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Structural investigations of phosphorus–nitrogen compounds. 4. Steric and electronic effects in dibenzylamino derivatives of hexachlorocyclotriphosphazatriene and 4,4,6,6-tetrachloro-2,2-diphenylcyclotriphosphazatriene[1]

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[1] Part 3: Alkubaisi *et al.* (1988).

A systematic study is presented on the products of aminolysis of $N_3P_3Cl_6$ (1) and $N_3P_3Ph_2Cl_4$ (4) with dibenzylamine. Two series of mono- and disubstituted derivatives of compounds (1) and (4), namely $N_3P_3Cl_5[N(CH_2Ph)_2]$ (2) and $N_3P_3Cl_4[N(CH_2Ph)_2]_2$ (3) and $N_3P_3Ph_2Cl_3[N(CH_2Ph)_2]$ (5) and $N_3P_3Ph_2Cl_2[N(CH_2Ph)_2]_2$ (6) [where (2), (3), (5) and (6) are new structures], are investigated in order to determine whether steric or electronic effects prevail in the formation of dibenzylamino-substituted cyclophosphazenes. The influence of an electron-releasing group (*i.e.* phenyl) on the stereochemistry and degree of substitution of the product is analysed by comparison of the above two series. The difference in unsymmetrically substituted endocyclic P—N bond lengths, Δ, is used as a measure of the degree of the electronic contribution, in combination with basicity constants, to quantify the degree of the electron-releasing capacity of the *R* group. In order to compare geminal *versus* non-geminal substitution, a difunctional secondary amine was used to form the compound $N_3P_3Cl_4[NMe(CH_2)_3NMe]$ (7) (a reinvestigation) for inclusion in this study. It is shown that electron-releasing groups have a greater effect on the lengthening of P—Cl bonds as opposed to endocyclic P—N bonds and that this effect is greater in the non-geminal P*R*Cl case than for geminal PCl_2. However, steric effects are shown to be dominant in the reactions of dibenzylamine with N_3P_3 derivatives, with a disposition to a *trans* stereochemistry in bisdibenzylamino derivatives.

1. Introduction

Aminolysis of $N_3P_3Cl_6$ (1) with secondary amines, NHR_2, to give $N_3P_3Cl_{6-n}(NR_2)_n$ has been extensively investigated (Shaw, 1976). Most of these investigations were designed to establish the degree of replacement, *n*, and the substitution pattern, which could be geminal, non-geminal or mixed (Shaw *et al.*, 1962). Although complete aminolysis was easily achieved with most amines, this was not attained with a few, even for reactions in boiling solvents and with an excess of reagents. For example, replacement of the chlorine atoms in $N_3P_3Cl_6$ (1) stopped at $n = 2$ with some secondary amines, such as dicyclohexylamine and dibenzylamine (Hasan *et al.*, 1975), and also for triphenylphosphazene, $Ph_3P{=}NH$ (Biddlestone & Shaw, 1973).

Reactions of (1) with most secondary amines follow a similar pattern. At the disubstitution stage, $n = 2$, the major product is non-geminal *trans*, although *cis* isomers have been observed in some systems, usually as minor products (Shaw,

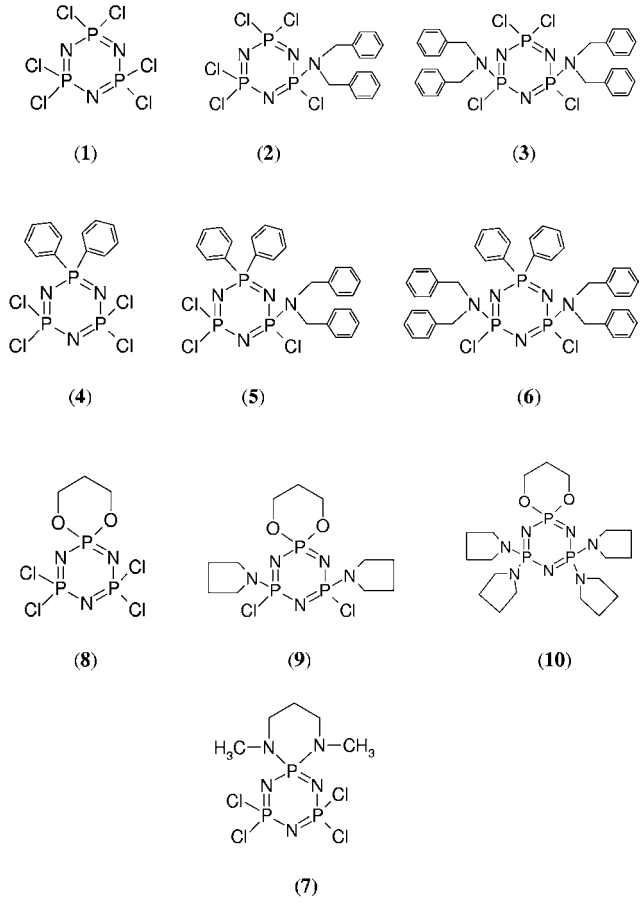
1976). As chloride ions have been shown to cause reversible *cis–trans* isomerizations (Keat & Shaw, 1965*b*), it is not clear whether the *cis* isomers are primary or secondary reaction products. For $NR_2 = NMe_2$, both isomers have been crystallographically characterized, namely *cis*- (Ahmed & Fortier, 1980) and *trans*-$N_3P_3Cl_4(NMe_2)_2$ (Ahmed & Fortier, 1980). The merest trace of geminal isomers has been observed in some systems (Shaw, 1976). At the trisubstituted stage, $n = 3$, all three isomers have been observed (Shaw, 1976) and crystallographically examined: geminal (Ahmed & Pollard, 1972), and *cis*- (Ahmed & Gabe, 1975) and *trans*-$N_3P_3Cl_3(NMe_2)_3$ (Ahmed & Gabe, 1975). The two main products are the non-geminal *trans* and the geminal isomers, the latter being favoured in aromatic solvents (Keat & Shaw, 1966). Again only traces of the non-geminal *cis* isomer were formed, although its yield could be increased by isomerization reactions. Earlier studies involving secondary amines found only one product at the tetrakis stage, $n = 4$, which was shown by proton NMR to be the *cis* isomer and proven crystallographically for the morpholino derivative, *cis*-$N_3P_3Cl_2[N(CH_2CH_2)_2O]_4$ (Ouagued *et al.*, 1991). The absence of pentakis derivatives, $n = 5$, has been noted (Keat & Shaw, 1965*b*), whereas the fully aminolysed derivatives, $n = 6$, are usually easily obtained and characterized, *e.g.* $N_3P_3(NMe_2)_6$ (Rettig & Trotter, 1973). In later studies with dimethylamine as reagent, small amounts of the tetrakis *trans* isomer were isolated (Green & Sowerby, 1971) and only traces of the pentakis derivative, $N_3P_3Cl(NMe_2)_5$ (Clare & Sowerby, 1974).

