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Cyclophosphazenes tethered together via N-ring centres with *ortho*-, *meta*- and *para*-xylylene linkers

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Abstract

Hexakis (organoamino) cyclotriphosphazenes $(RNH)_6P_3N_3$ {R = *i*-Bu (**1**), R = *i*-Pr (**2**)} react with *ortho*-, *meta*- and *para*-derivatives of α,α′-dibromo xylene in 2:1 ratio to form salts of compositions $[\{(RNH)_6P_3N_3\}_2xyl]Br_2$, {R = *i*-Bu, *o*-xyl (**3**); R = *i*-Pr, *m*-xyl (**4**); R = *i*-Pr, *p*-xyl (**5**)}. These contain dications consisting of two phosphazene rings, which are tethered together via ring N centres by a xylylene unit. X-ray structure analyses show that the substitution pattern at the xylylene bridge controls the orientation and distance between the two tethered phosphazene rings. The solid state structures exhibit dense networks of hydrogen bonds linking dications and anions. Direct N–H···N bonds between dications are observed in the crystal structure of **3**.

Keywords: Polycations; Phosphazene; Crystal structure; Hydrogen bonding

1. Introduction

Several routes have been pursued to link cyclophosphazenes via P-centres using difunctional reagents. The ease of side arm substitution of parent chloro derivatives, such as $P_3N_3Cl_6$, with alcohols and amines offers, in principle, a route towards macromolecular and polymeric species containing several phosphazene rings tethered together by organic linkers via P-centres. However, the *linked* binding mode is unselective and competes with geminal (*spiro*) and non-geminal (*ansa*) substitution modes (Scheme 1) [1]. The poor regio-selectivity of many of these reactions results in indistinct product mixtures. Nonetheless, some reagents featuring short C_2 or C_3 chains between functional sites exclusively form *spiro* products under certain reaction conditions [2]. Hence, appropriate polyfunctional reagents exhibiting short chains between binding sites, such as pentaerythritol (**a**) and spermine (**b**), react selectively to form links between two phosphazene rings via *spiro-linked-spiro* arrangements (Scheme 2) [3].

Recently, we started to explore pathways towards polycationic systems consisting of phosphazene rings tethered together via ring N centres. We found that 1,4-dibromobut-2-ene readily reacts with 2 equiv. of cyclotriphosphazene resulting in bromide salts that contain dications (**c**), in which a butenylene unit links two phosphazene rings via ring N centres [4]. A prerequisite of ring N quaternisation is the presence of electron rich side groups, such as RNH or R_2N, on the neighbouring P centres. Once one ring N site is quaternised, the nucleophilicity of the two vacant N sites is greatly reduced, which provides a highly selective reaction pathway towards linked dimers. Herein, we describe the syntheses of dications featuring *ortho*-, *meta*- and *para*-xylylene linkers between phosphazenes.

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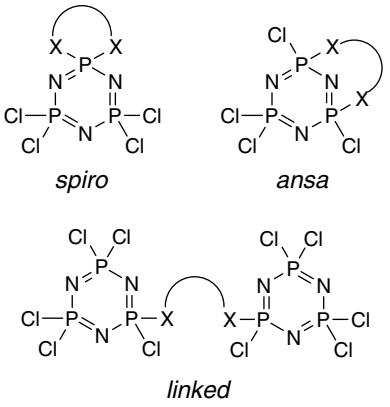
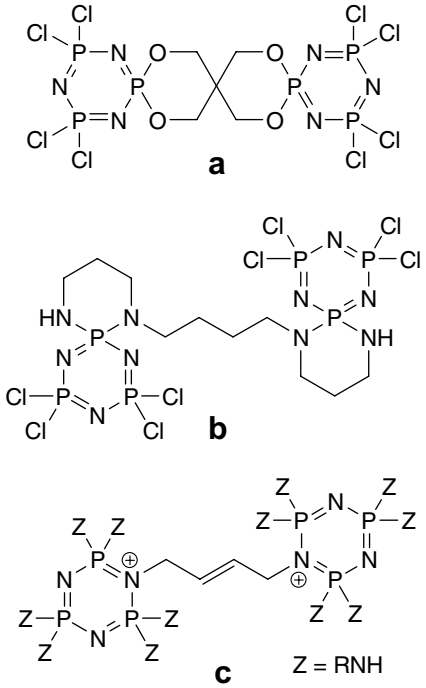


