Structural investigations of phosphorus–nitrogen compounds. 6. Relationships between molecular parameters in per-*X*-substituted bridged spermine derivatives and basicity constants Σ*aR* of substituents

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A systematic study is reported of the products of the nucleophilic substitution reactions of the spermine-bridged cyclotriphosphazene, $[N_3P_3X_4(NHCH_2CH_2CH_2N)CH_2CH_2]_2$ [where X = Cl (2a)], to give a number of new structures [(2b)–(2g)] in which X = OPh, [spiro-O(CH_2)_3O]_{0.5}, Ph, NHPh, NC_4H_8 and NHBu^t, respectively. A comparison has been made between the sum of the substituent basicity constants, $\Sigma\alpha_R$, obtained in nitrobenzene solution, and ten molecular parameters of the N_3P_3 ring (the internal bond angles α, β, γ, δ and θ, and the P—N bond lengths a, b, c, d and e) as well as the difference between the bond lengths a and b, $\Delta(P—N)$. It is found that the systematic change in molecular parameters of compounds (2a)–(2g) is in line with changes in α_R values, indicating the similarity in relative electron-releasing capacity of substituents X in the solid state and in solution. It is also found that the effect on molecular parameters of (2a)–(2g) with two X substituents in PX_2 groups is greater than that for one X substituent in $P(OR)X$ groups in an analogous series of compounds observed previously [Beşli *et al.* (2002). *Acta Cryst.* B**58**, 1067–1073].

1. Introduction

Changes in molecular parameters of a series of compounds {2,6-di-*X*-4,4-diphenyl-2,6-(3,6,9-trioxaundecane-1,11-dioxy)-cyclotriphosphazene, where X = phenoxy (1a), phenoxy (1b), methoxy (1c), anilino (1d), *tert*-butylamino (1e); 7,7′-butane-1,4-diylbis(2,2,2′,2′,4,4,4′,4′-octa-*X*-1,3,5,7,11-pentaaza-2,4,6-triphosphaspiro[5.5]undecane), where X = chloro (2a), phenoxy (2b), kis(3-hydroxypropoxy) (2c), phenyl (2d), anilino (2e), pyridino (2f), *tert*-butylamino (2g)} should reflect changes in electron distribution resulting from different substituents in the molecules. This expectation was confirmed for a series of molecules in which the two non-geminal Cl atoms adjacent to the *cis-ansa* macrocycle in the cyclotriphosphazene $N_3P_3Ph_2[O(CH_2CH_2O)_4]X_2$ (1), X = Cl) were replaced by other groups (X = OCH$_2$CF$_3$, OPh, OMe, NHPh and NHBu^t), see (I); the molecular parameters of (1a)–(1e) were related to the sum of the basicity constants, $\Sigma\alpha_R$, of the substituents (Beşli *et al.*, 2002). The changes in substituent basicity constants, α_R, are indicative of changes in electron distribution (Feakins *et al.*, 1965, 1968; Feakins, Last *et al.*, 1969; Feakins, Shaw *et al.*, 1969), which is also reflected in the changes in molecular parameters. An approximate linear relationship was demonstrated between $\Sigma\alpha_R$ and selected bond lengths and angles of compounds (1a)–(1e) in which the

Table 1
Experimental table.

	(2b)	(2c)	(2d)
Crystal data			
Chemical formula	$C_{58}H_{62}N_{10}O_8P_6$	$C_{22}H_{46}N_{10}O_8P_6$	$C_{64}H_{68}N_{10}P_6$
M_r	1213.00	764.51	1163.10
Cell setting, space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/c$	Monoclinic, $C2/c$
a, b, c (Å)	10.735 (2), 11.067 (3), 14.259 (4)	9.871 (2), 29.741 (6), 11.838 (2)	11.0388 (2), 30.2194 (5), 17.8858 (4)
α, β, γ (°)	75.650 (17), 83.84 (2), 61.096 (19)	90.00, 106.18 (3), 90.00	90.00, 93.0020 (10), 90.00
V (Å^3)	1436.6 (6)	3337.5 (12)	5958.3 (2)
Z	1	4	4
D_x (Mg m^{-3})	1.402	1.521	1.297
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
No. of reflections for cell parameters	22 022	25 012	19 360
θ range (°)	2.9–27.5	1.0–27.5	2.9–27.5
μ (mm^{-1})	0.25	0.38	0.23
Temperature (K)	120 (2)	120 (2)	120 (2)
Crystal form, colour	Plate, colourless	Plate, colourless	Block, colourless
Crystal size (mm)	$0.36 \times 0.20 \times 0.04$	$0.12 \times 0.08 \times 0.03$	$0.10 \times 0.08 \times 0.04$
Data collection			
Diffractometer	Bruker–Nonius KappaCCD area detector	Bruker–Nonius KappaCCD area detector	Bruker–Nonius KappaCCD area detector
Data collection method	φ and ω scans to fill Ewald Sphere	φ and ω scans	φ and ω scans
Absorption correction	Multi-scan (based on symmetry-related measurements)	Multi-scan (based on symmetry-related measurements)	Multi-scan (based on symmetry-related measurements)
T_{min}	0.865	0.956	0.977
T_{max}	0.992	0.989	0.991
No. of measured, independent and observed reflections	24 237, 6569, 5519	25 591, 7080, 3980	34 191, 6809, 5324
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.107	0.125	0.054
θ_{max} (°)	27.5	27.5	27.5
Range of h, k, l	$-13 \Rightarrow h \Rightarrow 13$	$-12 \Rightarrow h \Rightarrow 12$	$-14 \Rightarrow h \Rightarrow 14$
	$-14 \Rightarrow k \Rightarrow 14$	$-38 \Rightarrow k \Rightarrow 38$	$-38 \Rightarrow k \Rightarrow 39$
	$-18 \Rightarrow l \Rightarrow 18$	$-14 \Rightarrow l \Rightarrow 15$	$-22 \Rightarrow l \Rightarrow 23$
Refinement			
Refinement on	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.055, 0.152, 1.07	0.063, 0.154, 0.96	0.042, 0.110, 1.02
No. of reflections	6569	7080	6809
No. of parameters	375	424	366
H-atom treatment	Mixture of independent and constrained refinement	Mixture of independent and constrained refinement	Mixture of independent and constrained refinement
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0477P)^2 + 2.1319P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0701P)^2]$, where $P = (F_o^2 + 2F_2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0529P)^2 + 4.259P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.036	0.012	0.004
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.59, -0.40	0.43, -0.55	0.26, -0.40
Extinction method	None	None	SHELXL
Extinction coefficient	–	–	0.00103 (16)

