# Structural investigations of phosphorus–nitrogen compounds. 7. Relationships between physical properties, electron densities, reaction mechanisms and hydrogen-bonding motifs of $N_3P_3Cl_{(6-n)}(NHBu^t)_n$ derivatives

Stewart W. Bartlett,[a] Simon J. Coles,[a]* David B. Davies,[b] Michael B. Hursthouse,[a] Hanife İbişoğlu,[c] Adem Kiliç,[c] Robert A. Shaw[b] and İlker Ün[c]

[a]School of Chemistry, University of Southampton, Southampton SO17 1BJ, England, [b]Birkbeck College, University of London, Malet Street, Bloomsbury, London WC1E 7HX, England, and [c]Gebze Institute of Technology, Gabze, 41400 Kocaeli, Turkey

Correspondence e-mail: s.j.coles@soton.ac.uk

A series of compounds of the $N_3P_3Cl_{(6-n)}(NHBu^t)_n$ family (where $n$ = 0, 1, 2, 4 and 6) are presented, and their molecular parameters are related to trends in physical properties, which provides insight into a potential reaction mechanism for nucleophilic substitution. The crystal structures of $N_3P_3Cl_5(NHBu^t)$ and $N_3P_3Cl_2(NHBu^t)_4$ have been determined at 120 K, and those of $N_3P_3Cl_6$ and $N_3P_3Cl_4(NHBu^t)_2$ have been redetermined at 120 K. These are compared with the known structure of $N_3P_3(NHBu^t)_6$ studied at 150 K. Trends in molecular parameters [phosphazene ring, P—Cl and P—N(HBu$^t$) distances, PCl$_2$ angles, and endo- and exocyclic phosphazene ring parameters] across the series are observed. Hydrogen-bonding motifs are identified, characterized and compared. Both the molecular and the hydrogen-bonding parameters are related to the electron distribution in bonds and the derived basicities of the cyclophosphazene series of compounds. These findings provide evidence for a proposed mechanism for nucleophilic substitution at a phosphorus site bearing a PCl(NHBu$^t$) group.

## 1. Introduction

During extensive investigations of the replacement patterns of chloride substituents in $N_3P_3Cl_6$ by amines (Shaw, 1976; Krishnamurthy et al., 1976) the following conclusions were reached:

(i) Primary amines, $H_2NR$, show a greater degree of variation in substitution patterns than secondary amines, $HNR_2$.

(ii) Most secondary amines follow a predominantly non-geminal path, in which a PCl$_2$ group is attacked in preference to a PCl(N$R_2$) group.

(iii) At disubstitution, $N_3P_3Cl_4(NHR)_2$, both geminal and non-geminal replacements occur, depending on the $R$ group. For $R$ = Et only non-geminal cis and trans derivatives were observed, for $R$ = Pr$^i$ all three isomers, geminal and non-geminal, were obtained, whilst for $R$ = Bu$^t$ only the geminal derivative was isolated. Thus, under comparable conditions, the increasing steric bulk of the $R$ group causes a change from non-geminal to geminal substitution.

(iv) At tetra-substitution, $N_3P_3Cl_2(NHR)_4$, a geminal pattern prevails.

Thus, when a cyclotriphosphazene compound containing PCl$_2$ groups is allowed to react with tertiary butylamine, $H_2NBu^t$, geminal P(NHBu$^t$)$_2$ groups are formed with very few exceptions (Das et al., 1965; Begley et al., 1979; Krishnamurthy et al., 1980, Coles et al., 2001), and so tertiary butylamine is the preferred reagent to introduce geminal P(NH$R$)$_2$ groupings into a cyclotriphosphazene derivative. The different substitu-