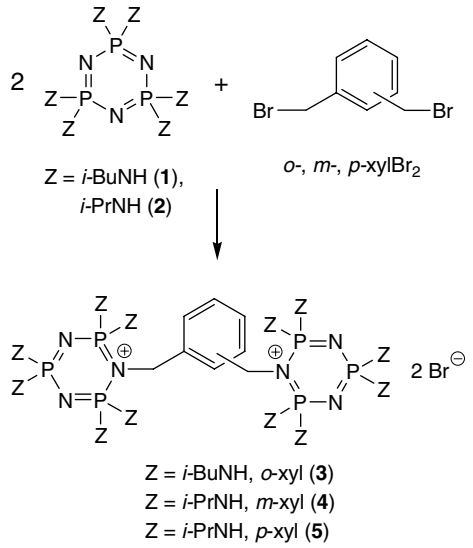
Scheme 1.



Scheme 2.

2. Results and discussion

Refluxing a 2:1 mixture of hexakis (organoamino) cyclotriphosphazene $(RNH)_6P_3N_3$ {R = *i*-Bu (**1**), R = *i*-Pr (**2**)} [5] and α,α′-dibromoxylene in either thf, toluene or chloroform for 24 h leads to exclusive formation of salts $[\{(RNH)_6P_3N_3\}_2xyl]Br_2$ (Scheme 3). The completeness of the reaction is indicated by the sole appearance of an AX_2 signal in the ^{31}P NMR spectra. The following species have been isolated and analysed: $[\{(i\text{-}BuNH)_6P_3N_3\}_2$-*o*-xyl$]Br_2$ (**3**), $[\{(i\text{-}PrNH)_6P_3N_3\}_2m$-xyl$]Br_2$ (**4**) and $[\{(i\text{-}PrNH)_6P_3N_3\}_2p$-xyl$]Br_2$ (**5**). Crystalline products were obtained after evaporation of the solvent and subsequent crystallisation from an appropriate solvent system. X-ray crystal structures were obtained of **3**, **4** · H_2O and **5** · 2 thf. Reactivity studies have shown that the dicationic units



Scheme 3. Syntheses of **3**, **4** and **5**.

in **3**, **4** and **5** are stable to air, water and mineral acids. Treatment with alkali metal hydroxides, however, slowly cleaves off the xylylene linkers resulting in the restoration of **1** and **2**.

The X-ray structures of salts $[\{(RNH)_6P_3N_3\}_2xyl]Br_2$ show that the substitution pattern around the xylylene core controls both the orientation and distance between the two tethered phosphazene rings. Fig. 1 displays the crystal structures of dicationic units of **3**, **4** and **5**. In the *ortho*-derivative **3** both phosphazene rings are forced into close proximity resulting in a coplanar arrangement. Apart from the external *iso*-butyl groups, the dication in **3** is C_2 symmetrical. The distance between the phosphazene ring centroids in **3** is 8.82 Å. The dication of the *meta*-derivative of **4** features crystallographic C_2 symmetry. Both phosphazene rings are oriented in a tilted arrangement with respect to each other; their mean planes intersect at an angle of 54.0°. The two ring centroids in **4** are 9.66 Å apart. The dication of the *para*-derivative **5** shows approximate C_i symmetry. The two phosphazene rings are aligned in parallel; their mean planes are 3.8 Å apart. The distance between ring centroids in **5** measures 10.15 Å.

The phosphazene rings in all three structures are slightly puckered. This could be a consequence of ring N quaternisation, which also affects the bond lengths within the phosphazene rings. The P–N bonds adjacent to the quaternised N centres measure on average 1.69 Å, which is long when compared to the P–N(ring) bond lengths in the parent phosphazenes **1** and **2**, which are in the range of 1.60 Å, [5] but very similar to the P–N bonds in cyclophosphazanes, which are regarded as P–N single bonds [6]. The remaining P–N(ring) bonds are less affected by quaternisation (see Fig. 2) and display bond lengths typical for cyclophosphazenes. The structure representation given in Fig. 2, which contains two P–N single bonds adjacent to the quaternised ring N position and four P–N bonds of ylidic character, suits the bonding scenario more fittingly.

