts are affected by proton coupling. This feature excludes the possibility of a bis-spiro structure for the isomers **5** and **6**, as in that case an AB_2 type spectrum, in which the PCl_2 signals would remain unsplit, could be expected. However an unambiguous assignment of the spiro-ansa or bis-ansa structure remains doubtful. Assuming the same sequence of elution as found for **3** and **4**, which means that under the experimental conditions used a spiro derivative has a higher R_f value than its ansa equivalent, the spiro-ansa structure can be ascribed to isomer **5** and consequently the bis-ansa structure to isomer **6** which has a lower R_f value. Another reason for this assignment may be provided by the fact that the yield of **5** is significantly smaller than that of **6**, similarly to the respective mono-crown derivatives, where the mono-ansa isomer was found to be formed preferentially.

^1H NMR spectra of compounds **3**–**6** showed resonance signals in the region 3.6–3.9 and 4.1–4.4 ppm corresponding to the $-CH_2OP$ and $-CH_2OC$ moieties, respectively. In all cases the integrated intensities were in line with the number of protons.

3.2. Structure of 3

Fig. 1 gives a view of the puckering of the title compound including the adopted numbering scheme. Each asymmetric unit contains one complete molecule with no atom setting at a special position. The triclinic unit cell contains two discrete molecules of the title compound separated by normal van der Waals distances [20].

The inorganic ring is almost planar, the largest deviation from the least-squares plane through P(1), N(1), P(2), N(2), P(3) and N(3) being 0.078(3) Å for P(1). The NP bond lengths are equal within experimental error with a mean value of 1.581(2) Å. The symmetrical conformation of the ring is also reflected by the PNP and NPN bond angles which show no significant deviations from their mean values, 120.6(2) and 118.5(4)°, respectively.

The organic ligand forms together with the atoms P(1), N(1) and P(2) a 16-membered ring with a distorted crown conformation. Roughly the 'crown' ring can be divided into two parts. One part, O(1)P(1)N(1)-P(2)O(5), is stiff as a consequence of the steric constraints caused by the geometry of the NP ring; the remaining part can be considered as more or less flexible. In a least-squares approach the angle between the 6-membered inorganic ring and the 16-membered ring turns out to be 64.01(7)°. This position makes the organic part freely accessible for any complexation reaction especially as the chlorine ligands are directed away from the organic moiety.

4. Supplementary material

Lists of structure factors, anisotropic thermal parameters, bond lengths and angles and an ORTEP plot have been deposited with the Cambridge Crystallographic Data Centre.

Acknowledgments

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