**Table 1**
Data collection and refinement parameters for structures (1)–(4).

| | (1) | (2) | (3) | (4) |
|---|---|---|---|---|
| **Crystal data** | | | | |
| Chemical formula | $Cl_6N_3P_3$ | $C_4H_{10}Cl_5N_4P_3$ | $C_8H_{20}Cl_4N_5P_3$ | $C_{16}H_{40}Cl_2N_7P_3$ |
| $M_r$ | 347.64 | 384.32 | 421.00 | 494.36 |
| Cell setting, space group | Orthorhombic, $Pnma$ | Monoclinic, $P2_1/c$ | Orthorhombic, $Pna2_1$ | Monoclinic, $P2_1/n$ |
| Temperature (K) | 120 (2) | 120 (2) | 120 (2) | 120 (2) |
| $a, b, c$ (Å) | 13.8572 (8), 12.8086 (11), 6.0801 (5) | 13.8045 (14), 10.7964 (16), 20.7719 (12) | 20.3441 (7), 11.9481 (4), 15.9661 (7) | 12.5207 (2), 16.1282 (2), 13.1311 (2) |
| $\beta$ (°) | 90 | 104.132 (7) | 90 | 95.9030 (10) |
| $V$ (Å$^3$) | 1079.17 (14) | 3002.1 (6) | 3880.9 (3) | 2637.59 (7) |
| $Z$ | 4 | 8 | 8 | 4 |
| $D_x$ Mg m$^{-3}$) | 2.140 | 1.701 | 1.441 | 1.245 |
| Radiation type | Mo $K\alpha$ | Mo $K\alpha$ | Mo $K\alpha$ | Mo $K\alpha$ |
| No. of reflections for cell parameters | 1403 | 6816 | 29 220 | 16 145 |
| $\theta$ range (°) | 2.9–27.5 | 2.9–27.5 | 2.9–27.5 | 2.9–27.5 |
| $\mu$ (mm$^{-1}$) | 1.99 | 1.27 | 0.85 | 0.45 |
| Crystal form, colour | Plate, colourless | Cut plate, colourless | Plate, colourless | Block, colourless |
| Crystal size (mm) | $0.50 \times 0.40 \times 0.10$ | $0.18 \times 0.10 \times 0.02$ | $0.16 \times 0.14 \times 0.06$ | $0.40 \times 0.25 \times 0.25$ |
| | | | | |
| **Data collection** | | | | |
| Diffractometer | Bruker–Nonius KappaCCD area detector | Bruker–Nonius 95 mm CCD camera on $\kappa$ goniostat | Bruker–Nonius KappaCCD area detector | Bruker–Nonius KappaCCD area detector |
| Data collection method | $\varphi$ and $\omega$ scans | $\varphi$ and $\omega$ scans | $\varphi$ and $\omega$ scans | $\varphi$ and $\omega$ scans |
| Absorption correction | Multi-scan (based on symmetry-related measurements) | Multi-scan (based on symmetry-related measurements) | Multi-scan (based on symmetry-related measurements) | Multi-scan (based on symmetry-related measurements) |
| $T_{min}$ | 0.437 | 0.804 | 0.875 | 0.842 |
| $T_{max}$ | 0.826 | 0.975 | 0.951 | 0.897 |
| No. of measured, independent and observed reflections | 7733, 1283, 1194 | 40 456, 6867, 5549 | 29 635, 8587, 5744 | 29 576, 5994, 5106 |
| Criterion for observed reflections | $I > 2\sigma(I)$ | $I > 2\sigma(I)$ | $I > 2\sigma(I)$ | $I > 2\sigma(I)$ |
| $R_{int}$ | 0.022 | 0.044 | 0.078 | 0.057 |
| $\theta_{max}$ (°) | 27.5 | 27.5 | 27.5 | 27.5 |
| Range of $h, k, l$ | $-16 \Rightarrow h \Rightarrow 18$ | $-17 \Rightarrow h \Rightarrow 17$ | $-26 \Rightarrow h \Rightarrow 24$ | $-16 \Rightarrow h \Rightarrow 16$ |
| | $-14 \Rightarrow k \Rightarrow 16$ | $-14 \Rightarrow k \Rightarrow 14$ | $-13 \Rightarrow k \Rightarrow 15$ | $-20 \Rightarrow k \Rightarrow 20$ |
| | $-7 \Rightarrow l \Rightarrow 7$ | $-26 \Rightarrow l \Rightarrow 26$ | $-20 \Rightarrow l \Rightarrow 20$ | $-17 \Rightarrow l \Rightarrow 17$ |
| | | | | |
| **Refinement** | | | | |
| Refinement on | $F^2$ | $F^2$ | $F^2$ | $F^2$ |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.028, 0.074, 1.26 | 0.034, 0.086, 1.07 | 0.053, 0.107, 1.02 | 0.038, 0.100, 1.04 |
| No. of reflections | 1283 | 6867 | 8587 | 5994 |
| No. of parameters | 62 | 370 | 414 | 270 |
| H-atom treatment | No H atoms present | Difmap | Mixture of independent and constrained refinement | Mixture of independent and constrained refinement |
| Weighting scheme | $w = 1/[\sigma^2(F_o^2) + (0.0403P)^2 + 0.3798P]$, where $P = (F_o^2 + 2F_c^2)/3$ | $w = 1/[\sigma^2(F_o^2) + (0.0415P)^2 + 1.5716P]$, where $P = (F_o^2 + 2F_c^2)/3$ | $w = 1/[\sigma^2(F_o^2) + (0.0134P)^2 + 2.2238P]$, where $P = (F_o^2 + 2F_c^2)/3$ | $w = 1/[\sigma^2(F_o^2) + (0.043P)^2 + 1.1457P]$, where $P = (F_o^2 + 2F_c^2)/3$ |
| $(\Delta/\sigma)_{max}$ | 0.005 | 0.001 | 0.011 | 0.030 |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.67, −0.68 | 0.49, −0.50 | 0.44, −0.43 | 0.27, −0.33 |
| Extinction method | $SHELXL$ | $SHELXL$ | $SHELXL$ | $SHELXL$ |
| Extinction coefficient | 0.0213 (18) | 0.0021 (2) | 0.0041 (3) | 0.0099 (11) |
| Flack parameter | – | – | Flack (1983) | – |

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

tion patterns have been explained by nucleophilic attack at different reaction sites, *viz.* at phosphorus or at the H atom of the PCl(NHR) grouping, giving rise to a proton abstraction/chloride ion elimination mechanism, which has been discussed elsewhere (Das *et al.*, 1965; Ganapathiappan & Krishnamurthy, 1987). If the P atom becomes more susceptible to nucleophilic attack, which occurs in $N_4P_4Cl_8$ (Krishnamurthy

*et al.*, 1977, 1978), the balance is tipped towards non-geminal replacements giving rise to PCl(NHBu$^t$) groups. $H_2$NBu$^t$ is the most sterically hindered of the primary amines discussed, which is also borne out by the fact that under many reaction conditions only tetra-substitution, $N_3P_3Cl_2(NHBu^t)_4$, is usually achieved (Das *et al.*, 1965), although the fully substituted derivative, $N_3P_3(NHBu^t)_6$, can be obtained under very drastic

conditions (Das *et al.*, 1965; Bickley *et al.*, 2003). Whilst many other phosphazene derivatives containing P—Cl and P—NHR groupings are rather unstable, this does not seem to apply to tertiary butylamino derivatives. Following previous work (Beşli, Coles, Davies, Hursthouse, Kiliç, Mayer & Shaw, 2002; Beşli, Coles, Davies, Hursthouse, Kiliç, Mayer, Shaw & Yenilmez, 2002; Coles, Davies, Eaton, Hursthouse *et al.*, 2004) the crystal structures of a series of tertiary butylamino derivatives of cyclophosphazene have been determined, and their molecular parameters and hydrogen-bonding motifs are discussed in the light of the chemical and physical properties of the compounds.

