Structural investigations of phosphorus–nitrogen compounds. 5. Relationships between molecular parameters of 2,2-diphenyl-4,6-*cis*-oxytetra(ethyleneoxy)-4,6-R_2-cyclotriphosphazatrienes (R = Cl, OCH$_2$CF$_3$, OPh, OMe, NHPh, NHBu^t) and substituent basicity constants[1]

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A systematic study of the products of nucleophilic substitution reactions of *cis-ansa* N$_3$P$_3$Ph$_2$[O(CH$_2$CH$_2$O)$_4$]Cl$_2$ (3) is reported. These reactions give a number of new structures with the general formula N$_3$P$_3$Ph$_2$[O(CH$_2$CH$_2$O)$_4$]R_2 [where R = OCH$_2$CF$_3$ (4), OPh (5), OMe (6), NHPh (7·H$_2$O), NHBu^t (8)]. A comparison has been made between the sum of the substituent basicity constants, $\sum \alpha_R$, that are obtained in nitrobenzene solution and eight molecular parameters of the N$_3$P$_3$ ring [the P—N bond lengths a, b, c; the internal bond angles α, β, γ, δ; and the difference between the bond lengths a and b, Δ(P—N)]. It is found that the systematic changes in the molecular parameters of (3)–(8) are in line with changes in α_R values. This result implies the similarity in relative electron-releasing capacity of substituents R in the solid state and in solution.

1. Introduction

Macrocyclic phosphazenes have aroused a good deal of interest recently, partly on account of their applications in supramolecular chemistry (Brandt, Porwolik *et al.*, 1997) and partly because they have been used to demonstrate the stereogenic properties of cyclophosphazenes (Davies *et al.*, 2000). Relatively few of these compounds have been fully characterized crystallographically (Brandt *et al.*, 1995, 1996, 1999; Brandt, Porwolik *et al.*, 1997; Brandt, Porwolik-Czomperlik *et al.*, 1997; Davies *et al.*, 2000) and many of them have been reported as oils (Brandt *et al.*, 1995; Beşli & Kılıç, 2002); even those that crystallize often exhibit disorder due to the high degree of torsional flexibility of the macrocyclic moiety. The main product of the reaction of the disodiumtetra(ethylene)-glycol (1) with the parent cyclophosphazene, hexachlorocyclo-triphosphazatriene (N$_3$P$_3$Cl$_6$), is N$_3$P$_3$Cl$_4$[O(CH$_2$CH$_2$O)$_4$], which has been demonstrated crystallographically to have a *cis-ansa* structure, whereas the spiro-isomer has been reported as an oil (Brandt *et al.*, 1995). We have been investigating the analogous reaction of the disodiumglycol (1) with the geminal diphenyl compound, N$_3$P$_3$Cl$_4$Ph$_2$ (2), in order to reduce the potential number of different reaction sites. In addition, it was hoped that the presence of two aromatic substituent groups would favour crystallization. The main product isolated from the reaction of the disodiumglycol (1) with the diphenyl derivative (2) was the ansa-derivative 2,2-diphenyl-4,6-oxytetra(ethyleneoxy)-4,6-dichlorocyclotriphosphazatriene, N$_3$P$_3$Ph$_2$[O(CH$_2$CH$_2$O)$_4$]Cl$_2$ (3), which is found to have the *cis-ansa* structure in line with other macrocyclic cyclophosphazene derivatives (Brandt *et al.*, 1995, 2001; Kruszynski *et al.*, 2001). Examination by ^{31}P NMR spectroscopy shows that
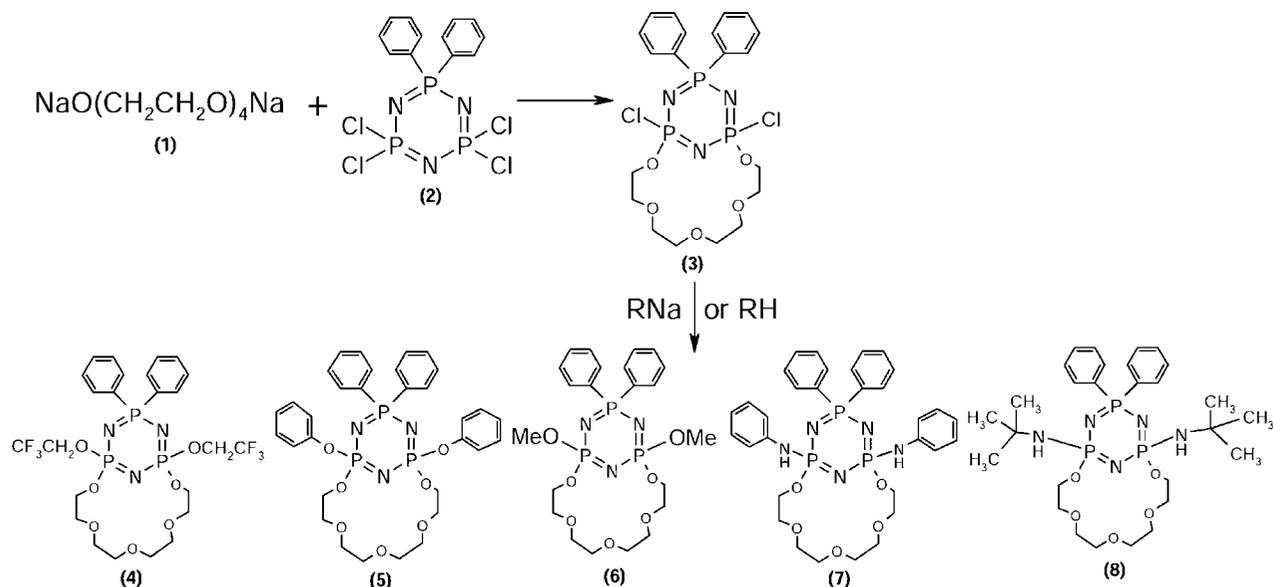
Scheme 1