Several questions are raised by the above observations. Among these are: why is a *trans* structure preferred for the two non-geminal amino groups at the bis stage, but a *cis* structure at the tetrakis stage? Is the *cis* configuration the usual sterochemistry when only two non-geminal chlorine atoms remain, as observed in previous studies (Ouagued *et al.*, 1991; Mani *et al.*, 1965)? Structural investigations have been undertaken to clarify some of these points and results are reported on the reactions of dibenzylamine with 2,2,4,4,6,6-hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$ (1) and 4,4,6,6-tetrachloro-2,2-diphenylcyclotriphosphazatriene, $N_3P_3Ph_2Cl_4$ (4).

In a previous study (Hasan *et al.*, 1975), the reaction of dibenzylamine with (1) was found to give only mono-substituted, $N_3P_3Cl_5[N(CH_2Ph)_2]$ (2) and disubstituted derivatives, $N_3P_3Cl_4[N(CH_2Ph)_2]_2$ (3), and even under very forcing conditions no further replacement was detected. Compound (3) was attributed a non-geminal structure from its NMR spectrum and a *trans* arrangement was proposed from indirect evidence (Hasan *et al.*, 1975). There were several reasons for further investigations of these dibenzylamino structures. Firstly, it was necessary to be certain of its structure because a non-geminal *trans*-disubstituted derivative of (1), namely $N_3P_3Cl_4(NR_2)_2$, was required as a starting material for other studies. Secondly, it was of interest to understand why the reaction with dibenzylamine appeared to stop at disubstitution and why disubstitution was stereospecific, because with many other secondary amines the *trans* product was accompanied by small, but varying quantities of its *cis* isomer (Shaw, 1976).

We have therefore studied crystallographically two series of compounds and compared their structures: (*A*) $N_3P_3Cl_6$ (1) (Bullen, 1971), $N_3P_3Cl_5[N(CH_2Ph)_2]$ (2), $N_3P_3Cl_4[N(CH_2Ph)_2]_2$ (3), (*B*) $N_3P_3Ph_2Cl_4$ (4) (Mani *et al.*, 1965), $N_3P_3Ph_2Cl_3[N(CH_2Ph)_2]$ (5) and $N_3P_3Ph_2Cl_2[N(CH_2Ph)_2]_2$ (6).

Comparison of the above series (*A*) and (*B*) will lead to greater understanding of the effect of electronic deactivation towards nucleophilic attack by the two electron-releasing phenyl groups of (4); this compound is readily available and has been characterized crystallographically.



2. Experimental

2.1. X-ray crystallography

Data were collected at low temperature 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 *SHELX* (Sheldrick, 1997) suite of programs. Data were corrected for absorption effects by means of comparison of equivalent reflections using the program *SORTAV* (Blessing, 1997). Non-H atoms were refined anisotropically, while H atoms were fixed in idealized positions with their displacement parameters riding on the values of their parent atoms. Pertinent data collection and refinement parameters are collated in Table 1,

Table 1
Experimental details.