## 2. Experimental

### 2.1. Preparation of compounds

Hexachlorocyclotriphosphazene (1) (15 g, 43.16 mmol) and *tert*-butylamine (12.6 g, 173 mmol) were dissolved in dichlor-

omethane (200 ml) under argon pressure in a 250 ml three-necked round-bottomed flask. The reaction mixture was stirred and refluxed in an oil-bath for 6 d. *tert*-Butylamine hydrochloride was filtered off and the solvent was removed at 303 K. Two compounds were detected by thin-layer chromatography [$R_f$ = 0.6 (2) and 0.3 (3), $N_3P_3Cl_4(NHBu^t)_2$], using dichloromethane–*n*-hexane (1:2) as the mobile phase. The crude product was subjected to column chromatography on silica gel using dichloromethane–*n*-hexane (1:2) as the eluant. 1-*tert*-Butylamino-1,3,3,5,5-pentachlorocyclotriphosphazatriene (2) was separated and recrystallized from *n*-hexane. Found: C 12.56, H 2.74, N 14.66%; $(M+H)^+$, 384 $C_4H_{10}Cl_5N_4P_3$; requires: C 12.50, H 2.62, N 14.58%; *M* 383.34. M.p. 319 K [literature 262–263 K (Das *et al.*, 1965); 383 K (Begley *et al.*, 1979)]. Yield 2 g, 21%. 1,1-Bis(*tert*-butylamino)-3,3,5,5-tetrachlorocyclotriphosphazene (3) was separated and recrystallized from *n*-hexane–dichloromethane (1:1). Found: C 22.74, H 4.68, N 16.15%; $(M+H)^+$, 421 $C_8H_{20}Cl_4N_5P_3$; requires: C 22.82, H 4.79, N 16.63%; *M* 421. M.p. 393–395 K [literature 393–395 K (Das *et al.*, 1965); 394 K (Begley *et al.*, 1979)]. Yield 4.35 g, 24%.

Details of the preparation of $N_3P_3Cl_2(NHBu^t)_4$ (4) have been reported elsewhere (Das *et al.*, 1965), with m.p. = 429 K from light petroleum.

### 2.2. 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 ($\lambda_{Mo\,K\alpha}$ = 0.71073 Å). Structures were solved and refined using the *SHELX97* (Sheldrick, 1997) suite of programs. Data were corrected for absorption effects by means of comparison of equivalent reflections using the program *SORTAV* (Blessing, 1997). Non-H atoms were refined anisotropically, whilst H atoms were located from a difference map and freely refined isotropically for all N-bound H atoms, whereas all methyl H atoms were located in idealized positions according to a riding model, with their displacement parameters based on the values of their parent atoms. Compound (3) exhibited some rotational disorder in one Bu$^t$ group. It also crystallized in a chiral space group with a Flack (1983) parameter that refined to a value of 0.08 (8), and hence it can be assumed that the correct absolute structure has been determined. Pertinent data collection and refinement parameters are collated in Table 1.[1]

## 3. Discussion

### 3.1. Molecular structures

Changes in molecular parameters of cyclophosphazene derivatives have been investigated as a function of substituents at fixed positions (Coles, Davies, Hursthouse *et al.*, 2004); the overall architecture of these molecules remained
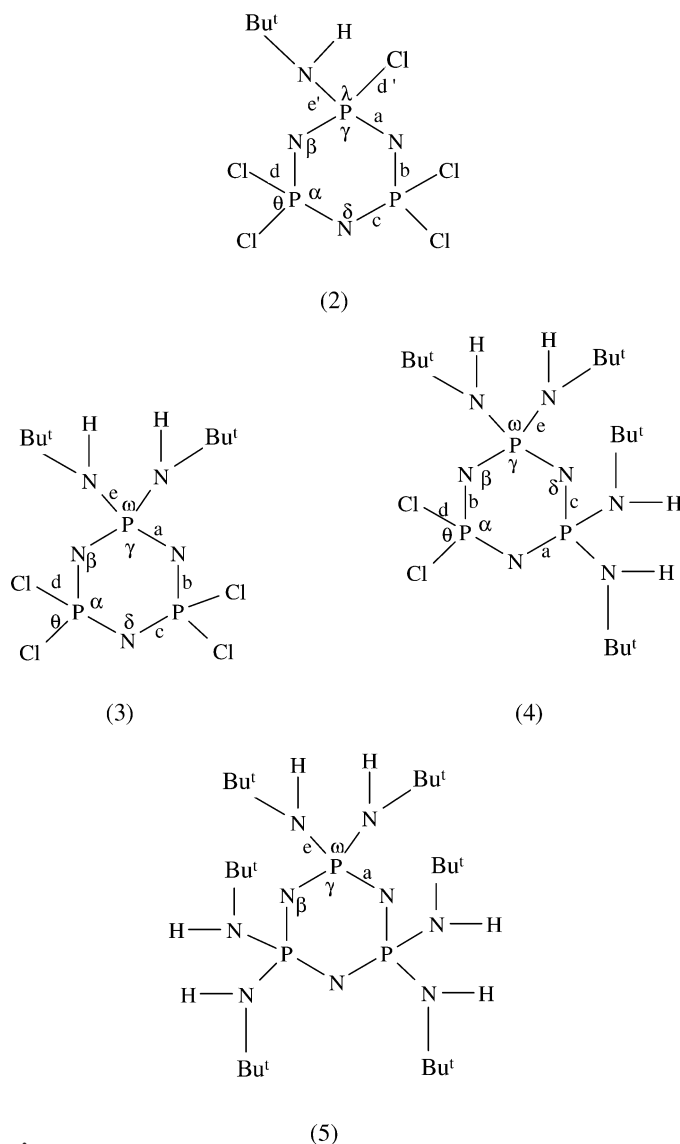