there are other minor products in the reaction mixture, and these are currently being investigated.

It has been demonstrated previously that when two (or more) different substituents are present in cyclotriphosphazatriene derivatives, $N_3P_3Cl_{6-n}R_n$, these substituents can produce differential changes in molecular parameters (Mani *et al.*, 1965, 1966; Ahmed & Pollard, 1972; Ahmed & Gabe, 1975; Ahmed & Fortier, 1980; Contractor *et al.*, 1985; Fincham *et al.*, 1986; Alkubaisi *et al.*, 1988; Beşli *et al.*, 2002). A similar observation has been made for geminal $N_3P_3F_4Ph_2$, where different P—N bond lengths were also noted (Allen *et al.*, 1969). These observations were made a little more quantitative by the introduction of the parameter Δ(P—N), which is the difference between the bond lengths of two adjacent P—N bonds that form part of the same three-centre P—N—P island in a cyclophosphazene ring (Contractor *et al.*, 1985; Fincham *et al.*, 1986; Alkubaisi *et al.*, 1988). These differential changes have recently been used to demonstrate the electron-density transfer in two series of N_3P_3 derivatives (Beşli *et al.*, 2002).

In order to understand in more detail the effect of substituent groups on the molecular parameters of cyclophosphazenes we have synthesized and examined crystallographically a series of 2,2-diphenyl-4,6-*cis*-oxytetra(ethyleneoxy)-4,6-R_2-cyclotriphosphazatriene derivatives (Scheme 1), where the substituents R = Cl, OCH_2CF_3, OPh, OMe, NHPh and $NHBu^t$ represent a wide range of electron-supplying properties (relative to Cl), as demonstrated by basicity measurements in a nitrobenzene solution (Feakins *et al.*, 1965; Feakins, Last *et al.*, 1969; Feakins, Shaw *et al.*, 1969).