	(2)	(3)	(5)	(6)	(7)
Crystal data					
Chemical formula	$C_{14}H_{14}Cl_5N_4P_3$	$C_{28}H_{28}Cl_4N_5P_3$	$C_{26}H_{24}Cl_3N_4P_3$	$C_{40}H_{38}Cl_2N_5P_3$	$C_5H_{12}Cl_4N_5P_3$
Chemical formula weight	508.45	669.26	591.75	752.56	376.91
Cell setting, space group	Monoclinic, $P2_1/n$	Orthorhombic, $Pbca$	Monoclinic, Pn	Monoclinic, $P2_1/n$	Orthorhombic, $P2_12_12_1$
a, b, c (Å)	11.125 (2), 8.1671 (16), 23.585 (5)	18.294 (4), 17.411 (4), 19.047 (4)	11.657 (2), 8.5838 (17), 13.783 (3)	10.2810 (1), 21.0219 (3), 17.3783 (2)	7.8379 (2), 13.4076 (3), 14.0752 (4)
β (°)	99.61 (3)	90	96.41 (3)	99.047 (1)	90
V (Å^3)	2112.9 (7)	6067 (2)	1370.5 (5)	3709.18 (8)	1479.13 (7)
Z	4	8	2	4	4
D_x (Mg m^{-3})	1.598	1.465	1.434	1.348	1.693
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
No. of reflections for cell parameters	8236	12 469	10 134	44 308	4103
θ range (°)	2.91–27.48	2.49–27.49	2.49–27.49	2.91–27.48	2.91–27.48
μ (mm^{-1})	0.922	0.577	0.534	0.342	1.110
Temperature (K)	120 (2)	150 (2)	150 (2)	120 (2)	150 (2)
Crystal form, colour	Block, colourless	Block, colourless	Block, colourless	Block, colourless	Plate, colourless
Crystal size (mm)	0.35 × 0.20 × 0.16	0.625 × 0.625 × 0.325	0.2 × 0.1 × 0.05	0.40 × 0.20 × 0.18	0.30 × 0.18 × 0.05
Data collection					
Diffractometer	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
Absorption correction	Multi-scans	Multi-scans	Multi-scans	Multi-scans	Multi-scans
T_{min}	0.7386	0.7142	0.9008	0.8755	0.7318
T_{max}	0.8666	0.8345	0.9738	0.9411	0.9466
No. of measured, independent and observed parameters	11 630, 4790, 4054	22 246, 5347, 3833	13 855, 4508, 3152	42 554, 8451, 7150	7531, 3272, 3093
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.0426	0.0592	0.1006	0.0618	0.0406
θ_{max} (°)	27.48	25.03	24.71	27.48	27.48
Range of h, k, l	$-14 \rightarrow h \rightarrow 14$ $-8 \rightarrow k \rightarrow 10$ $-30 \rightarrow l \rightarrow 23$	$-21 \rightarrow h \rightarrow 21$ $-20 \rightarrow k \rightarrow 20$ $-22 \rightarrow l \rightarrow 14$	$-13 \rightarrow h \rightarrow 13$ $-10 \rightarrow k \rightarrow 10$ $-16 \rightarrow l \rightarrow 16$	$-13 \rightarrow h \rightarrow 13$ $-27 \rightarrow k \rightarrow 27$ $-22 \rightarrow l \rightarrow 20$	$-8 \rightarrow h \rightarrow 10$ $-17 \rightarrow k \rightarrow 14$ $-18 \rightarrow l \rightarrow 17$
Refinement					
Refinement on	F^2	F^2	F^2	F^2	F^2
$R[F^2>2\sigma(F^2)]$, $wR(F^2)$, S	0.0311, 0.0823, 1.048	0.0385, 0.1043, 0.873	0.0461, 0.081, 0.978	0.0354, 0.0941, 1.007	0.0272, 0.0647, 0.908
No. of reflections and parameters used in refinement	4790, 236	5347, 466	4508, 414	8451, 452	3272, 157
H-atom treatment	Mixed	Mixed	Mixed	Mixed	Mixed
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0394P)^2 + 0.4555P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0695P)^2 + 0.6558P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/\sigma^2(F_o^2)$	$w = 1/[\sigma^2(F_o^2) + (0.0429P)^2 + 2.2200P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0318P)^2 + 0.6613P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.056	0.023	0.003	0.003	0.015
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.385, −0.431	0.341, −0.321	0.232, −0.28	0.435, −0.406	0.275, −0.38
Extinction method			*SHELXL*		*SHELXL*
Extinction coefficient			0.0037 (6)		0.0068 (10)

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

while full details have been deposited with the Cambridge Crystallographic Data Centre as well as the IUCr.[2]

[2] Citations on the basis of CSD Refcodes (Allen & Kennard, 1993) for all crystal structures discussed, but not determined, in this study, as well as full crystallographic data (CIF format) for the structures determined, are available from the IUCr's electronic archives (Reference: BM0049). Services for accessing these data are described at the back of the journal.

2.2. Preparation of compounds

Compounds (2) and (3) have been described previously (Hasan *et al.*, 1975), as has (4) (Acock *et al.*, 1964). The procedure for (5) and (6) is reported here. The structure of (7) had been determined previously (Deutsch *et al.*, 1987) at room temperature; however, a redetermination at 120 K was deemed necessary in order to increase the accuracy for inclusion in this study.

Table 2
Comparison of averaged N and P geometries (Å, °) for compounds with $R = N(CH_2Ph)_2$.