**Figure 1**
Designation of molecular parameter descriptors for (1)–(5).

**Table 2**
Selected molecular parameters for structures (1)–(5).

|  | (1) | (2) | (3) | (4) | (5) |
|---|---|---|---|---|---|
| $a$ | 1.577 (3) | 1.594 (2) | 1.619 (1) | 1.623 (2) | 1.578 (4) |
| $b$ | – | 1.567 (2) | 1.556 (1) | 1.560 (2) | – |
| $\Delta$(P–N) = $a - b$ | – | 0.027 (2) | 0.063 (1) | 0.063 (2) | – |
| $c$ | – | 1.575 (2) | 1.577 (1) | 1.598 (2) | – |
| $d$ | 1.986 (3) | 1.991 (1) | 2.003 (2) | 2.034 (1) | – |
| $d'$ | – | 2.017 (1) | – | – | – |
| $e$ | – | – | 1.616 (1) | 1.644 (2) | 1.638 (4) |
| $e'$ | – | 1.600 (2) | – | – | – |
| $\alpha$ | 118.5 (2) | 119.2 (1) | 119.9 (3) | 121.3 (1) | – |
| $\beta$ | 121.1 (2) | 121.6 (1) | 123.5 (2) | 121.9 (1) | 121.9 (2) |
| $\gamma$ | – | 116.9 (1) | 112.3 (2) | 114.4 (1) | 115.9 (2) |
| $\delta$ | – | 120.6 (1) | 118.4 (2) | 126.7 (1) | – |
| $\theta$ | 101.9 (1) | 101.2 (1) | 99.3 (1) | 98.0 (1) | – |
| $\omega$ | – | – | 104.8 (2) | 102.5 (1) | 101.7 (2) |
| $\lambda$ | – | 107.4 (1) | – | – | – |
| $\Sigma$N | – | 358.3 (1) | 358.8 (2) | 353.7 (1) | 355.1 (2) |

the same, and so the designation of bond length and bond angle parameters was unambiguous for such a series of compounds. The molecules in the present study have different degrees of substitution of Cl atoms by NHBu$^t$ residues, and this situation requires some modifications in the designation of their molecular parameters, as summarized in Fig. 1. The endocyclic bond angle $\alpha$ is defined as N—P$(X)_2$—N, the endocyclic bond angle $\beta$ as $(Y)_2$P—N—P$(X)_2$ or $(XY)$P—N—P$(X)_2$, the endocyclic bond angle $\gamma$ as N—P$(XY)$—N or N—P$(Y)_2$—N and the endocyclic bond angle $\delta$ as $(X)_2$P—N—P$(X)_2$ or $(Y)_2$P—N—P$(Y)_2$, where $X$ = Cl and $Y$ = NHBu$^t$. Analogous descriptions apply to definitions of the endocyclic bond lengths $a$, $b$, $c$ etc., as summarized in Fig. 1. Selected molecular parameters for all the crystal structures used in this comparison are given in Table 2.

Although the room-temperature molecular structure of $N_3P_3Cl_6$ (1) had been reported (Bullen, 1971), a low-temperature structure (depicted in Fig. 2) was determined for the purposes of accurate comparison in this study.

The structures of the two chemically equivalent molecules in the asymmetric unit of $N_3P_3Cl_5(NHBu^t)$ (2) are shown in Fig. 3, and a number of structural differences from (1) are observed. There is a significant decrease in $\gamma$, with a corresponding increase in $\beta$, and smaller changes are observed in $\alpha$ and $\delta$. There is a marked increase in bond length $a$ and a marked decrease in $b$, whereas $c$ is largely unaffected. The non-geminal P—Cl bond, $d'$, is longer than the corresponding bond lengths, $d$, of the PCl$_2$ group. The opposite behaviour is observed for the exocyclic P—N bond length $e'$, which is substantially shorter than those in geminal groups, $e$. Both effects have been observed in similar structures (Ahmed & Pollard, 1972; Ahmed & Gabe, 1975; Ahmed & Fortier, 1980; Alkubaisi et al., 1988; Beşli, Coles, Davies, Hursthouse, Kilic, Mayer, Shaw & Yenilmez, 2002; Coles, Davies, Eaton et al., 2004; Beşli, Coles, Davies, Hursthouse et al., 2004; Beşli, Coles, Davies, Eaton et al., 2004). The sum of the bond angles around the exocyclic N atom [358.3 (1)°] shows that it has trigonal planar character.

Although the crystal structure of $N_3P_3Cl_4(NHBu^t)_2$ (3) had been previously determined (Begley et al., 1979), the study was performed at room temperature and the data were of insufficient quality to determine H-atom positions. As (3) is a typical example of a geminally disubstituted derivative of the type, $N_3P_3Cl_4R_2$, where $R$ is a strongly electron-releasing substituent, an accurate structure (shown in Fig. 4) was determined at low temperature, so that the molecular parameters could be included in this work. The structure exhibits two chemically equivalent molecules in the asymmetric unit. The bond lengths $a$ of 1.619 (1) Å are relatively long, whereas those for $b$ of 1.556 (1) Å are relatively short, giving a $\Delta$(P—N) (= $a - b$) value of 0.063 (1) Å, one of the largest observed from a survey of the Cambridge Structural Database (CSD; Allen, 2002). Concomitantly, there is a very small bond angle $\alpha$ of 112.3 (2)° and a very large $\beta$ angle of 123.5 (2)°. The exocyclic P—N bond length, $e$, of 1.616 (1) Å is quite short for this type of bond, indicating extensive back-donation of the
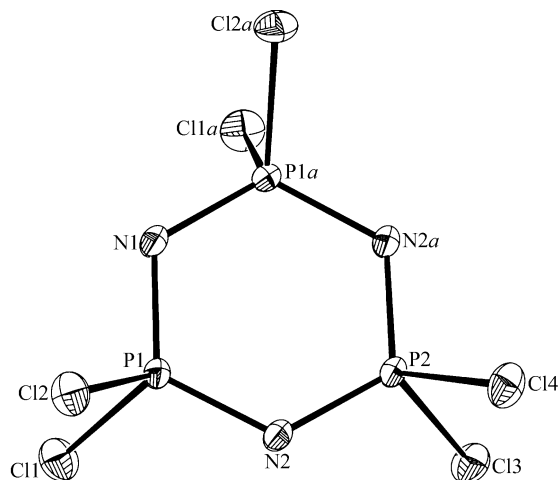