	(2e)	(2f)	(2g)
Crystal data			
Chemical formula	$C_{58}H_{70}N_{18}OP_6$	$C_{42}H_{54}N_{18}P_6$	$C_{42}H_{102}N_{18}P_6$
M_r	1221.14	996.85	1045.24
Cell setting, space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/c$	Triclinic, $P\bar{1}$
a, b, c (Å)	13.112 (3), 15.160 (3), 17.546 (4)	30.586 (10), 9.660 (2), 18.449 (5)	13.476 (3), 14.437 (3), 16.340 (3)
α, β, γ (°)	81.67 (3), 74.73 (3), 67.08 (3)	90.00, 94.599 (10), 90.00	111.28 (3), 96.87 (3), 93.69 (3)
V (Å^3)	3095.4 (11)	5433 (3)	2921.1 (10)
Z	2	4	2
D_x (Mg m^{-3})	1.310	1.219	1.188
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
No. of reflections for cell parameters	70 927	38 071	68 138
θ range (°)	2.9–27.5	2.9–27.1	2.9–27.5
μ (mm^{-1})	0.23	0.25	0.23
Temperature (K)	150 (2)	120 (2)	150 (2)
Crystal form, colour	Block, colourless	Needle, colourless	Block, colourless
Crystal size (mm)	$0.20 \times 0.20 \times 0.15$	$0.24 \times 0.05 \times 0.03$	$0.28 \times 0.28 \times 0.28$
Data collection			
Diffractometer	Nonius KappaCCD	Bruker–Nonius KappaCCD area detector	Bruker–Nonius KappaCCD area detector

Table 1 (continued)

	(2e)	(2f)	(2g)
Data collection method	φ and ω scans	φ and ω scans	φ and ω scans
Absorption correction	Multi-scan (based on symmetry-related measurements)	Multi-scan (based on symmetry-related measurements)	Multi-scan (based on symmetry-related measurements)
T_{min}	0.789	0.944	0.886
T_{max}	0.975	0.993	0.922
No. of measured, independent and observed reflections	44 336, 13 705, 5294	10 652, 5213, 2316	47 815, 10 292, 7658
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.187	0.129	0.071
θ_{max} (°)	27.5	25.0	25.0
Range of h, k, l	$-17 \Rightarrow h \Rightarrow 17$	$-36 \Rightarrow h \Rightarrow 35$	$-16 \Rightarrow h \Rightarrow 16$
	$-19 \Rightarrow k \Rightarrow 19$	$-9 \Rightarrow k \Rightarrow 9$	$-17 \Rightarrow k \Rightarrow 17$
	$-22 \Rightarrow l \Rightarrow 22$	$-20 \Rightarrow l \Rightarrow 21$	$-19 \Rightarrow l \Rightarrow 19$
Refinement			
Refinement on	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.066, 0.168, 0.93	0.117, 0.277, 1.10	0.041, 0.110, 1.02
No. of reflections	13 705	5213	10 292
No. of parameters	797	595	659
H-atom treatment	Mixture of independent and constrained refinement	Mixture of independent and constrained refinement	Mixture of independent and constrained refinement
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0561P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0439P)^2 + 22.223P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_2) + (0.0585P)^2 + 0.4011P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.012	0.254	0.003
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.68, -0.36	0.35, -0.27	0.28, -0.37
Extinction method	None	None	None

Computer programs used: *DENZO* (Otwinowski & Minor, 1997), *COLLECT* (Hooft, 1998), *SHELXS*97 (Sheldrick, 1997), *SHELXL*97 (Sheldrick, 1997), *PLATON* (Spek, 1990).

substituent X varies in the moiety $PX(Om)$ (m = macrocycle; Beşli *et al.*, 2002, Part 5 of the series).

In the present study we report on changes in analogous molecular parameters in the series of tetra-substituted spermine-bridged cyclotriphosphazenes [N$_3$P$_3$X$_4$(NHCH$_2$CH$_2$-CH$_2$N)CH$_2$CH$_2$]$_2$, (2) {where X = Cl, OPh, [spiro-O(CH$_2$)$_3$O]$_{0.5}$, Ph, NHPh, pyr (pyrrolidino) and NHBu^t for (2a)–(2g) respectively}, see (I). For (2a)–(2g) the X substituent varies for the moiety PX_2, where two geminal substituents are replaced on one P atom, compared with the replacement of one X substituent on one P atom in (1a)–(1e).
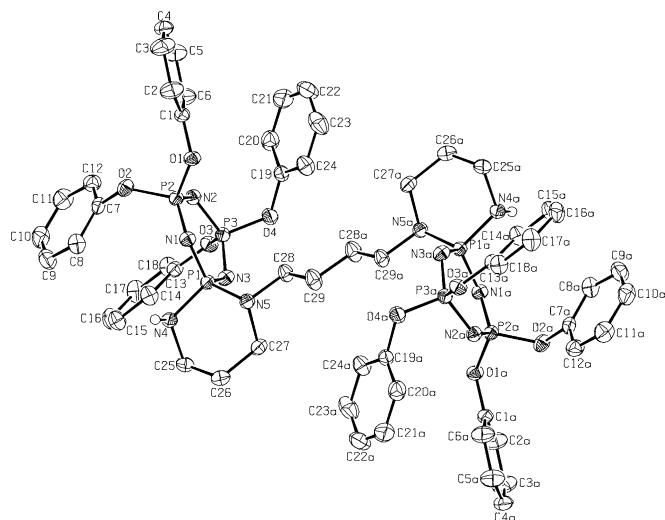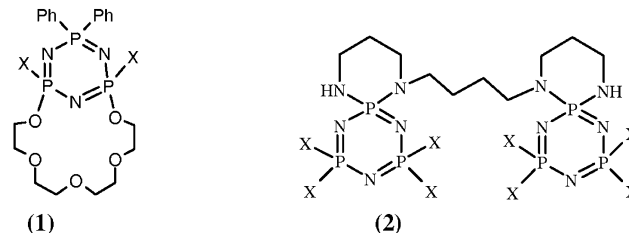