	(1)	(2)	(3)	(4)	(5)	(6)
Endocyclic P—N—P						
P—N	1.581 (3)	1.584 (5)		1.587 (1)		
Cl_2P—N—PCl_2	121.4 (3)	120.15 (9)		119.2 (2)		
Cl_2P—N—PCl*R*		1.594 (5)/1.567 (5)	1.594 (2)/1.564 (2)		1.598 (4)/1.577 (4)	
Δ		0.027 (7)	0.030 (3)		0.021 (6)	
Cl_2P—N—PCl*R*		120.72 (10)	120.40 (15)		119.3 (2)	
P—N			1.582 (2)			1.587 (4)
*R*ClP—N—PCl*R*			121.37 (14)			119.93 (8)
P—N				1.615 (2)/1.555 (1)	1.610 (4)/1.555 (4)	
Δ				0.060 (2)	0.055 (6)	
Ph_2P—N—PCl_2				122.0 (3)	122.2 (2)	
P—N					1.618 (4)/1.564 (4)	1.603 (4)/1.578 (4)
Δ					0.054 (6)	0.025 (6)
Ph_2P—N—PCl*R*					121.5 (2)	121.82 (8)
Endocyclic N—P—N						
N—PCl_2—N	118.4 (2)	119.67 (8)	119.52 (12)	119.75 (9)	120.4 (2)	
N—PCl*R*—N		117.55 (8)	118.25 (12)		119.2 (2)	119.41 (7)
N—PPh_2—N				115.2 (1)	115.8 (2)	116.72 (7)
N_3P_3 planarity (maximim deviation from mean plane)	0.04 (N1)	0.077 (N2)	0.087 (N3)	0.078 (P6)	0.082 (P3)	0.056 (P2)

Table 3
Geometrical parameters (Å, °) for P–Cl and P–*R* groups, where $R = N(CH_2Ph)_2$.

	(1)	(2)	(3)	(4)	(5)	(6)
Geminal	1.984 (2)	1.998 (3)	2.002 (3)	1.998 (12)	2.007 (2)	
Non-geminal		2.041 (2)	2.042 (3)		2.049 (2)	2.056 (5)
Cl—P—Cl	101.44 (9)	101.56 (3)	100.89 (4)	100.3 (1)	99.87 (8)	
Exocyclic P—N		1.618 (4)	1.623 (2)		1.630 (4)	1.629 (4)
Cl—P—*R*		107.20 (6)	105.82 (9)		102.9 (2)	104.42 (5)
Sum of angles about exocyclic N		357.08 (9)	357.7 (4)		356.2 (3)	359.53 (8)

2.2.1. Preparation of 4-dibenzylamino-2,2,4-trichloro-6,6-diphenylcyclotriphosphazatriene (5). 2,2,4,4-Tetrachloro-6,6-diphenylcyclotriphosphazatriene (4) (1.075 g, 2.5 mmol) was dissolved 15 ml of dry thf in a 100 ml three-necked round-bottomed flask and dibenzylamine (2 g, 10 mmol) dissolved in 15 ml of dry thf was added dropwise to a stirred solution. The reaction mixture was refluxed and followed by TLC. After 72 h, the reaction mixture was cooled to room temperature, filtered and the solvent removed under reduced pressure. 100 ml of distilled water was added and the mixture extracted twice with dichloromethane. The organic layer was dried over anhydrous Na_2SO_4, concentrated to 10 ml and the crude product was subjected to column chromatography, using thf–hexane (1:1) as eluant. Compound (5) was isolated as a solid (yield 0.8 g, 54%) and crystallized from hexane–dichloromethane as colourless crystals, m.p. 412 K. Analysis found: C, 52.79; H, 4.11; N, 9.30%; M^+, 591. $C_{26}H_{24}Cl_3N_4P_3$ requires: C, 52.77; H, 4.09; N, 9.47%; *M* 591.79.

2.2.2. Preparation of 2,4-dichloro-2,4-bis(dibenzylamino)-6,6-diphenylcyclotriphosphazatriene (6). Compound (4) (1.075 g, 2.5 mmol) was dissolved 10 ml of dry thf in a 50 ml three-necked round-bottomed flask and dibenzylamine (9.85 g, 50 mmol) was added dropwise to a stirred solution. The refluxed reaction mixture was followed by TLC and after 12 h the reaction mixture was cooled to room temperature, filtered and the solvent removed under reduced pressure. 100 ml of distilled water was then added and the mixture extracted three times with dichloromethane. The organic layer was dried over anhydrous Na_2SO_4, concentrated to 10 ml and the crude product was subjected to column chromatography, using dichloromethane as eluant. Compound (6) was isolated as an oil, which eventually solidified. Crystalization of this solid from hexane yielded (1.13 g, 60%) colourless crystals, m.p. 391 K. Analysis found: C, 63.80; H, 5.10; N, 9.30%; M^+, 752.1. $C_{40}H_{38}Cl_2N_5P_3$ requires: C, 63.84; H, 5.09; N, 9.31%; *M* 752.61.

3. Data analysis

A comparison is made for the two series of compounds, (*A*) (1)–(3) and (*B*) (4)–(6), in terms of the structural parameters for the N and P geometries of the cyclophosphazene ring (Table 2) and for the exocyclic PCl and P*R* groups (Table 3). In series (*A*) the bond lengths and angles show a slight, but consistent trend indicating the electron-releasing capacity of the dibenzylamino group(s). In order to investigate electronic effects in cyclophosphazenes in more detail the parameter Δ has been defined as the difference between the two P—N bond lengths in a given endocyclic P—N—P segment. (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 differing *R* groups (Feakins *et al.*, 1965) and as the Δ values follow a similar trend they may be taken as a reliable struc-

Table 4
Δ values (Å) and basicity constants.