**Figure 2**
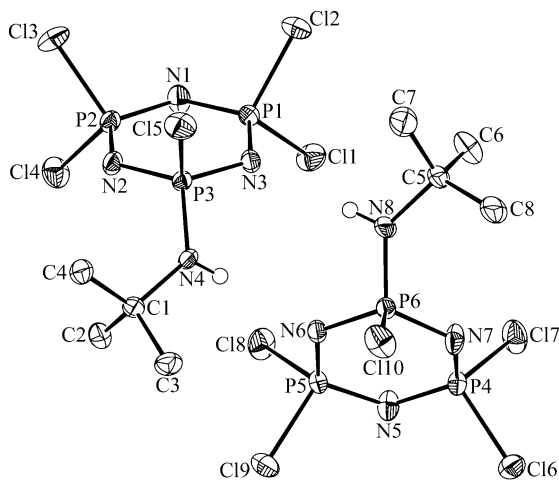The molecular structure and numbering scheme of (1).



**Figure 3**
The molecular structure and numbering scheme of (2).

**Table 3**
Geometric parameters for NH—Bu$^t$ groups.

| Compound | Torsion angles of NHBu$^t$ substituents to both adjacent ring N atoms | | C···C separations between central atoms on adjacent NHBu$^t$ groups |
|---|---|---|---|
| (2) Molecule A | 31.9 (5) | 162.5 (4) | |
| Molecule B | −41.1 (5) | −171.5 (5) | |
| | | | |
| (3) Molecule A | 41.2 (5) | −82.1 (5) | 4.72 |
| | 49.0 (5) | 172.5 (5) | |
| Molecule B | −37.8 (5) | 86.8 (5) | 4.68 |
| | −51.3 (6) | −174.4 (5) | |
| | | | |
| (4) Molecule A | −43.07 (16) | 84.84 (16) | 4.74 |
| | −42.2 (2) | 85.23 (19) | 4.75 |
| | −37.63 (17) | −162.53 (15) | |
| | −32.4 (2) | −158.29 (17) | |
| | | | |
| (5) Molecule A | −63.84 | 79.70 | 4.579 |
| | −61.85 | −83.88 | 4.605 |
| | −51.52 | 83.18 | 4.548 |
| | 59.28 | 170.73 | |
| | 45.75 | 171.70 | |
| | −45.32 | −173.10 | |
| | | | |
| Molecule B | 59.80 | 79.12 | 4.575 |
| | −63.30 | −81.27 | 4.569 |
| | −60.85 | 84.54 | 4.554 |
| | −49.67 | 169.13 | |
| | 48.31 | 172.77 | |
| | −45.01 | 173.10 | |

lone-pair of electrons on the N atom towards the P atom. This bond shortening might have been even greater were it not for the conformation of the NHBu$^t$ substituents, one of which is in almost a complete Type II conformation, while the other is between Type I and III [an explanation of these conformational types is given by Fincham *et al.* (1986)]. The back-donation is also demonstrated by the sum of the bond angles around the exocyclic N atoms of 358.8 (2)°, showing their trigonal planar character. Increases in P—Cl bond lengths, *d*, and a decrease in bond angle Cl—P—Cl, *ω*, are also noted.

The crystal structure of N$_3$P$_3$Cl$_2$(NHBu$^t$)$_4$ (4) is presented in Fig. 5. The effect on molecular parameters resulting from the large electron-releasing capacity of the NHBu$^t$ substituents is also demonstrated in this compound, as the changes in some parameters are further enhanced compared with the disubstituted compound (3). The bond angle *α* of 114.4 (1)° bears this out, as do the respective bond lengths *a* and *b* of 1.623 (2) and 1.560 (2) Å, giving a Δ(P—N) value of 0.063 (2) Å. The averaged sum of bond angles around the exocyclic N atoms of 353.7 (1)° is the lowest in this series of compounds and indicates the greatest deviation from a trigonal planar structure.

The low-temperature structure of N$_3$P$_3$(NHBu$^t$)$_6$ (5) has been reported previously (Bickley *et al.*, 2003) with the CSD refcode GUZVIG, and is used for comparison in this study. As expected for such a symmetrically substituted derivative, there are no statistically significant variations in the endocyclic P—N bond lengths. The averaged sum of the bond angles around the exocyclic N atoms of 355.1 (2)° is also somewhat lower than those for (2) and (3).

A measure of the conformational orientation of the NHBu$^t$ groups relative to each other is given by the torsion angle to both adjacent ring N atoms. A measure of the close-packed nature of the NHBu$^t$ groups is given by the non-bonded separation of the central C atoms between adjacent moieties (Table 3). It can be seen from Table 3 that there is a general decrease in this C···C distance for a corresponding increase in the number of NHBu$^t$ groups situated about the N$_3$P$_3$ core. This trend is indicative of the fact that these groups are more tightly clustered around the core and hence impede any interactions with it, owing to an increase in steric hindrance. Another indication of the close-packed nature of the NHBu$^t$ groups is the dihedral angle between the plane of the N$_3$P$_3$ ring and the orientation of the NHBu$^t$ group with respect to the P—N bond (Table 3). With an increasing number of NHBu$^t$ groups there is, on average, a corresponding increase in the torsion angle, indicating that this group must increasingly twist away from its sterically unhindered optimal position.