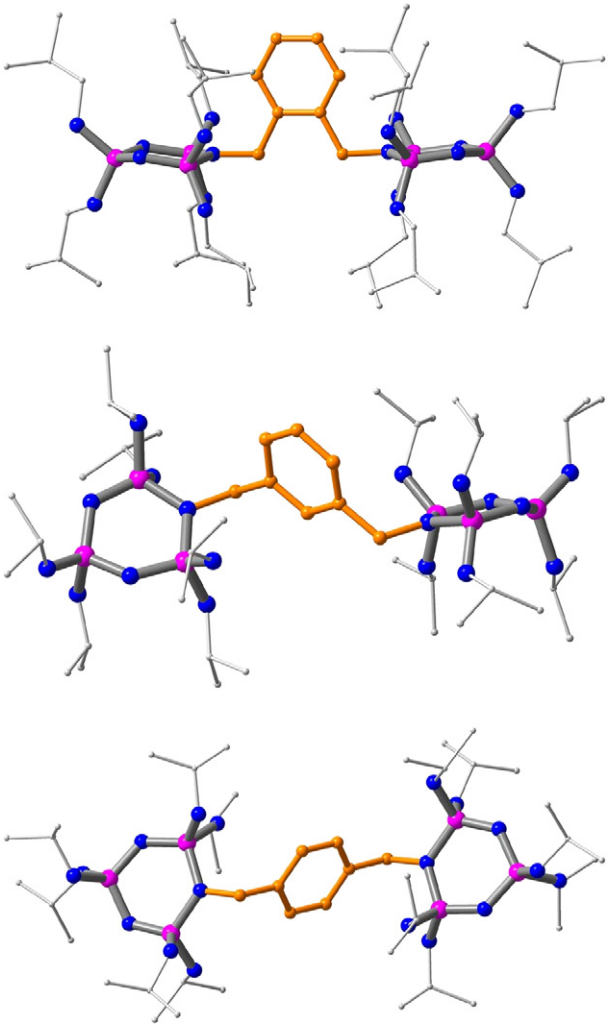


Fig. 1. Crystal structures of dicationic units of **3** (top), **4** (centre) and **5** (bottom). H-atoms are omitted.

All three structures exhibit extensive hydrogen bonding in the solid state owing to the ability of dications to act as both H-donors via 12 amino side groups and H-acceptors via the vacant ring N sites (see Fig. 3). The salt lattices are held together by N–H···Br bonds. In addition, **3** features N–H···N bridges between dications, which is facilitated by the low steric demand of *iso*-butyl groups in **3**

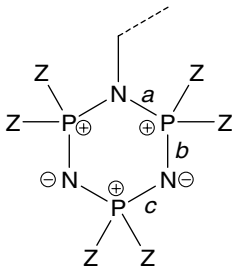


Fig. 2. Representation of quaternised phosphazene rings containing single (*a*) and ylidic (*b* and *c*) P–N bonds. Average P–N(ring) bond lengths from crystal structures of **3**, **4** and **5**: *a*, 1.687; *b*, 1.565; *c*, 1.598 Å.

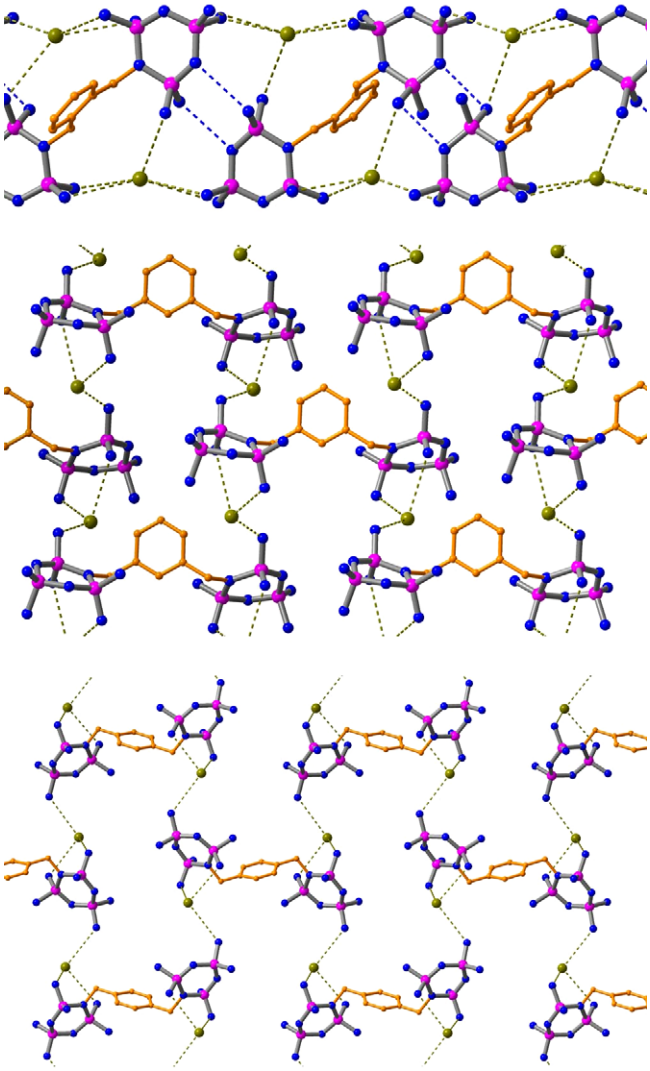


Fig. 3. Supramolecular structures of **3** (top), **4** (centre) and **5** (bottom); H-bonds are drawn as dashed lines; *iso*-propyl and *iso*-butyl groups, water molecules (in **4**) and thf molecules (in **5**) are omitted for clarity.