	X		X
(1a)	Cl	**(2a)**	Cl
(1b)	OPh	**(2b)**	OPh
(1c)	OMe	**(2c)**	O(CH$_2$)$_3$O
(1d)	NHPh	**(2d)**	Ph
(1e)	NHBu^t	**(2e)**	NHPh
		(2f)	NC$_4$H$_4$ (pyr)
		(2g)	NHBu^t

Figure 1
The molecular structure of (2b).

2. Experimental

2.1. Preparation of compounds

Compounds (2b), (2c), (2e) and (2f) were synthesized by reaction of the known compound (2a) (Labarre *et al.*, 1984) with an excess of the appropriate nucleophile (phenol, 1,3-propanediol, aniline and pyrrolidine, respectively), whereas
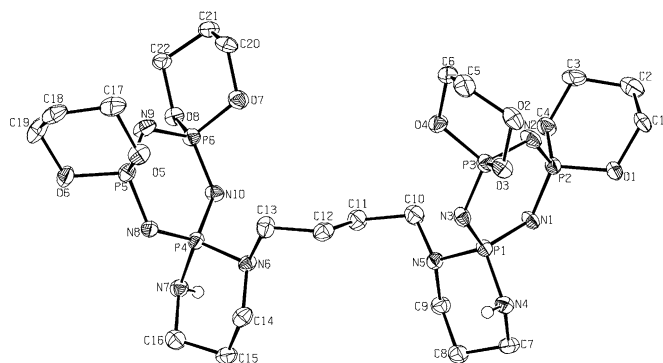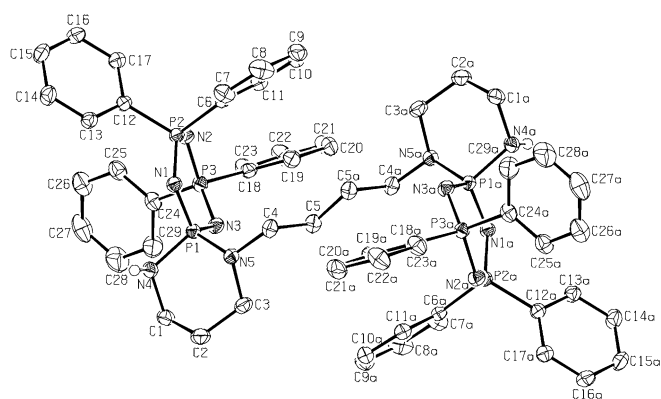
Figure 2
The molecular structure of (2c).

Figure 3
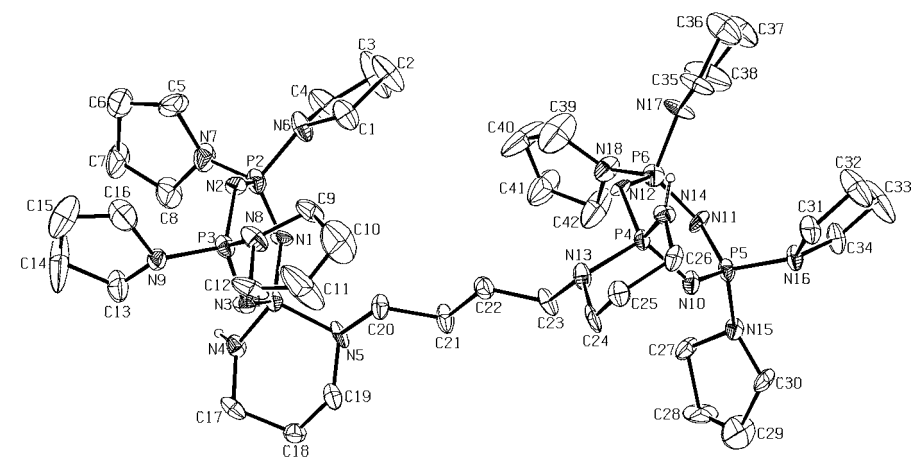The molecular structure of (2d) with the benzene solvate molecule removed for clarity.

Figure 4
The molecular structure of compound (2e) with water molecules omitted for clarity.

(2d) and (2g) were synthesized by reaction of spermine with the known di-gem, tetra-substituted cyclophosphazene precursors 2,2-dichloro-4,4,6,6-tetraphenylcyclotriphosphazene (Acock et al., 1964) and 2,2-dichloro-4,4,6,6-tetra-tert-butylaminocyclotriphosphazene (Das et al., 1965). Full details of the synthetic procedures for (2b)–(2g) are being reported elsewhere (Yenilmez-Çiftçi, 2004).