### 3.2. Hydrogen bonding

The hydrogen bonding in the crystal structure of (2) is depicted in Fig. 6, which shows the formation of discreet head-to-tail dimers containing an eight-membered ring as a result of
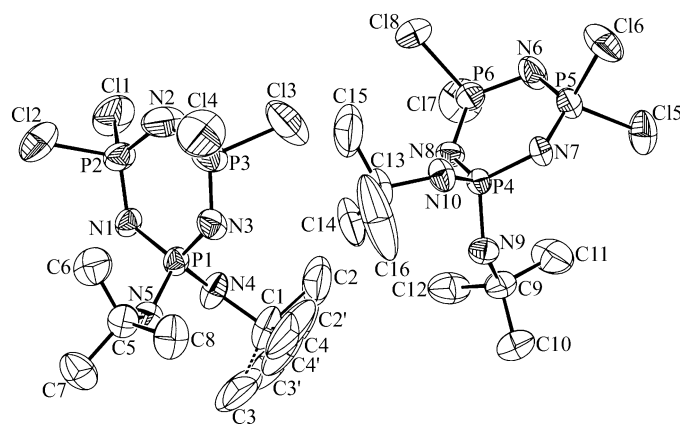


**Figure 4**
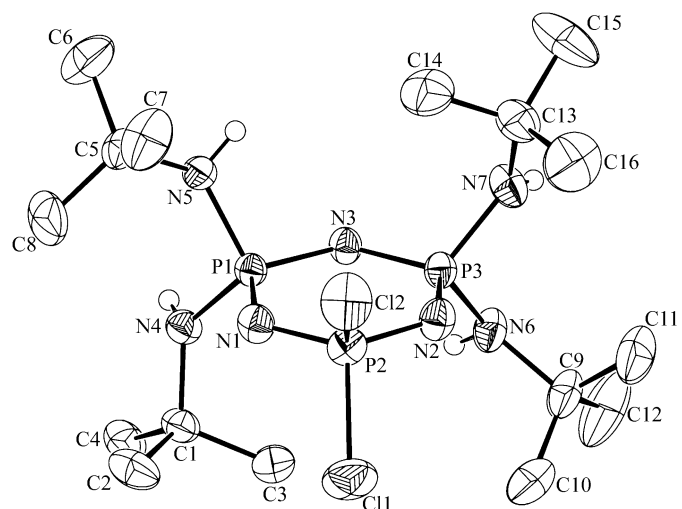The molecular structure and numbering scheme of (3).



**Figure 5**
The molecular structure and numbering scheme of (4).

donation from the Bu$^t$N—H group to the ring N atom of another molecule. The conformation of this ring is approximately saddle-shaped, with slightly different distances between donor and acceptor atoms, of 3.079 (4) and 3.095 (4) Å, respectively.

The hydrogen bonding in the crystal structure of (3) is presented in Fig. 7 and leads to the formation of a similar structural arrangement to (2), where the intermolecular hydrogen bonds form an eight-membered ring of complementary dimers. The corresponding donor–acceptor separation distances of (3) are 3.123 (3) and 3.167 (4) Å, respectively, making them somewhat longer than those in (2).

The hydrogen bonding exhibited by (4) forms a similar dimer motif (Fig. 8), although the conformation of the eight-membered ring differs in that it is a boat form with the P atoms at the apices and the central six atoms coplanar. The symmetric N$\cdots$N distances, with a value of 3.392 (4) Å, are even longer than in (3), indicating weaker hydrogen bonding, which presumably arises from an increase in steric hindrance in the hydrogen-bonding region.

Bickley et al. (2003) reported no hydrogen bonding in the crystal structure of $N_3P_3(NHBu^t)_6$ (5). As the shortest N$\cdots$N separation in the structure is 4.950 (5) Å there is certainly no sign of a hydrogen bond from any Bu$^t$N—H group to a ring N atom. There may be a very weak intramolecular interaction from one NHBu$^t$ group to another NHBu$^t$ group in a cis non-geminal position, because there are two of these interactions having separations of 3.751 (5) and 3.766 (5) Å in chemically identical environments in the two molecules composing the asymmetric unit.

## 3.3. Structure–property relationships

The molecular parameters of (2)–(5) are discussed in terms of the basicity of each molecule. The NHBu$^t$ substituent is one of the most base-strengthening primary amino residues so far investigated, with a substituent constant $\alpha_R$ value of 5.9 (Feakins et al., 1969). The basicities of the more basic compounds $N_3P_3(NHBu^t)_6$ and $N_3P_3Cl_2(NHBu^t)_4$ have been measured in nitrobenzene solution with values of 8.0 and 4.35, respectively (Feakins et al., 1964). In fact, the basicity of 8.0 for

(4) would be $\sim$ 9.9, if allowance were made for the saturation effect (Feakins et al., 1969). The basicity values of the remaining derivatives have been obtained by summation of known substituent basicity constants ($\Sigma\alpha_R$) according to the previously described (Beşli, Coles, Davies, Hursthouse, Kilic, Mayer & Shaw, 2002), viz. −20.3, −14 and −8 for (1), (2) and (3), respectively. These $\Sigma\alpha_R$ values span a range of 30 p$K_a$ units.

**3.3.1. Molecular structures.** Although the preparation of (2) has been published on two occasions, different physical properties were reported; the first report (Das et al., 1965) gave a melting point of 262–263 K and later a $^{31}$P NMR spectrum with absorptions at 16.0 and −5.3 p.p.m. (Keat et al., 1976). The sample of (2) prepared for this study has a melting point of 319 K and a $^{31}$P NMR spectrum with absorptions at 21.1 and 13.45 p.p.m. The fact that the structure is confirmed by X-ray crystallography (Fig. 3) indicates that the former report must have been incorrectly assigned to a different product. The second report (Begley et al., 1979) gave a melting point of 383 K for (2), which may indicate a different polymorph, and investigations into this result are underway.