	Δ	Basicity constant	Structure reference
Geminally disubstituted *R*		$2\alpha_R$	
$[O(CH_2)_2O]$	0.019 (6)	7.2[a]	CUNPOQ (Contractor *et al.*, 1985)
$[O(CH_2)_3O]$	0.021 (8)	7.5[a]	CUNPUW (Contractor *et al.*, 1985)
$[O(CH_2)_4O]$	0.031 (8)	7.8[a]	CUNRAE (Contractor *et al.*, 1985)
Ph_2	0.060 (6)	8.4[b]	PCLPAZ (Mani *et al.*, 1965)
$(NH^tBu)_2$	0.070 (6)	11.8[c]	TCBAPZ (Deutsch *et al.*, 1986)
$(NPPh_3)_2$	0.094 (4)	14.4[d]	PHSPAZ (Krishnaiah *et al.*, 1981)
Non-geminally mono-substituted *R*		α_R	
$N(CH_2Ph)_2$	0.027 (7)	5.4[e]	This work (2)
$N(CH_2)_5$	0.034 (5)	5.6[b]	POTKEO (Adam *et al.*, 1997)
NH^iPr	0.041 (5)	5.9[c]	BEVWEE (Bullen, 1982)
Non-geminally disubstituted *R*		$2\alpha_R$	
cis-$N_3P_3Cl_4(NMe_2)_2$	0.011 (7)	11.2[b]	CLPHZB (4) (Ahmed & Fortier, 1980)
trans-$N_3P_3Cl_4(NMe_2)_2$	0.018 (5)	11.2[b]	CLPHZA (4) (Ahmed & Fortier, 1980)
trans-$N_3P_3Cl_4[N(CH_2Ph)_2]_2$	0.030 (3)	10.8[e]	This work (3)

Basicity-constant notes: (*a*) by comparison with α_{OMe} and α_{OEt} (Das, Shaw, Smith & Woods, 1973); (*b*) Nabi & Shaw (1974); (*c*) Feakins *et al.* (1969); (*d*) Shaw (1986); (*e*) $N(Alk)_2$ are generally 5.6, and allowance has been made for the electron-withdrawing effect of the Ph groups.

tural indicator of an electronic effect. The sequence of bonds used to calculate Δ is chosen arbitrarily, but must be consistent in the series being compared. Hence both positive and negative values of Δ may be observed (*see below*).

The series (*B*) is more complicated than (*A*) because the two phenyl groups are pushing in electrons in the opposite direction to that of the dibenzylamino group(s). The opposing electronic effects are demonstrated by the decreasing Δ values for similar molecular fragments in comparing (4) with (5), and (5) with (6) (Table 2).

4. Discussion

The molecular structures and atomic numbering schemes for (2), (3), (5), (6) and (7) are presented in Figs. 1–5. The crystal structure of (3) shows unambiguously that it is the non-geminal *trans* disubstituted derivative, thus confirming the structure proposed from NMR studies (Hasan *et al.*, 1975). The molecule, which belongs to a structural type that is predicted to be chiral (Shaw *et al.*, 1962), is found to be a racemate existing in *RR*/*SS* configurations because it has two stereogenic centres. Similarly, (6) has a non-geminal *trans*-disubstituted structure with two stereogenic centres and is found to exist as a racemate in *RR*/*SS* configurations. The *cis* isomers of (3) and (6), which would be *meso*, have not been observed, indicating the reluctance of the two dibenzylamino groups to be *cis* on steric grounds. Compound (5) has only one stereogenic centre and crystal structure analysis shows the molecule to be chiral; it too exists as a racemate.

Theoretical studies have suggested (Cameron *et al.*, 1994, and references therein) that electron delocalization in phosphazenes is largely confined to three-centre P—N—P islands and that electron transmission beyond these is much reduced. Basicity studies support this conclusion, as the effect of an electron-releasing substituent on the adjacent N atom (α_R) is about double that at the remote N atom (γ_R) (Feakins *et al.*, 1969). Ahmed and co-workers were the first to demonstrate that replacement of Cl atoms by electron-releasing groups, such as phenyl, caused significant and differential changes in

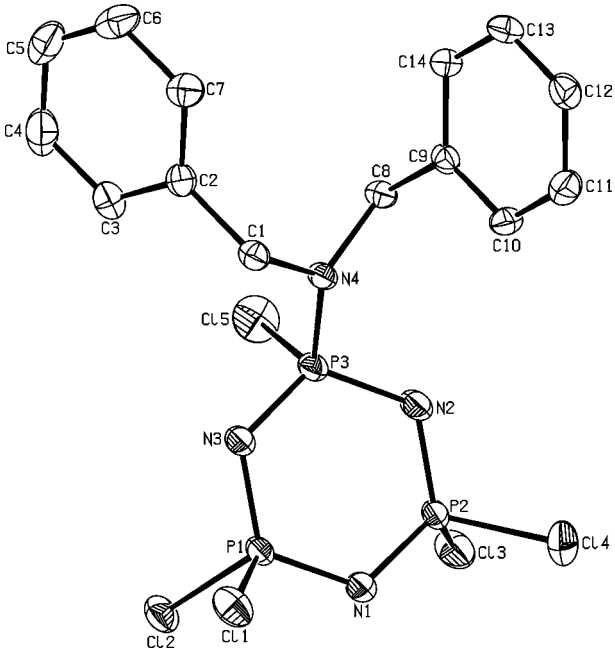


Figure 1
The molecular structure and atomic numbering scheme for (2), with protons omitted for clarity and ellipsoids shown at 30% probability.