2.2. Crystallography

Data were collected at 120 K on an Nonius KappaCCD area-detector diffractometer located at the window of a Nonius FR591 rotating anode X-ray generator, equipped with a molybdenum target [λ(Mo $K\alpha$) = 0.71073 Å]. Structures were solved and refined using the SHELX97 (Sheldrick, 1997) suite of programs. Data were corrected for absorption effects by comparing equivalent reflections using the program SORTAV (Blessing, 1997). Non-H atoms were refined aniso-tropically, whilst H atoms were generally fixed in idealized positions (with the exception of some N—H protons, whose positions were determined from a difference map) with their displacement parameters riding on the values of their parent atoms. The structure of (2e) contains a disordered water molecule split over two sites, neither of which could be assigned reliably with H atoms, and the structure of compound (2d) contains a benzene solvate molecule. There are a number of potentially serious validation errors, mainly for structures (2c), (2e) and (2f), which are discussed below:

(i) The crystal of (2c) used in the experiment was a small platelet of the dimensions 0.12 × 0.08 × 0.03 mm, which diffracted weakly and only achieved a data completeness of 93%, despite 40 second exposure times for each image.

(ii) The amido H atoms on atoms N4 and N13 of (2e) were somewhat poorly defined in the difference map and had to be restrained in the model to conform to a regular geometry.

(iii) The crystal quality of (2f) was extremely poor (fibrous needle 0.24 × 0.05 × 0.03 mm), resulting in a weak diffraction pattern that did not extend to high angles and could only produce a very limited dataset. The structure derived for (2f) from this data is somewhat poor, however, the core N_3P_3 rings and areas of interest in the molecular structure are defined reasonably well and the structure is considered to be pertinent and important to this study and is therefore included. Pertinent data collection and refinement parameters are collated in Table 1.[1] The data for (2a) were extracted from the Cambridge Structural Database (Allen et al., 1983) as a CIF, with the refcode COPTUW (Labarre et al., 1984).

3. Results

3.1. Molecular structures

Displacement ellipsoid plots for (2b)–(2g) [see (I)] are shown in Figs. 1–6, respectively. The common factors between all seven molecular systems are the facts that the halves of the bridged molecule have the same substitution pattern in each N_3P_3 ring, and that one P atom in

Table 2
Parameters of the molecular frameworks of (2a)–(2g) defined in Fig. 8.

$\Sigma\alpha_R$ = sum of substituent basicity constants; $\Delta(P{-}N) = a - b$; $\Sigma NHsp$ and $\Sigma NCsp$ are the sums of three internal bond angles for the N atoms of NHsp and NCsp, respectively. The spiro ring puckering amplitude is derived by standard methods (Cremer & Pople, 1975). Conformation corresponds to the syn or anti conformation of the cyclophosphazene rings about the $NCH_2CH_2CH_2CH_2N$ bridge. Values of molecular parameters for (2a) are taken from Labarre et al. (1984).

	(2a)	(2b)	(2c)	(2d)	(2e)	(2f)	(2g)
X	Cl	OPh	$O(CH_2)_3O$	Ph	NHPh	NC_4H_8	$NHBu^t$
$\Sigma\alpha_R$	0	12.4	15	16.8	17.6	23.6	23.6
α	112.98 (2)	116.1 (1)	116.3 (1)	116.2 (1)	116.2 (2)	118.3 (4)	117.5 (1)
β	123.14 (2)	122.0 (1)	122.3 (2)	120.4 (1)	122.3 (1))	121.5 (4)	121.6 (1)
γ	120.49 (2)	118.1 (1)	118.6 (1)	117.0 (1)	117.8 (1)	117.1 (3)	115.9 (1)
δ	119.24 (2)	121.3 (1)	121.4 (1)	120.7 (1)	121.0 (2)	122.1 (5)	123.2 (1)
θ	104.49 (4)	105.1 (1)	105.0 (1)	103.4 (1)	101.8 (2)	101.6 (4)	101.6 (6)
a	1.613 (1)	1.612 (1)	1.610 (2)	1.600 (1)	1.596 (3)	1.594 (5)	1.589 (1)
b	1.562 (2)	1.580 (1)	1.571 (2)	1.603 (1)	1.597 (2)	1.597 (5)	1.597 (1)
c	1.575 (1)	1.590 (1)	1.583 (2)	1.597 (1)	1.592 (3)	1.593 (5)	1.599 (1)
d	1.635 (2)	1.660 (2)	1.637 (3)	1.653 (2)	1.656 (4)	1.670 (6)	1.660 (1)
e	1.631 (1)	1.674 (2)	1.674 (2)	1.665 (2)	1.664 (3)	1.670 (7)	1.686 (1)
$\Delta(P{-}N)$	0.051	0.032	0.039	−0.003	−0.001	−0.003	−0.008
$\Sigma NHsp$	360.0 (2)	336.2 (3)	340.8 (3)	335.4 (2)		360.0 (1)	335.0 (2)
$\Sigma NCsp$	354.59 (7)	336.8 (3)	342.1 (3)	349.6 (2)	340.1 (6)	338.2 (1)	340.4 (4)
Pucker	0.505	0.5646	0.5303	0.5551	0.5715	0.5688	0.5303
amplitude, Q			0.5403		0.5891	0.5793	0.5766
Conformation	anti	anti	syn	anti	anti	syn	anti

each N_3P_3 ring has a common pair of substituents consisting of a six-membered spiro ring with one primary and one secondary N atom joined at one end by the P atom and linked at the other by a trimethylene chain, $CH_2CH_2CH_2$. These spiro rings all adopt a chair configuration. The other two P atoms in (2a)–(2g) have the same substituents (X_2) on each P atom in each N_3P_3 ring, in which X differs from compound to compound. The bridging moiety consists of a five-bond chain, $NCH_2CH_2CH_2CH_2N$, about which rotation can occur and giving, in principle, a range of conformations for the two cyclophosphazene rings with respect to each other. In practice it is found that the two substituted cyclophosphazene rings take up either syn or anti conformations; (2a), (2b), (2d), (2e) and (2g) adopt an anti conformation, whilst (2c) and (2f) are present as syn conformers. In (2b) two non-geminal OPh (O2 and O3) groups adopt a conformation above the N_3P_3 ring, making them almost parallel. However, with a centroid separation of approximately 4.2 Å this is most likely to be a packing effect. In the anti structures (2a) and (2b) the two N_3P_3 rings are in almost parallel planes, whilst in the syn structures (2c) and (2f) the two N_3P_3 rings are slightly tilted