The electron-donating power of the NHBu$^t$ group is demonstrated by the $\Delta$(P—N) values of (2), (3) and (4), which are 0.027 (2), 0.063 (1) and 0.063 (2) Å, respectively (Table 2).
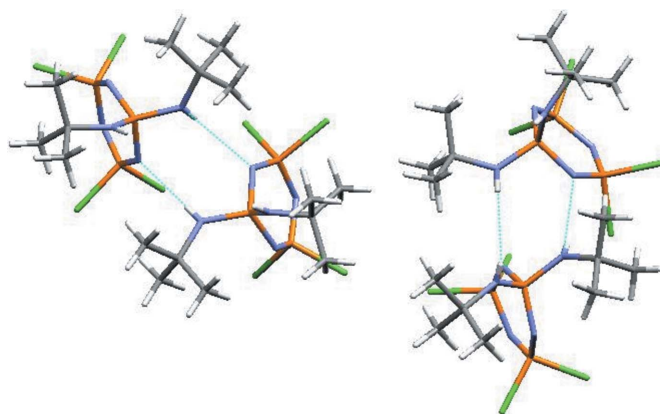


**Figure 7**
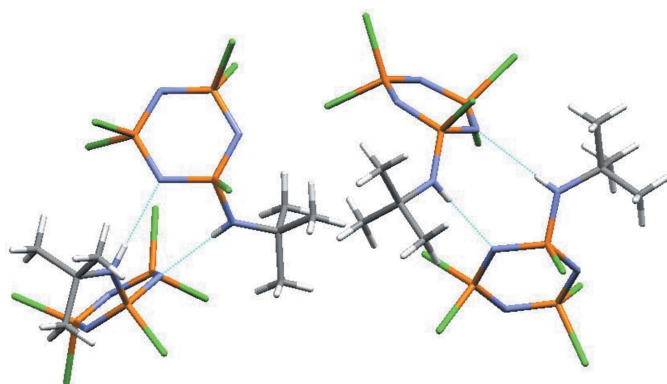The hydrogen-bonded structure formed by (3).



**Figure 6**
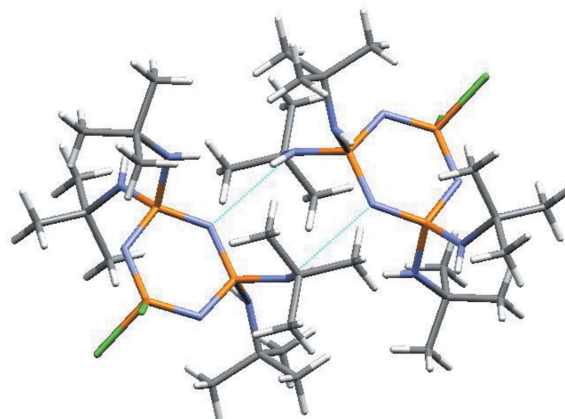The hydrogen-bonded structure formed by (2).



**Figure 8**
The hydrogen-bonded structure formed by (4).

**Table 4**
Sum of substituent basicity constants ($\sum \alpha_R$), geometric parameters and averaged $^{35}Cl$ NQR frequencies of the $PCl_2$ group of (1)–(4), (6) and (7).

Compounds $N_3P_3Cl_4Ph_2$ (6) and $N_3P_3Cl_2Ph_4$ (7) are included for comparison purposes.

| Compound | Molecular formula | P—Cl (Å) | Cl—P—Cl (°) | $\sum \alpha_R$ | Averaged $^{35}Cl$ NQR frequencies (77 K) (MHz) |
|---|---|---|---|---|---|
| (1) | $N_3P_3Cl_6$ | 1.986 (3) | 101.9 (1) | 0.0 | 28.482 |
| (2) | $N_3P_3Cl_5(NHBu^t)$ | 1.991 (1) | 101.2 (1) | 5.9 | – |
| (6) | $N_3P_3Cl_4Ph_2$ | 1.998 (6) | 100.3 (2) | 8.4 | 27.759 |
| (3) | $N_3P_3Cl_4(NHBu^t)_2$ | 2.003 (2) | 99.3 (1) | 11.8 | 27.481 |
| (7) | $N_3P_3Cl_2Ph_4$ | 2.017 (4) | 98.5 (2) | 16.8 | 26.511 |
| (4) | $N_3P_3Cl_2(NHBu^t)_4$ | 2.034 (1) | 98.0 (1) | 23.6 | 26.398 |

As indicated by the results above, a simple additive behaviour is not expected for endocyclic parameters. For (2), in particular, some of the electron density appears to be diverted into lengthening the $P(NHBu^t)$—Cl bond, which at 2.017 (1) Å is considerably longer than the other P—Cl bonds in this compound. There are substantial changes in some bond angles, but again these are non-uniform, e.g. reduction in $\alpha$.

In contrast to the non-uniform changes in endocyclic parameters, the exocyclic values follow uniform and consistent trends. The effect of the electron-releasing capacity of the substituents on the average values of the P—Cl bonds and the Cl—P—Cl bond angles in the remaining $PCl_2$ groups are compared with the sum of the substituent basicity constants ($\sum \alpha_R$) in Table 4, where the structures of some related $PPh_2$

derivatives have been included, viz. $N_3P_3Cl_4Ph_2$ (6) (Mani et al., 1965) and $N_3P_3Cl_2Ph_4$ (7) (Mani et al., 1966). In this series of compounds there is a good correlation between the increase in P—Cl bond length and the increase in $\sum \alpha_R$, as shown graphically in Fig. 9(a). Although the changes are small for the disubstituted compounds in this sequence, they are in keeping with the electron-supplying properties discussed above. For the tetrasubstituted compounds the effects on the P—Cl bond lengths are rather larger, as expected, because the effects of four donor groups are spread over only two P—Cl bonds, whereas the effects of two donors are spread over four P—Cl bonds for the disubstituted derivatives. A similar explanation can account for the concomitant decrease in Cl—P—Cl bond angles with $\sum \alpha_R$ (shown graphically in Fig. 9a), which is expected from a lengthening of the P—Cl bonds.

The above linear relationships are mirrored in a number of other physical properties. In a study of the Faraday effect of some aminochlorocyclotriphosphazenes in $CCl_4$ solution, it was noted that in a plot of the number of amino substituents versus the molecular magnetic rotation geminal derivatives gave a good straight-line relationship, whilst non-geminal derivatives showed positive deviations (Bruniquel et al., 1973). A possible explanation of these observations is that the former only depends on electron distributions within the plane of the $N_3P_3$ ring, whereas in the latter there is ample evidence from crystallographic data that there is an electron transfer, which changes the parameters of substituents above and below this ring.