2. Experimental

2.1. Preparation of compounds

A brief general description of the synthetic methods is given in this section, whereas the complete synthetic details are

provided as supplementary information.[2] The sodium derivative of tetraethyleneglycol (1) in tetrahydrofuran solution was allowed to react with 2,2-diphenyl-4,4,6,6-tetrachlorocyclotriphosphazatriene (2) (Acock *et al.*, 1964) at room temperature. After column chromatography, 2,2-diphenyl-4,6-dichloro-4,6-[oxytetra(ethyleneoxy)]cyclotriphosphazatriene (3) was crystallized from hexane:dichloromethane (50:50). Compound (3) was then treated in tetrahydrofuran solution with either the amine (reflux) or the sodium salts of different alcohols/phenol (room temperature) to give the products (4)–(8) (Scheme 1), which were purified in the same way as (3).

2.2. X-ray crystallography

The data for all compounds except (6) (see below) were collected at low temperature on a Nonius KappaCCD area-detector diffractometer located at the window of a Nonius FR591 rotating-anode X-ray generator and equipped with a molybdenum target [λ(Mo $K\alpha$) = 0.71073 Å]. Structures were solved and refined using the *SHELX*97 (Sheldrick, 1997) suite of programs. Absorption corrections were estimated from comparisons of equivalent reflections using the program *SORTAV* (Blessing, 1997). Non-H atoms were refined anisotropically, while H atoms were generally fixed in idealized positions (with the exception of some N—H protons, whose positions were determined from a difference map) and refined with their displacement parameters riding on those of their parent atoms. The data for (6) were collected at room temperature, because on cooling the crystal appeared to undergo a mildly destructive phase transition, which produced a very disordered structure. Pertinent data collection and refinement parameters are collated in Table 1.

Table 1
Experimental details.