towards each other. The tetramethylene chain, $CH_2CH_2CH_2CH_2$, bridging the two cyclophosphazene rings exhibits a near zigzag structure in all compounds, except in the syn conformer (2c), where it is rather distorted. The structures of partially substituted spermine-bridged derivatives have been reported previously: whilst those with Ph groups mirrored the anti conformation of its per-substituted derivative (2d) (Coles et al., 2001), interestingly those with spiro-$[O(CH_2)_3O]$ [where spiro = $-NH(CH_2)_3N(CH_2)_4$-$N(CH_2)_3HN-$] and $NHBu^t$ substituents (Beşli et al., 2003) had the opposite conformation from those of their per-derivatives [(2c), syn] and $NHBu^t$ [(2g), anti], respectively. From Table 2 one can see that these compounds exhibit both syn and anti conformations. Further work to rationalize this observation is currently in progress.

3.2. Crystal structures

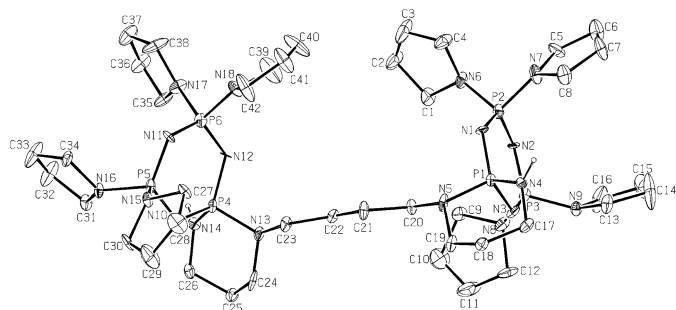The hydrogen-bonding schemes for (2a)–(2g) are summarized in Fig. 7. In (2a) and (2c) the N−H of the spiro group

Figure 5
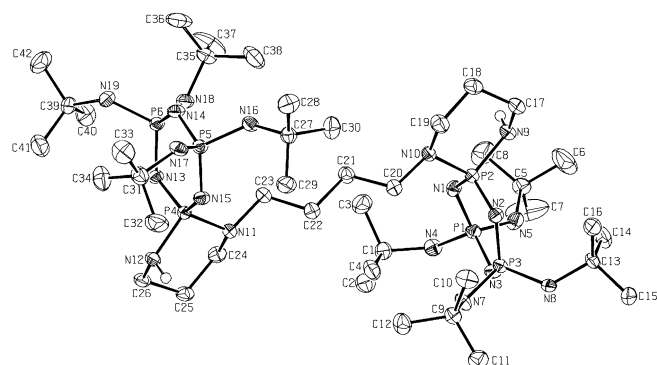The molecular structure of compound (2f). Ellipsoids are displayed at 20% probability for clarity.

Figure 6
The molecular structure of (2g).

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Table 3
Comparison of the difference (Δ) in the molecular framework parameters of (2g) and (2a) with those for (1e) and (1a).

	Δ(2g)–(2a)	Δ(1e)–(1a)
Moiety	PX_2	P(Om)X
$\Sigma\alpha_R$	23.6	9.8
α	4.52	3.0
β	−1.54	−0.7
γ	−4.59	−3.2
δ	3.96	3.8
θ	−2.89	−3.7
a	−0.024	−0.011
b	0.035	0.026
c	0.024	0.015
d	0.025	0.028
Δ(P—N)	−0.059	−0.037

Molecular framework parameters are defined in Fig. 8 and in the footnote to Table 2. Values of molecular parameters for (1a) and (1e) taken from (Beşli et al., 2002).