over the more hindering *iso*-propyl groups in **4** and **5**. The parent phosphazenes also exhibit a strong correlation between the steric demand of side groups and the extensiveness of H-bonding networking [5]. The supramolecular structure of **3** exists as 1D ribbons in the solid state, whereas the networks consisting of dications and bromide anions of **4** and **5** form 2-D sheets. Crystals of **4** contain one molecule of water per formula unit, which is disordered over two positions and connects the above mentioned sheets via N–H···O bonds. There are two molecules of thf in **5** binding to the dication via N–H···O bonds.

3. Conclusion

We have shown that cyclophosphazenes are readily bridged by *ortho*-, *meta*-, and *para*-xylylene units to form dications. We are currently utilising this approach to develop novel polycationic systems based on N-tethered

phosphazenes. There is an on-going search for new and improved materials based on polycations, which find uses in many areas including polyelectrolytes, dendrimers, membranes, ion exchangers and drug delivery [7]. In particular, well-defined macromolecular polycations promise interesting applications as building blocks in nano-structures or as hosts for highly ordered anion arrays.

4. Experimental

All manipulations were carried out in dry nitrogen atmosphere using dry solvents. Precursors **1** and **2** were synthesised as described previously [5]. Dibromo xylenes were employed as purchased. FT-IR spectra were recorded on a Perkin–Elmer Paragon 1000 spectrometer as nujol mull between CsI plates. NMR spectra were recorded on a Bruker AMX 400 Spectrometer [^{1}H NMR (400.13 MHz, TMS), ^{13}C{^{1}H} NMR (100.62 MHz, TMS), ^{31}P{^{1}H} NMR (161.97 MHz, 85%) H_3PO_4(ext.)] operating at 25 °C.

4.1. Synthesis of *3*

One gram (1.76 mmol) of **1** was dissolved in toluene (20 ml). To this 0.23 g (0.88 mmol) of α,α′-dibromo-*o*-xylene was added. The reaction mixture was refluxed for 2 days giving a clear solution. Subsequently, the solvent was removed under vacuum. Colourless crystals were obtained from slow evaporation of a methanol solution. Yield: 0.96 g (0.69 mmol, 78%); m.p.: 217–218 °C. ^{1}H NMR ($CDCl_3$): δ 0.87 (br, 12H, CH_3), 0.96 (m, 24H, CH_3), 1.67 (br, 2H, CH), 1.77 (m, 4H, CH), 2.81 (m, 12H, CH_2), 4.19 (br, 6H, NH), 5.29 (t, 4H, aryl-CH_2, $^3J_{HP} = 14$ Hz), 7.21–7.29 (m, 4H, arylH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 20.5 (CH_3), 30.2 (CH), 43.9 (N^+CH_2), 49.2(CH_2), 124.7, 125.7, 136.7 (aryl); ^{31}P{^{1}H} NMR (thf): δ 15.2 (t), 18.6 (d), $^2J_{PP} = 47$ Hz. IR (nujol): ν (cm^{-1}) 3209, 1689, 1266, 1215, 1091, 1058, 1031, 958, 918, 865, 819, 777, 758, 723. Anal. Calc. for $C_{56}H_{128}N_{18}P_6Br_2$ (1399.40): C, 48.06; H, 9.22; N, 18.02. Found C, 47.24; H, 9.14: N, 17.77%.