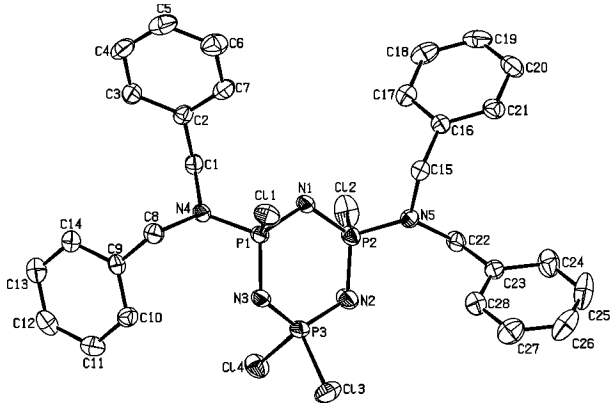


Figure 2
The molecular structure and atomic numbering scheme for (3), with protons omitted for clarity and ellipsoids shown at 30% probability.

endocyclic P—N bonds (Mani *et al.*, 1965); this corresponds to $\Delta = 0.060\ (6)$ Å for (4). For geminal derivatives, *i.e.* PR_2, both substituents supply a similar amount of electron density, which is pushed into the adjacent endocyclic PNP segments of the N_3P_3 ring; this causes a lengthening in the nearer P—N bond and a shortening in the more distant P—N bond. In other geminally disubstituted derivatives, $N_3P_3R_2Cl_4$, different Δ values were observed, as summarized in Table 4. It is found that Δ values vary from approximately 0.020 (6) Å for a spiro $P[O(CH_2)_3O]$ group (Contractor *et al.*, 1985; Alkubaisi *et al.*, 1988), to approximately 0.094 (4) Å for $P(NPPh_3)_2$ (Fincham *et al.*, 1986).

Basicity constants give a reliable indication of relative electron availability at given ring N atoms, when approached by a proton. Although electron availability in nitrobenzene solution, when the base is approached by a proton, may differ somewhat from that in the ground state as observed by crystallography, it is likely that the trend is the same when the molecule is perturbed by the approach of a positive charge (Koppel *et al.*, 2001). The α_R basicity values for the geminally disubstituted derivatives, *i.e.* $2\alpha_R$, are summarized in Table 4. Although small variations in Δ values are not very significant, it is found that the large increase in Δ values for a series of structurally related compounds (OAlk < Ph $\leq$ NR_2 < $NPPh_3$) parallels that for α_R values. In the present study this applies to (4), for which a Δ value of 0.060 (6) Å is observed (Table 4).

The results of NQR spectroscopy are directly comparable with those from crystallography, both being solid-state techniques applied to crystalline materials, and the above findings, in Table 4, are mirrored in ^{35}Cl NQR studies. A comparison has been made of the different ^{35}Cl NQR frequencies in a phosphazene molecule, where the two electron-donating substituents, *R*, in $N_3P_3Cl_4R_2$ are, respectively, geminal or non-geminal (Keat *et al.*, 1972). A straight-line relationship between P—Cl bond length and ^{35}Cl NQR frequency in chlorocyclophosphazenes has been established (Keat *et al.*, 1972) with an equation $y = -0.128x + 2.355$ [y = P—Cl bond length (Å); x = NQR frequency (MHz)]. Lower frequency values imply greater ionic character of the P—^{35}Cl bond and correspond to longer P—Cl bond lengths. Electron-donating substituents in geminal derivatives do lower the ^{35}Cl frequencies (and increase the bond lengths), namely at 77 K the mean frequencies for $N_3P_3Cl_6$ (1), $N_3P_3Cl_4Ph_2$ (4) and $N_3P_3Cl_2Ph_4$ decrease from 28.482 to 27.759 to 26.510 MHz, respectively, and the mean bond length for the same set of compounds increases from 1.984 (2) to 1.998 (3) to 2.017 (2) Å. The effect for non-geminal structures is much greater, with reductions in the ^{35}Cl NQR frequencies to 23–24 MHz and an increase in bond lengths to approximately 2.05 Å (Keat *et al.*, 1972).

In non-geminal $N_3P_3Cl_4R_2$ derivatives there is an electron donor, *R*, and electron acceptor, Cl, on the same phosphorus atom, *i.e.* P*R*Cl. The electron supply from the donor group could take one of two routes: (i) into the adjacent endocyclic PNP segments of the N_3P_3 ring, and/or (ii) into the adjacent P—Cl bonds. Investigations of the preferred route may be made by comparison of Δ values (Tables 2 and 4) and P—Cl bond lengths (Table 3). In the present study, it is observed that there are relatively minor differences between the Δ values of mono- and non-geminally disubstituted compounds (Tables 2 and 4), because the two P*R*Cl groups affect different P—N—P segments, *i.e.* for (2) $\Delta = 0.027\ (7)$ Å and for (3) $\Delta = 0.030\ (3)$ Å. Hence, for related structures having substituents with similar electron-releasing power, Δ values for P*R*Cl groups are considerably less than those for PR_2 groups, because electron density in the P*R*Cl group is diverted to the adjacently located P—Cl bond, which shows considerable bond-lengthening compared with those of PCl_2 groups (Table 3). In addition, the exocyclic P—N bond in non-geminal amino groups is shorter than comparable bonds in similar geminal structures [see values for (9) and (10) below]. The electron supply from the donor group could also take both routes and the evidence clearly indicates that both routes are operative, *i.e.* electron supply into the endocyclic segment and into the adjacent P—Cl bond.