bonds to a ring N atom in another molecule. This occurs in both halves of the molecule and leads to infinite ladders linked by single hydrogen bonds, where the rungs are the tetra-methylene chains, $CH_2CH_2CH_2CH_2$. In (2b) and (2d) the N—H of the spiro group bonds to a ring N atom in another molecule. In this case, however, the two molecules form eight-membered hydrogen-bonded rings. Again leading through the other half of the molecule to infinite chains, which are held by two hydrogen bonds, in this case there is no ladder arrangement as both hydrogen bonds are involved in the eight-membered rings. The hydrogen bonding in (2e) is complex, involving mainly the N—H parts of the NHPh groups. The strongest of these interactions are two N—H···N bonds with a phosphazene ring N atom, which forms a zigzag chain. This chain then interacts through close contacts and weaker hydrogen bonds with other chains and the water molecules to form a sheet-like structure. In (2f) the situation is also complicated. Two molecules bind together as head-to-tail dimers through hydrogen bonding (C18···N12 and C25···N1). This association facilitates N—H···N interactions, where the N13—H of the spiro group of one molecule (A) bonds intramolecularly to the secondary N atom (N4) of the spiro group of another molecule (B). This other molecule (B)
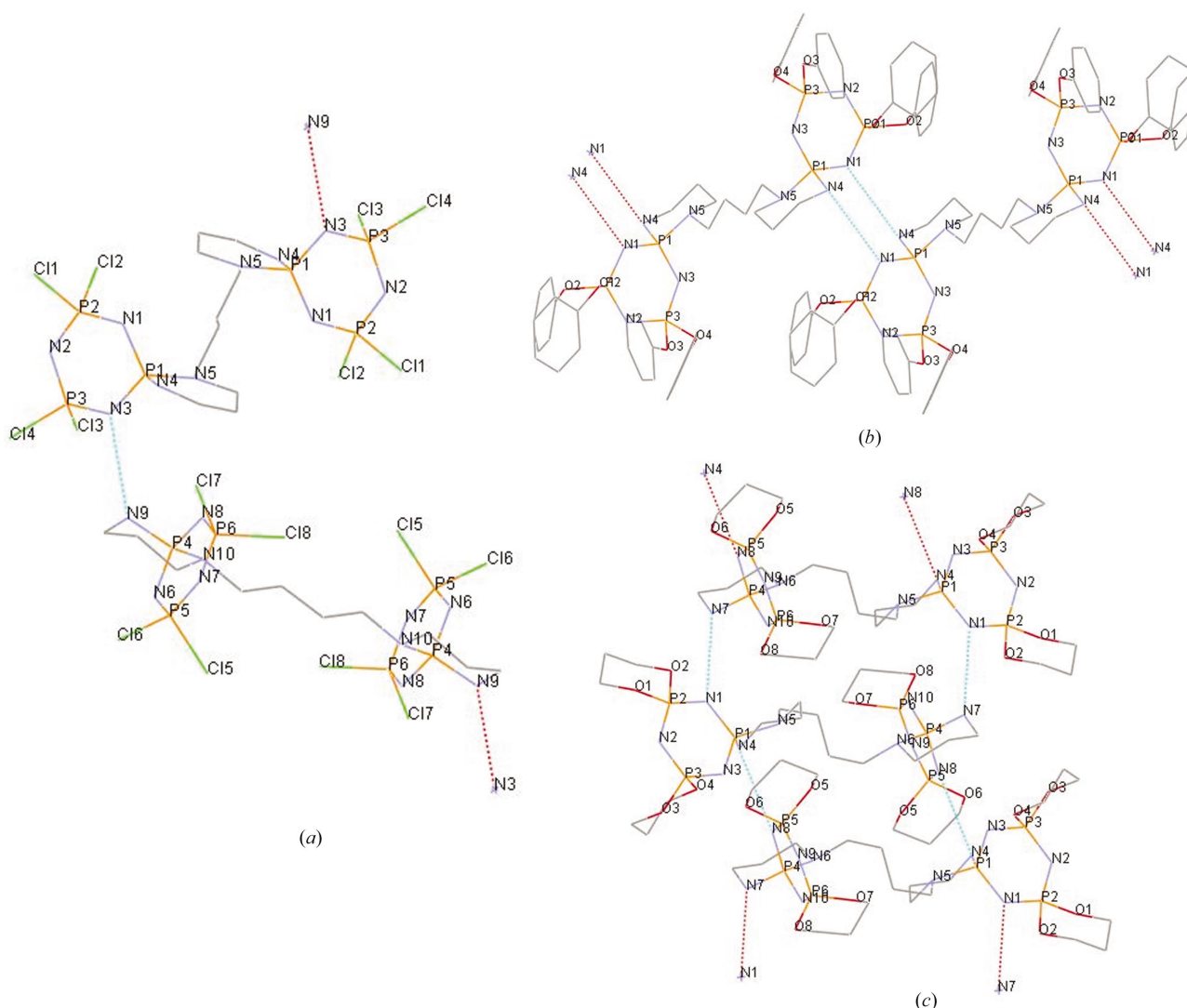

Figure 7
Hydrogen-bonding schemes for (2a)–(2g).

in turn forms a bifurcated hydrogen bond from N14*B* to a ring N atom, N1 in molecule *A*, as well as to the secondary N atom (N5) of the spiro group of molecule *A*. In (2*g*) there are again eight-membered hydrogen-bonded rings, which differ from those in (2*b*) and (2*c*) in that the N—H of the spiro group does not bond to a ring N atom in another molecule, but to the secondary N atom of the spiro group forming an infinite zigzag structure. Interestingly, the N—H of the NHBu^t groups in (2*g*) do not form any significant hydrogen bonds.

4. Discussion

Early crystallographic studies have provided evidence that cyclotriphosphazenes carrying two or more different substituents show significant differences in bond lengths (Mani *et al.*, 1965, 1966; Allen *et al.*, 1969; Ahmed & Pollard, 1972; Ahmed & Gabe, 1975; Ahmed & Fortier, 1980) and later studies revealed trends in both bond lengths and angles, which could

be related to a variety of different physical and chemical properties (Contractor *et al.*, 1985; Fincham *et al.*, 1986; Alkubaisi *et al.*, 1988). It is known that substituent basicity constants give a reliable indication of the relative electron-releasing capacity of different substituent *X* groups (Feakins *et al.*, 1965; Feakins, Last *et al.*, 1969; Feakins, Shaw *et al.*, 1969) and it was found that changes in bond lengths and angles of the series of cyclophosphazene derivatives (1*a*)–(1*e*) varied with the sum of the substituent basicity constants $\Sigma\alpha_R$ (Beşli *et al.*, 2002). A similar analysis is made for (2*b*)–(2*g*) in this work and the results are compared with those for (2*a*) (Labarre *et al.*, 1984).