	(3)	(4)	(5)	(6)	(7)·H_2O	(8)
Crystal data						
Chemical formula	$C_{20}H_{26}Cl_2N_3O_5P_3$	$C_{24}H_{30}F_6N_3O_7P_3$	$C_{32}H_{36}N_3O_7P_3$	$C_{22}H_{32}N_3O_7P_3$	$C_{32}H_{40}N_5O_6P_3$	$C_{28}H_{46}N_5O_5P_3$
Chemical formula weight	552.25	679.42	667.55	543.42	683.6	625.61
Cell setting, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$	Triclinic, $P1$	Monoclinic, $P2_1/n$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
a, b, c (Å)	17.618 (4), 8.1109 (16), 19.284 (4)	15.3839 (4), 8.0685 (2), 24.1935 (9)	10.166 (2), 12.105 (2), 13.313 (3)	11.8293 (2), 10.3312 (2), 21.6318 (5)	10.519 (2), 12.694 (3), 14.340 (3)	9.5003 (2), 10.4210 (3), 17.1257 (3)
α, β, γ (°)	90, 114.44 (3), 90	90, 105.877 (1), 90	88.86 (3), 86.54 (3), 78.14 (3)	90, 100.203 (1), 90	114.81 (3), 93.81 (3), 103.59 (3)	92.598 (2), 90.645 (2), 108.799 (1)
V (Å^3)	2508.8 (9)	2888.46 (15)	1600.4 (6)	2601.84 (9)	1659.6 (6)	1602.79 (6)
Z	4	4	2	4	2	2
D_x (Mg m^{-3})	1.462	1.562	1.385	1.387	1.368	1.296
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
No. of reflections for cell parameters	7188	10029	13461	8163	11413	12052
θ range (°)	2.91–27.48	2.91–27.48	2.91–27.48	2.91–27.48	2.91–27.48	2.91–27.48
μ (mm^{-1})	0.487	0.294	0.238	0.275	0.231	0.230
Temperature (K)	150 (2)	120 (2)	150 (2)	293 (2)	150 (2)	120 (2)
Crystal form, colour	Block, colourless	Plate, colourless	Block, colourless	Plate, colourless	Block, colourless	Block, colourless
Crystal size (mm)	$0.32 \times 0.28 \times 0.13$	$0.18 \times 0.10 \times 0.03$	$0.20 \times 0.15 \times 0.10$	$0.26 \times 0.20 \times 0.07$	$0.30 \times 0.17 \times 0.08$	$0.27 \times 0.18 \times 0.12$
Data collection						
Diffractometer	Nonius KappaCCD	Nonius KappaCCD	Nonius KappaCCD	Nonius KappaCCD	Nonius KappaCCD	Nonius KappaCCD
Data collection method	φ and ω scans	φ and ω scans	φ and ω scans	φ and ω scans	φ and ω scans	φ and ω scans
Absorption correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan	Multi-scan	Multi-scan
T_{min}	0.8598	0.9491	0.9539	0.9319	0.9340	0.9406
T_{max}	0.9394	0.9912	0.9766	0.9810	0.9829	0.9730
No. of measured, independent and observed reflections	17345, 5657, 4268	22797, 6488, 3777	24220, 12306, 8751	18814, 5841, 4160	19478, 7460, 6157	20859, 7079, 5682
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.0446	0.0825	0.0609	0.0376	0.0326	0.0909
θ_{max} (°)	27.48	27.47	27.48	27.47	27.47	27.50
Range of h, k, l	$-22 \rightarrow h \rightarrow 22$ $-9 \rightarrow k \rightarrow 10$ $-24 \rightarrow l \rightarrow 25$	$-19 \rightarrow h \rightarrow 19$ $-10 \rightarrow k \rightarrow 8$ $-31 \rightarrow l \rightarrow 31$	$-13 \rightarrow h \rightarrow 11$ $-15 \rightarrow k \rightarrow 13$ $-17 \rightarrow l \rightarrow 16$	$-14 \rightarrow h \rightarrow 15$ $-12 \rightarrow k \rightarrow 13$ $-27 \rightarrow l \rightarrow 28$	$-13 \rightarrow h \rightarrow 13$ $-16 \rightarrow k \rightarrow 15$ $-17 \rightarrow l \rightarrow 18$	$-12 \rightarrow h \rightarrow 12$ $-13 \rightarrow k \rightarrow 13$ $-22 \rightarrow l \rightarrow 19$
Refinement						
Refinement on	F^2	F^2	F^2	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.039, 0.1023, 1.013	0.0496, 0.1144, 0.977	0.0505, 0.1141, 0.933	0.0518, 0.1525, 1	0.0392, 0.1203, 0.647	0.0452, 0.1248, 1.007
No. of reflections and parameters in refinement	5657, 299	6488, 389	12306, 920	5841, 319	7460, 431	7079, 385
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	Mixed	H-atom parameters constrained	Mixed	Mixed
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0421P)^2 + 1.1841P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0463P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0472P)^2 + 0.0555P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0776P)^2 + 1.3016P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0981P)^2 + 3.4222P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0461P)^2 + 1.1656P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.002	0.006	0.295	0.061	0.005	0.029
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.321, -0.461	0.377, -0.375	0.393, -0.351	0.459, -0.312	0.283, -0.454	0.718, -0.482
Extinction method	*SHELXL*	*SHELXL*	*SHELXL*	*SHELXL*	None	*SHELXL*
Extinction coefficient	0.0041 (7)	0.0013 (3)	0.0063 (8)	0.0061 (11)	0	0.0032 (15)

3. Results

Displacement ellipsoid plots for the structures determined [(3)–(8), Scheme 1] are shown in Figs. 1–6, respectively. All six molecular systems are shown to have the macrocyclic polyether in a *cis-ansa* configuration about the P1 and P2 centres; concomitantly, both *R* group substituents are arranged *cis* to

Table 2
Parameters of the molecular frameworks of compounds (3)–(8).

$\Delta(P-N) = a - b$.