4.2. Synthesis of *4*

One gram (2.06 mmol) of **2** was dissolved in thf (20 ml). To this 0.27 g (1.03 mmol) of α,α′-dibromo-*m*-xylene was added. The reaction solution was refluxed for 2 days resulting in a clear solution. Subsequently, the solvent was removed under vacuum. Colourless crystals were obtained by slow evaporation of a methanol solution. Yield: 0.99 g (0.08 mmol, 78%); m.p.: 109–110 °C. ^{1}H NMR ($CDCl_3$): δ 1.11 (m, 72H, CH_3), 2.04 (m, 12H, CH), 3.34 (br, 12H, NH), 4.64 (t, 4H, N^+CH_2, $^3J_{HP} = 11.6$ Hz), 7.25 (s, 2H, Ph), 7.52 (d, Ph), 7.96 (s, arylH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 23.9 (CH_3), 24.6 (CH_3), 42.3 (CH), 43.0 (CH), 47.5 (arylCH_2), 129.1, 133.2, 136.6 (aryl). ^{31}P{^{1}H} NMR (toluene): δ 12.3 (t), 15.7 (d), $^2J_{PP} = 43$ Hz. IR (nujol): ν (cm^{-1}) 3396, 3132, 1772, 1261, 1167, 1040, 913, 867, 806, 738, 680. Anal. Calc. for $C_{44}H_{104}N_{18}P_6Br_2 \cdot H_2O$ (1249.11): C, 42.31; H, 8.55; N, 20.18. Found C, 43.33; H, 8.63; N, 19.88%.

4.3. Synthesis of *5*

One gram (2.06 mmol) of **2** was dissolved in thf (20 ml). To this 0.27 g (1.03 mmol) of α,α′-dibromo-*p*-xylene was added. The reaction mixture was refluxed for 2 days yielding a white precipitate which was filtered and washed with hexane. Colourless crystals were obtained from methanol/thf solution. Yield: 0.95 g (0.77 mmol, 75%); m.p.: 269–271 °C. ^{1}H NMR ($CDCl_3$): δ 1.19 (m, 72H, CH_3), 3.42 (m, 12H, CH), 3.67 (m, 12H, NH), 4.71 (t, 4H, arylCH_2, $^3J_{HP} = 15.88$ Hz), 7.5 (s, 4H, arylH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 24.1 (CH_3), 24.7 (CH_3), 42.4 (CH),

Table 1
Crystallographic data

Compound	**3**	**4** · H_2O	**5** · 2 thf
Chemical formula	$C_{56}H_{128}Br_2N_{18}P_6$	$C_{44}H_{106}Br_2N_{18}OP_6$	$C_{52}H_{120}Br_2N_{18}O_2P_6$
Formula weight	1399.40	1249.11	1375.30
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$	$P2_1$
Unit cell dimensions			
a (Å)	21.634(2)	18.4190(11)	12.2216(7)
b (Å)	18.594(2)	12.9296(7)	17.5188(10)
c (Å)	18.887(2)	28.4439(17)	18.1643(10)
β (°)	98.585(2)	102.6760(10)	106.3850(10)
V (Å^3)	7512.1(14)	6608.8(7)	3731.2(4)
Z	4	4	2
μ (Mo Kα) (cm^{-1})	1.253	1.417	1.262
ρ_{calc} (g cm^{-1})	1.237	1.255	1.224
Reflections, total	38,940	17,020	23,281
Reflections, unique	13,261	5846	13,867
R_{int}	0.062	0.058	0.022
R_1 ($F > 4\sigma(F)$)	0.032	0.064	0.047
wR_2 (all data)	0.069	0.178	0.127

43.2 (CH), 48.4 (arylCH$_2$), 129.1 (aryl). $^{31}P\{^1H\}$ NMR (toluene): δ 8.61 (t), 11.1 (d), $^2J_{PP} = 43$ Hz. IR (nujol): ν (cm^{-1}) 3389, 3106, 1653, 1301, 1273, 1228, 1165, 1138, 1044, 1020, 1005, 908, 870, 848, 824, 764, 730, 617. Anal. Calc. for: $C_{44}H_{104}N_{18}P_6Br_2 \cdot 2$ thf (1375.30): C, 45.13; H, 8.79; N, 18.33. Found C, 44.39; H, 8.91; N, 18.15%.

4.4. Crystallography

Crystallographic data (see Table 1) were recorded on a Bruker Smart Apex diffractometer ($T = 100$ K) using Mo Kα radiation ($\lambda = 0.71073$ Å). Structures were refined by full-matrix least squares against F^2 using all data [8]. Apart from disordered atoms, non-hydrogen atoms were refined anisotropically and hydrogen atoms were fixed geometrically. Disordered groups were split in two positions and refined using similar distance and similar U restraints. Compound **4** contains three disordered *iso*-propyl amino groups and one disordered water molecule. Compound **5** contains two disordered *iso*-propyl groups and one disordered thf molecule. It was also possible to refine the structure of **5** in the higher space group symmetry $P2_1/c$. This refinement, however, showed extensive disorder of *iso*-butyl groups and a high R-value of 13%.

Acknowledgement

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Appendix A. Supplementary material

CCDC 623943, 623944 and 623945 contain the supplementary crystallographic data for **3**, **4** and **5**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.11.052.

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