The structural parameters considered for (2*a*)–(2*g*) are the bond lengths (*a*, *b*, *c*, *d* and *e*) and angles (α, β, γ, δ and θ), which are defined in the generalized structure for (2) shown in Fig. 8. The structural data for (2*a*)–(2*g*) summarized in Table 2 show a small, but moderately consistent, trend of bond lengths and angles in the series of molecules which reflects the elec-
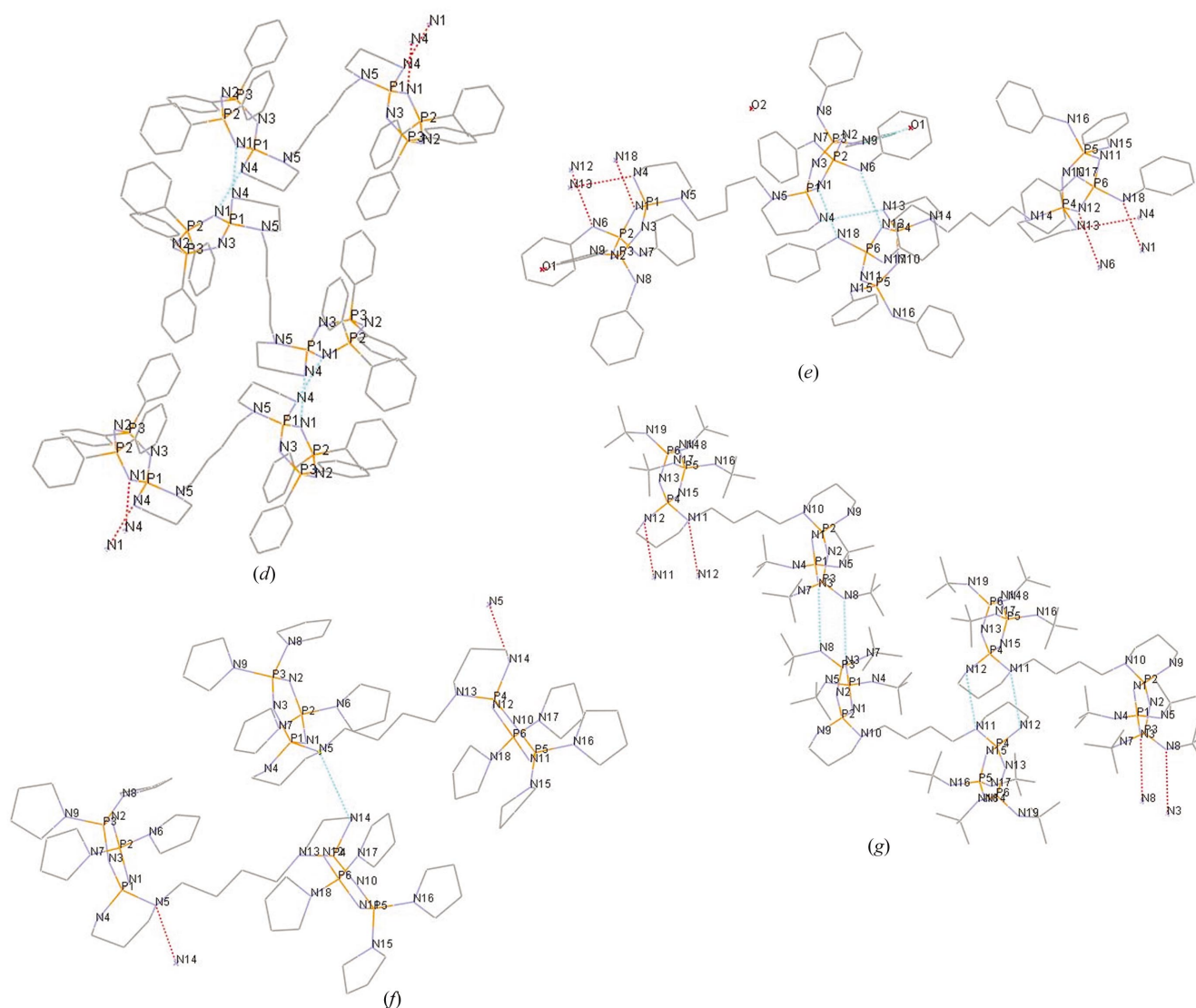

Figure 7 (continued)

tron-releasing capacity of the substituents X = Cl, OPh, [spiro-O(CH$_2$)$_3$O]$_{0.5}$, Ph, NHPh, pyr and NHBu^t. The values of the sum of the substituent basicity constants, $\Sigma\alpha_R$, for (2a)–(2g) are also summarized in Table 2. In general it is found that, with the increasing value of $\Sigma\alpha_R$, the bond angles α and δ increase, whilst those for β, γ and θ decrease; concomitantly, the bond length a decreases, whilst b, c, d and e increase. Although the present structural data refer to molecules in their unperturbed ground state in the crystalline solid and the basicity measurements were made in nitrobenzene solution (Feakins *et al.*, 1965, 1968; Feakins, Last *et al.*, 1969; Feakins, Shaw *et al.*, 1969), where the molecule is perturbed by the approach of a proton (Koppel *et al.*, 2001), there is a definite relationship between the molecular parameters of (2a)–(2g) and the substituent basicity constant, analogous to the effects observed previously (Beşli *et al.*, 2002). Other molecular parameters, such as Δ(P—N) values and the sum of the bond angles $\Sigma NHsp$ and $\Sigma NCsp$ in the series of molecules (2a)–(2g), also decrease as $\Sigma\alpha_R$ increases, indicating a similar trend in increasing electron density provided by the X substituents, from X = Cl through to X = NHBu^t.

The results on the variation of molecular parameters with two substituents in PX_2 groups in (2a)–(2g) can be compared with previous work (Beşli *et al.*, 2002) on the variation of molecular parameters with one substituent X in PX(Om) groups of (1) (Fig. 8). The difference in molecular parameters of (2g), X = NHBu^t, $\Sigma\alpha_R$ = 23.6, and (2a), X = Cl, $\Sigma\alpha_R$ = 0, is summarized in Table 3, together with the values for the analogous compounds (1). It can be seen that for each parameter the sign of the difference is the same in the two series, but the magnitude of the change is greater for (2) than for (1). Given the changes in the basic molecular structure in which a PPh$_2$ moiety in (1) is replaced by a nitrogenous spiro group compound (2) and the presence of the macrocyclic ring in (1), these results are consistent with a larger change in molecular parameters in those of (2) with two substituents in PX_2 groups compared with those of (1) having one substituent X in P(OR)X groups.

We have also compared the values of the difference in bond lengths, Δ(P—N), resulting from substitution in the cyclo-phosphazene ring (Beşli *et al.*, 2002). The choice of the two bond lengths which are subtracted from each other is somewhat arbitrary (other than being adjacent P—N bonds), but Δ(P—N) must be consistent for the set of compounds discussed and compared. In the present context, Δ(P—N) is taken as bond lengths a–b, as defined in Fig. 8. Again, it is shown in Table 3 that there is a greater change in Δ(P—N) for (2) with two X substituents per P atom compared with those of (1) having one substituent X.