R		$\sum \alpha_R$	α	β	γ	δ	a	b	c	$\Delta(P-N)$	Maximum deviation from mean N_3P_3 plane
Cl	(3)	0	115.37 (9)	122.08 (7)	119.65 (6)	119.86 (10)	1.609 (1)	1.566 (1)	1.575 (1)	0.043	0.076
OCH$_2$CF$_3$	(4)	2	117.27 (11)	122.03 (10)	117.41 (8)	122.76 (13)	1.604 (1)	1.567 (1)	1.584 (1)	0.037	0.054
OPh	(5)	6.2	117.27 (12)	121.57 (10)	117.58 (8)	122.37 (14)	1.603 (2)	1.579 (2)	1.578 (2)	0.024	0.074/0.122
OMe	(6)	7.2	117.33 (11)	121.11 (9)	116.92 (8)	122.96 (13)	1.602 (1)	1.575 (1)	1.585 (1)	0.027	0.126
NHPh	(7·H$_2$O)	8.8	117.25 (8)	119.85 (7)	116.25 (6)	121.03 (9)	1.600 (1)	1.592 (1)	1.599 (1)	0.008	0.197
NHBu^t	(8)	9.8	118.32 (8)	121.38 (7)	116.47 (6)	123.56 (10)	1.598 (1)	1.593 (1)	1.590 (1)	0.005	0.106
Correlation with $\sum \alpha_R$			0.896	0.848	0.527	0.662	0.522	0.773	0.290	0.899	0.404

each other. The third phosphorus position, P3, is diphenyl-substituted in all structures. The phenyl groups are oriented approximately face-to-face except in (3), which adopts a face-to-edge conformation. The polyether moiety generally adopts the classic 'crown' conformation, with the O atoms in an alternating *syn/anti* arrangement. This ideal relaxed conformation is perturbed in (7) because of intermolecular hydrogen-bonding effects that arise from the presence of a guest water molecule.

A comparison has been made of the structural parameters of the cyclophosphazene moiety for the series of compounds (3)–(8). The structural parameters that are considered (bond lengths *a*, *b*, *c* and bond angles α, β, γ, δ) are defined in the generalized structure shown in Scheme 2.
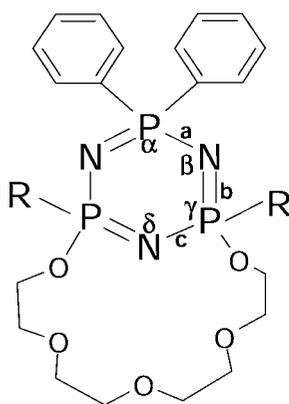
Scheme 2

Data for compounds (3)–(8) are summarized in Table 2, which also shows the correlation coefficients between these parameters and $\sum \alpha_R$ and which contains data on the N_3P_3 ring planarity. The bond lengths and bond angles in Table 2 show small but moderately consistent trends that reflect the electron-releasing capacity of the substituents *R* (Cl, OCH$_2$CF$_3$, OPh, OMe, NHPh and NHBu^t). We have also compared the values of $\Delta(P-N)$ (Beşli *et al.*, 2002). The choice of which of the two bond lengths are subtracted from each other is somewhat arbitrary (other than being adjacent P—N bonds) but $\Delta(P-N)$ must be consistent for the set of compounds discussed and compared. In the present context, $\Delta(P-N)$ is

taken as $\Delta(a - b)$, where *a* and *b* are the bond lengths as shown in Scheme 2.