**Figure 9**
Correlation between (a) the sum of substituent basicity constants ($\sum \alpha_R$) and (b) averaged $^{35}Cl$ NQR frequencies (MHz) for P—Cl bond lengths and Cl—P—Cl bond angles for data presented in Table 4.

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In this study a significant correlation has been observed between molecular parameters and $^{35}Cl$ NQR frequencies of $PCl_2$ groups of cyclophosphazene derivatives, perhaps because this technique deals with crystalline substances as does crystallography. It has been shown previously that a linear relationship exists between $^{35}Cl$ NQR frequencies and the P—Cl bond lengths both for Ph derivatives (Keat et al., 1972) and for NHBu$^t$ derivatives (Sridharan et al., 1980). It is found that such a relationship holds for the compounds reported in this study and that it also extends to their Cl—P—Cl bond angles (Fig. 9b). These results are also important because the observed linear correlations between molecular parameters and a physical parameter ($^{35}Cl$ NQR frequency) for molecules in the solid state are mirrored in the analogous dependence on a physical parameter (sum of substituent basicity constants, $\sum\alpha_R$) for molecules in the solution state.

The structural data also permit some tentative conclusions to be drawn as to why there is a mono, $N_3P_3Cl_5(NHBu^t)$, but no tris derivative, $N_3P_3Cl_3(NHBu^t)_3$, because the successive substitutions of the cyclophosphazene group change molecular parameters, particularly the P—Cl bond lengths. There is now a good deal of evidence for a hydrogen abstraction/chloride ion elimination mechanism leading to a trigonal planar intermediate, which then reacts rapidly with any nucleophile present (Das et al., 1965; Ganapathiappan & Krishnamurthy, 1987). The proposed mechanism for nucleophilic substitution at a phosphorus site bearing an NHBu$^t$ group is shown in Fig. 10. When $X$ = Cl, which is electron withdrawing, the proton abstraction by base is reversible, which was clearly shown by a $D_2O$ shake-up in proton NMR spectroscopy to eliminate the N–H coupling in (3) and (4) (Das et al., 1965). If $X$ = NHBu$^t$, which is a strongly electron-supplying group, proton abstraction is irreversible and thus prevents isolation of the tris derivative.

**3.3.2. Hydrogen-bonding trends.** Compounds (2), (3) and (4) form eight-membered-ring hydrogen-bonded dimers, with the rings in a saddle shape for (2) and (3) and a boat
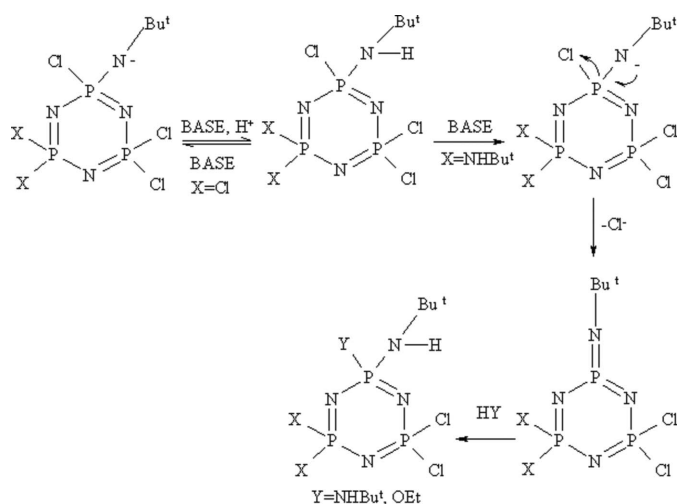
conformation for (4). The increase in average N···N distances for (2) (3.087 Å), (3) (3.145 Å) and (4) (3.392 Å) are probably due to steric crowding. There are no intermolecular hydrogen bonds for (5), which is a result of the steric shielding of the potential acceptor N atoms in the cyclophosphazene core of the molecule.

The position of protonation of cyclophosphazene derivatives was originally deduced to be the ring N atoms from potentiometric studies, and this hypothesis was later proven by crystallography (Mani & Wagner, 1971; Shaw, 1976). These same N atoms are involved in the observed hydrogen-bonding patterns. However, the weakest base (2) seems to form the strongest hydrogen bonds, and the strongest base (5) does not form any intermolecular hydrogen-bonded interactions. Undoubtedly steric hindrance must be the cause, a conclusion supported by the geometric and conformational results (see above) regarding the relative conformations of the NHBu$^t$ groups.

## 4. Conclusions

This is the first series of products from reaction of $N_3P_3Cl_6$ with a given amine (in this case a bulky primary amine, $H_2NR$), where all the compounds have been characterized crystallographically. The three hydrogen-bonded dimers show two types of eight-membered ring conformation; one is saddle shaped with slightly different hydrogen bridges for $N_3P_3Cl_5(NHBu^t)$ and $N_3P_3Cl_4(NHBu^t)_2$, whereas for $N_3P_3Cl_2(NHBu^t)_4$ the two intermolecular hydrogen-bonded bridges are identical and the conformation is that of a boat. The changes in observed molecular parameters show good correlation with changes in other physical properties, such as the substituent basicity constants, the Faraday effect, some $^{31}P$ NMR parameters and $^{35}Cl$ NQR frequencies. In spite of the much increased basicity of the ring N atoms, the capacity for intermolecular hydrogen-bonding decreases from the mono-substituted compound, $N_3P_3Cl_5(NHBu^t)$, to $N_3P_3Cl_2(NHBu^t)_4$ and has disappeared altogether for $N_3P_3(NHBu^t)_6$. This behaviour is attributed to steric hindrance. The change in molecular parameters with increasing replacement of Cl atoms by NHBu$^t$ groups gives rise to regular changes for exocyclic parameters, but is somewhat erratic for endocyclic parameters because of the different degrees and positions of substitution.

**Figure 10**
Proposed mechanism for nucleophilic substitution at a phosphorus site bearing an NHBu$^t$ group.

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