5. Conclusions

Structural investigations of the molecular framework [bond angles α, β, γ, δ and θ, and bond lengths a, b, c, d and e, as well as Δ(P—N) values] of (2a)–(2g) have revealed a fairly consistent trend of changes in molecular parameter, which mirror the electron release of the substituents X, as measured by basicity measurements in nitrobenzene solution. The changes in molecular parameters reported here for two di-geminal substituted X_2 groups (*i.e.* four substituents) are approximately twice those observed in an earlier study, where two non-geminal substituents X (*i.e.* two substituents) were varied. Ellipsoids are displayed at the 50% level in this and the following five figures, except where noted.

References

Acock, K. G., Shaw, R. A. & Wells, F. B. G. (1964). *J. Chem. Soc.* pp. 121–130.
Ahmed, F. R. & Fortier, S. (1980). *Acta Cryst.* B**36**, 1456–1461.
Ahmed, F. R. & Gabe, E. J. (1975). *Acta Cryst.* B**31**, 1028–1031.
Ahmed, F. R. & Pollard, D. R. (1972). *Acta Cryst.* B**28**, 513–517.
Alkubaisi, A. H., Hursthouse, M. B., Shaw, L. S. & Shaw R. A. (1988). *Acta Cryst.* B**44**, 16–22.
Allen, C. W., Faught, J. B., Moeller, T. & Paul, I. C (1969). *Inorg. Chem.* **8**, 1719–1727.
Allen, F. H., Kennard, O. & Taylor, R. (1983). *Acc. Chem. Res.* **16**, 146–153.
Beşli, S., Coles, S. J., Davies, D. B., Eaton, R. J., Hursthouse, M. B., Kılıç, A., Shaw, R. A., Çiftçi, G. Y. & Yeşilot, S. (2003). *J. Am. Chem. Soc.* **125**, 4943–4950.
Beşli, S., Coles, S. J., Davies, D. B., Hursthouse, M. B., Kılıç, A., Mayer, T. A. & Shaw, R. A. (2002). *Acta Cryst.* B**58**, 1067–1073.
Blessing, R. H. (1997). *J. Appl. Cryst.* **30**, 421–426.
Coles, S. J., Davies, D. B., Eaton, R. J., Hursthouse, M. B., Kılıç, A., Mayer, T. A., Shaw, R. A. & Çiftçi, G. Y. (2001). *J. Chem. Soc. Dalton Trans.* pp. 365–370.
Contractor, S. R., Hursthouse, M. B., Shaw, L. S., Shaw, R. A. & Yılmaz, H. (1985). *Acta Cryst.* B**41**, 122–131.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Das, S. K., Keat, R., Shaw, R. A. & Smith, B. C. (1965). *J. Chem. Soc.* pp. 5032–5036.
Feakins, D., Last, W. A., Neemuchwala, N. & Shaw, R. A. (1965). *J. Chem. Soc.* pp. 2804–2811.
Feakins, D., Last, W. A., Nabi, S. N., Shaw, R. A. & Watson, P. (1969). *J. Chem. Soc. A*, pp. 196–202.
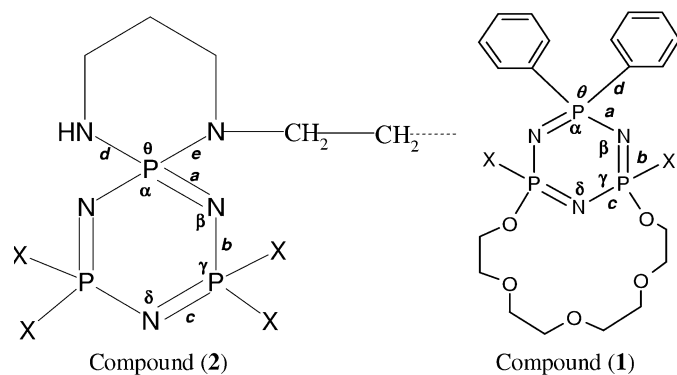
Figure 8
Generalized schemes for the definition of the molecular-framework parameters of (2a)−(2g) studied in this work and comparison with previous work on (1) (Beşli *et al.*, 2002).

Feakins, D., Nabi, S. N., Shaw, R. A. & Watson, P. (1968). *J. Chem. Soc. A*, pp. 10–15.

Feakins, D., Shaw, R. A., Watson, P. & Nabi, S. N. (1969). *J. Chem. Soc. A*, pp. 2468–2475.

Fincham, J. K., Hursthouse, M. B., Parkes, H. G., Shaw, L. S. & Shaw, R. A. (1986). *Acta Cryst.* B**42**, 462–472.

Hooft, R. (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.

Koppel, I. A., Schwesinger, R., Breuer, T., Burk, P., Herodes, K., Koppel, I., Leito, I. & Mishima, M. (2001). *J. Phys. Chem. A*, **105**, 9575–9586.

Labarre, J. F., Guerch, G., Sournies, F., Lahana, R., Enjalbert, R. & Galy, J. (1984). *J. Mol. Struct.* **116**, 75–88.

Mani, N. V., Ahmed, F. R. & Barnes, W. H. (1965). *Acta Cryst.* **19**, 693–697.

Mani, N. V., Ahmed, F. R. & Barnes, W. H. (1966). *Acta Cryst.* **21**, 375–382.

Otwinowski, Z. & Minor, W. (1997). *Methods Enzymol.* **276**, 307–326.

Sheldrick, G. M. (1997). *SHELX*97. University of Göttingen, Germany.

Spek, A. L. (1990). *Acta Cryst.* A**46**, C34.

Yenilmez-Çiftçi, G. (2004). In the press.