4. Discussion

Careful crystallographic studies by Ahmed and co-workers, on phosphazenes synthesized by our group, provided the first evidence that cyclotriphosphazatrienes carrying two or more different substituents show significant differences of bond lengths (Mani *et al.*, 1965, 1966; Ahmed & Pollard, 1972; Ahmed & Gabe, 1975; Ahmed & Fortier, 1980). Subsequent studies have revealed trends in bond lengths and angles, and these trends could be related to a variety of different physical and chemical properties (Contractor *et al.*, 1985; Fincham *et al.*, 1986; Alkubaisi *et al.*, 1988). Earlier studies have shown that substituent basicity constants give a reliable indication of the relative electron-releasing capacity of different substituent *R* groups (Feakins *et al.*, 1965; Feakins, Last *et al.*, 1969; Feakins, Shaw *et al.*, 1969). These constants are defined in the following manner for the six-membered N_3P_3 ring system. A
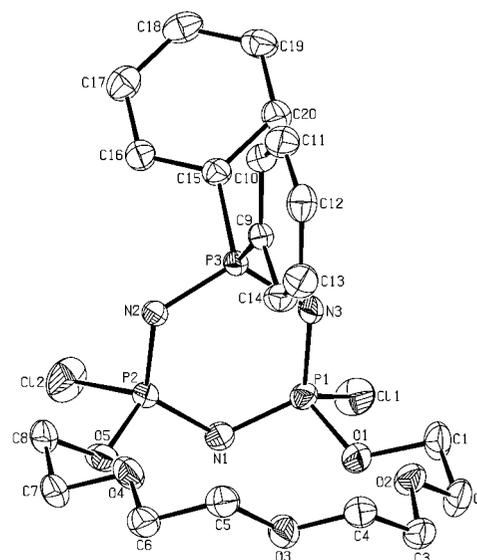
Figure 1
The molecular structure and atomic-numbering scheme for compound (3) with H atoms omitted for clarity and ellipsoids shown at the 30% probability level.

substituent R on a given P atom will supply a base-strengthening amount of electron density to the adjacent N atoms, and this is denoted as α_R. The same substituent will also supply some base strengthening to the remote N atom, which is denoted as γ_R. The most widely accepted model of electronic structure of phosphazenes is that proposed by Dewar *et al.* (1960), in which the structure consists of three-centre islands (Cameron *et al.*, 1994). However, there is a body of evidence, including crystallographic data, that effects, probably diluted, can be transmitted beyond these three-centre islands. For instance, in basicity studies the measured basicity constants indicate that values of γ_R are only about half those of α_R (Feakins *et al.*, 1968; Feakins, Last *et al.*, 1969; Feakins, Shaw *et al.*, 1969). However, in the present work on the symmetrically disubstituted compounds (3)–(8) it will be sufficient to use the sum of the basicity constants for both substituents, *i.e.* $\sum \alpha_R = 2\alpha_R$ [*e.g.* for (5) $\alpha_{OPh} = 3.1$, hence for this compound $\sum \alpha_R = 6.2$.]

In Table 2 we compare the sum of the substituent basicity constants, $\sum \alpha_R$, with the bond lengths (a, b, c), bond angles (α, β, γ, δ) and $\Delta(\mathrm{P-N})$ values for (3)–(8). In general it is found that, with increasing value of $\sum \alpha_R$, the bond angles α and δ increase, while β and γ decrease; similarly, the bond length a decreases while b and c increase. All of these trends fit a pattern that parallels the increase in basicity, where there is a similar trend in electron density provided by the substituents R. Our structural data refer to molecules in their unperturbed ground state in the crystalline solid, whereas the basicity measurements (Feakins *et al.*, 1965, 1968; Feakins, Last *et al.*, 1969; Feakins, Shaw *et al.*, 1969) were made in a nitrobenzene solution where the molecule is perturbed by the approach of a proton (Koppel *et al.*, 2001). Nevertheless, there is a definite relationship between the molecular parameters of (3)–(8) and

the substituent basicity constant, and this relationship is analogous to the effects observed previously (Shaw, 1986).