For further comparison with the non-geminal dialkylamino derivative (3), an analogous geminal derivative was needed.

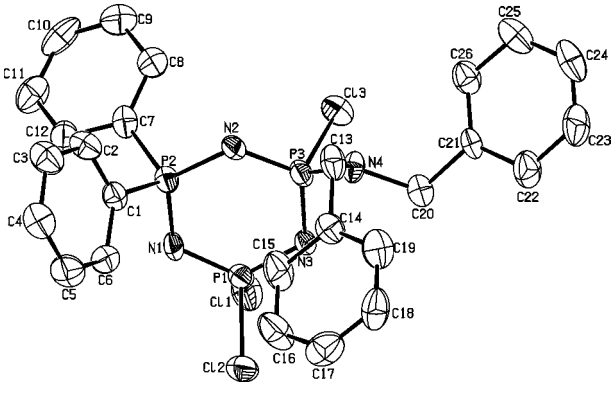


Figure 3
The molecular structure and atomic numbering scheme for (5), with protons omitted for clarity and ellipsoids shown at 30% probability.

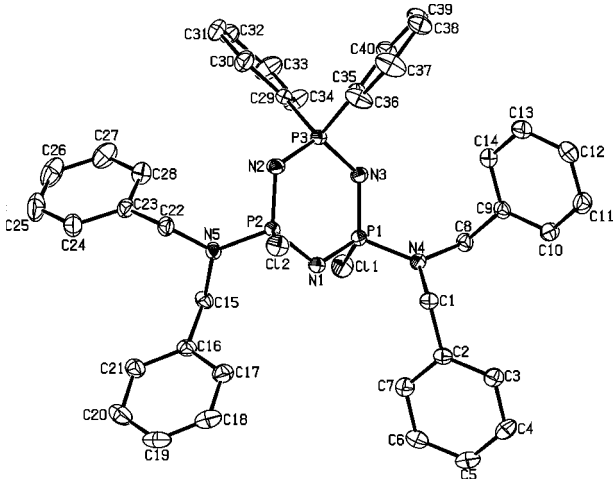


Figure 4
The molecular structure and atomic numbering scheme for (6), with protons omitted for clarity and ellipsoids shown at 30% probability.

As monofunctional dialkylamines tend to give non-geminal substitution (Shaw, 1976), a derivative of the difunctional amine $HNMe(CH_2)_3NHMe$, which tends to give spiro derivatives (Deutsch *et al.*, 1987; Deutsch & Shaw, 1988), was considered suitable. The low-temperature structure of $N_3P_3Cl_4[NMe(CH_2)_3NMe]$ (7) has been determined, giving a Δ value of 0.062 (7) Å, which is a great deal larger than the Δ value of 0.030 (3) Å of the non-geminal disubstituted compound (3), as expected. Compound (7) also shows that its four geminal P—Cl bonds have an average bond length of 2.007 (4) Å, compared with the two geminal P—Cl bonds in (3) of 2.002 (3) Å.

If the averaged endocyclic P—N bonds and the averaged P—Cl bonds of (1) are taken as standards, it can be seen that the relative bond-length changes are different in the two structurally related, but not strictly isomeric, geminal, (7), and non-geminal compounds, (3). In (7) the P—N bond is lengthened from 1.589 (2) to 1.620 (2) Å, *i.e.* by 0.031 (3) Å, while in (3) the increase is from 1.582 (2) to 1.594 (2) Å, *i.e.* by only 0.014 (3) Å. In (7) the four geminal P—Cl bonds increase from 1.984 (3) to 2.007 (3) Å, *i.e.* by 0.023 (4) Å, compared with the two geminal ones in (3), *i.e.* by 0.018 (3) Å. By contrast, the two non-geminal P—Cl bonds in this compound increase significantly to 2.042 (3) Å, *i.e.* by 0.058 (4) Å. It is concluded that electron-releasing substituents in N_3P_3 derivatives have a much greater lengthening effect on P—Cl bonds than on the endocyclic P—N bonds, and the effect is most marked in non-geminal P—Cl bonds.

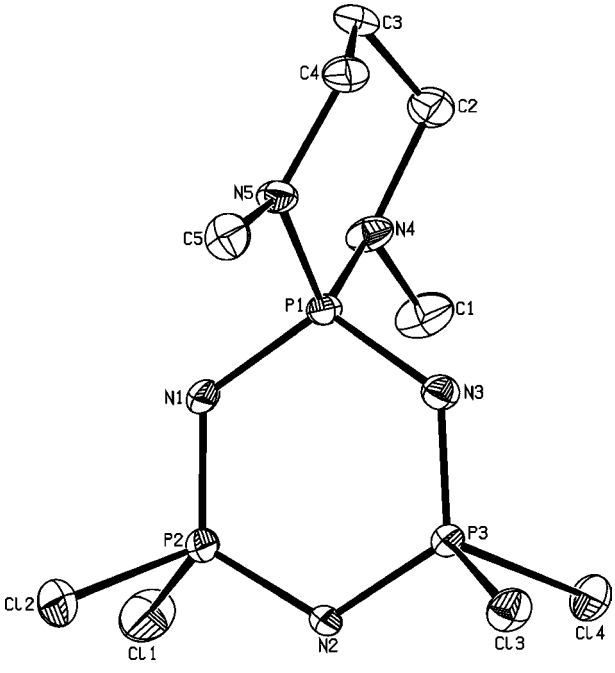


Figure 5
The molecular structure and atomic numbering scheme for (7), with protons omitted for clarity and ellipsoids shown at 30% probability.