As an example, the variations in the bond lengths a and b with $\sum \alpha_R$ are presented in graphical form in Fig. 7. It can be readily observed that the bond lengths b increase with increasing $\sum \alpha_R$, while the bond lengths a decrease, and that the two lines appear to converge; *i.e.* $\Delta(\mathrm{P-N})$ is largest for (3), where the difference in electron-releasing capacity of the PCl(Om) and PPh$_2$ groups is greatest, whereas at the higher $\sum \alpha_R$ values the relative electron-release from the PX(Om) group is similar to that of the PPh$_2$ group and so $\Delta(\mathrm{P-N}) \to 0$.

Compound (7) exhibits deviations from the curves in the graphs for the angles δ. A closer examination of its crystal
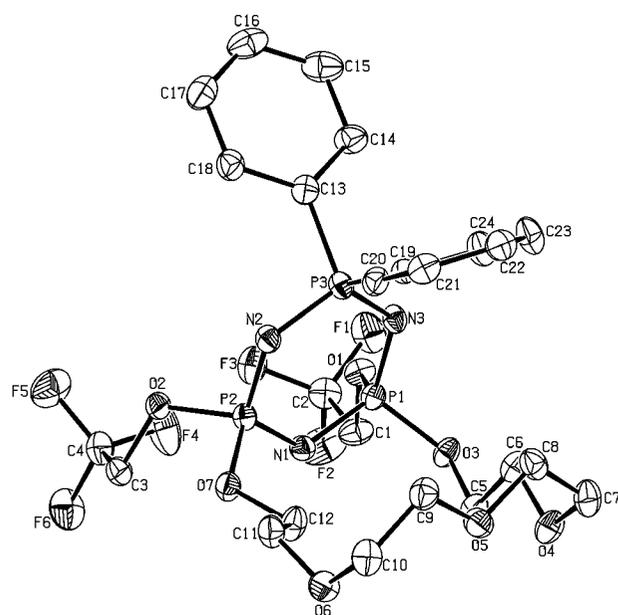
Figure 2
The molecular structure and atomic-numbering scheme for compound (4) with H atoms omitted for clarity and ellipsoids shown at the 30% probability level.
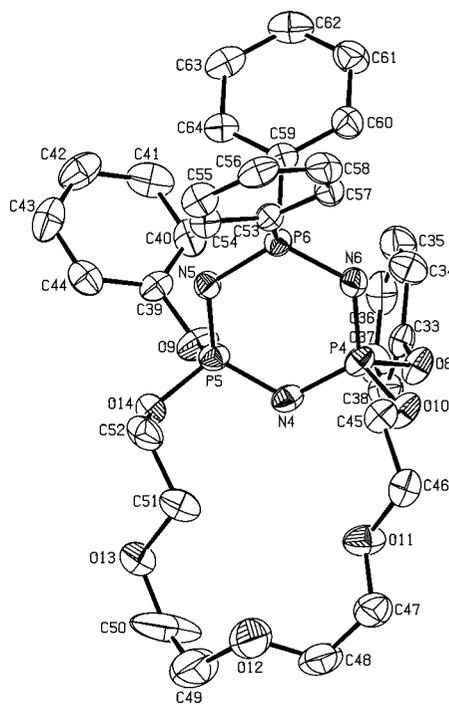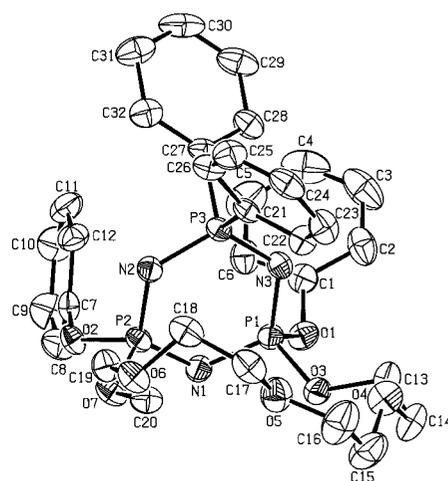
Figure 3
The two crystallographically independent molecules in the molecular structure and atomic-numbering scheme for compound (5) with H atoms omitted for clarity and ellipsoids shown at the 30% probability level.

structure indicates the likely reason for this effect: the compound crystallizes with one molecule of water, which forms four hydrogen bonds. Two hydrogen bonds are formed by using its lone pairs to interact with the N—H protons of two separate anilino groups of a molecule above the plane

of the water molecule [$D \cdots A$: N4$\cdots$O6 = 2.884 (1), N5$\cdots$O6 = 2.982 (1) Å]. Below the plane of the water molecule the two other hydrogen bonds affect not only the macrocyclic ring, with the H atoms of the water molecule interacting with the central O atom of the macrocyclic ring [$D \cdots A$: O6$\cdots$O3 = 2.860 (1) Å], but also the cyclophosphazene ring by interaction with the lone pairs of electrons on N1 [$D \cdots A$: O6$\cdots$N1 = 2.857 (1) Å], which is the central atom of the P—N—P bond whose bond angle is δ. It has been shown previously that hydrogen bonding has significant effects on such molecular parameters (Fincham *et al.*, 1986), and so hydrogen-bonding effects most probably explain these small deviations for (7).

5. Conclusions

Structural investigations of the molecular frameworks [bond lengths a, b, c, bond angles α, β, γ, δ and Δ(P—N) values] of

Figure 4
The molecular structure and atomic-numbering scheme for compound (6) with H atoms omitted for clarity and ellipsoids shown at the 30% probability level.
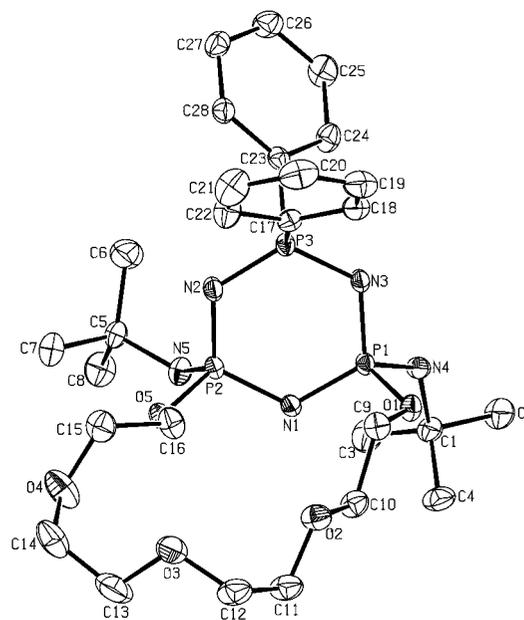
Figure 6
The molecular structure and atomic numbering scheme for compound (8) with H atoms omitted for clarity and ellipsoids shown at the 30% probability level.

Figure 5
The molecular structure and atomic-numbering scheme for compound (7) with H atoms omitted for clarity and ellipsoids shown at the 30% probability level. The water molecule is included to demonstrate the effect of hydrogen bonding on the geometry of the N₃P₃ ring.
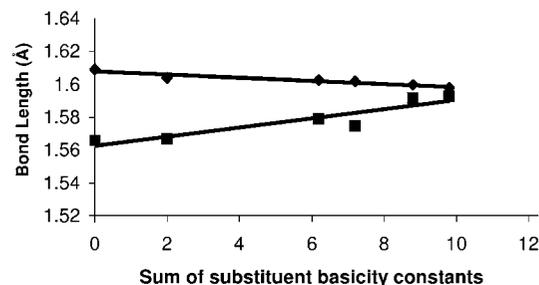
Figure 7
Graph of bond lengths a (♦) and b (■) against the sum of substituent basicity constants, $\sum \alpha_R$

(3)–(8) have revealed a fairly consistent trend of changes in the molecular parameters. These changes mirror the electron-releasing capacities of the substituents R as measured by basicity measurements in nitrobenzene solution. Deviations from these trends are observed for (7), and these deviations may be rationalized by considering the hydrogen bonding from an included water molecule.

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