4.1. Chemical consequences of the observed structural variations observed

A greater ionic character of the P—Cl bond in PCl*R* compared with PCl_2 moieties is also indicated by ^{35}Cl NQR measurements (Keat *et al.*, 1972). This conclusion is elegantly demonstrated by the behaviour of geminal $N_3P_3Cl_3(NMe_2)_3$, which has a PCl_2 and a $PCl(NMe_2)$ group in the same molecule (Ahmed & Pollard, 1972). It is found from the crystal structure that the P—Cl bond in the $PCl(NMe_2)$ group is considerably longer than those of the PCl_2 group. These two groups also exhibit different reactivities towards nucleophilic (*e.g.* $HNMe_2$) and electrophilic (*e.g.* Friedel–Crafts phenylation) reagents. The former reagent attacks the more electrophilic PCl_2 centre (Keat & Shaw, 1965*a*), while the latter initially attacks the more ionic P—Cl bond in the $PCl(NMe_2)$ group; further phenylation at the PCl_2 centre only takes place after this initial attack (Das, Shaw & Smith, 1973).

Treatment of (2) with an excess of dimethylamine gave rise to $N_3P_3Cl(NMe_2)_4[N(CH_2Ph)_2]$ (Hasan *et al.*, 1975), one of the few examples of a monochloropentaamino derivative, which can be readily isolated (Shaw, 1976). Under more forcing conditions, the fully aminolysed product $N_3P_3(NMe_2)_5[N(CH_2Ph)_2]$ was obtained (Hasan *et al.*, 1975). Compound (3) with the same reagent gave a monosubstituted product, $N_3P_3Cl_3(NMe_2)[N(CH_2Ph)_2]_2$, and under very forcing conditions only small amounts of a disubstituted derivative, $N_3P_3Cl_2(NMe_2)_2[N(CH_2Ph)_2]_2$.

Although (4) has a Δ value of 0.060 (3) Å, which indicates a greater deactivation towards nucleophilic attack than for (3) with Δ = 0.030 (3) Å, it does react with dibenzylamine to give (5) and (6), demonstrating that this degree of deactivation is not sufficient to prevent reaction. Hence, the smaller reduction in electrophilicity of the P atom of the PCl_2 group in (3) compared with that in (4) is unlikely to be the reason why no further reaction with dibenzylamine occurs in (3). All of the above points to the conclusion that steric effects are dominant in the reactions of dibenzylamine described in this work. Steric effects seem to limit the degree of substitution and define the stereospecificity of the reaction, as well as the stereochemistry of the products.

As a result of these studies, it is feasible to rationalize some earlier results (Alkubaisi *et al.*, 1988) on the investigation of a similar series of structures with pyrrolidine (pyr) as reagent, namely $N_3P_3Cl_4[O(CH_2)_3O]$ (8), its non-geminal dipyrrolidino derivative, $N_3P_3Cl_2(pyr)_2[O(CH_2)_3O]$ (9), and the fully aminolysed compound, $N_3P_3(pyr)_4[O(CH_2)_3O]$ (10). The respective Δ values are 0.021 (6), 0.012 (6) and −0.029 (4) Å, the negative value indicating that the relative bond lengths are now inverted and that the two geminal $P(pyr)_2$ groups push the electrons towards the $P[O(CH_2)_3O]$ moiety. The change in Δ value between (8) and (9) of 0.009 (6) Å is only a fraction of the difference of 0.041 (7) Å between those of (9) and (10), although in each case two P—Cl bonds are replaced by two P(pyr) bonds. Concomitant with the small difference in Δ value, there is the expected increase in average P—Cl bond length (see discussion above) from 1.987 (5) Å in (8)

(Contractor *et al.*, 1985) to 2.060 (8) Å (average) in (9) (Alkubaisi *et al.*, 1988). This increase in P—Cl bond length for the PCl(pyr) group over that in the PCl_2 group is accompanied by a decrease in the exocyclic bond length in the PCl(pyr) group to 1.612 (3) Å in (9) from that of 1.641 (4) Å in the geminal group $P(pyr)_2$ in (10).

5. Conclusions

Structural investigations make it clear that the apparent difficulty of introducing more than two dibenzylamino groups into the chlorocyclotriphosphazatriene molecules (1) and (4) is steric in nature. It is a combination of two effects: (i) the bulk of the substituent and (ii) the bulk of the attacking nucleophile, which is effectively demonstrated by the behaviour of (2) and (3) towards dimethylamine, as discussed above. The relative changes in P—Cl bond lengths and Δ values of endocyclic P—N bonds also explain the different points of attack preferred by nucleophilic and electrophilic reagents to geminal and non-geminal disubstitution. Electronic effects play only a minor role in this system; they affect the rates of reaction, but not the overall pattern of products. The steric bulk of the dibenzylamino group determines the *trans* disposition of disubstitution in an N_3P_3 ring, which accounts for the presence of racemates and the absence of *meso* derivatives.

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