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# Aminolysis of *P*-Trichloro-*N*-dichlorophosphorylmonophosphazene and the Crystal Structure of 1-(Dichlorophosphinyl)-2-chloro-2,2-bis(diisopropylamino)phosphazene

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## ABSTRACT

*The reactions of $Cl_3P{=}N{-}P(O)Cl_2$ (**1**) with primary and secondary amines have been studied. The following monophosphazenes, $(RRN)_3P{=}N{-}P(O)(NRR)_2$, and bis(phosphinoyl)amines, $[(RRN)_2P(O)]_2NH$ were isolated: NRR = $NHCH_2Ph$, $NEt_2$, $NH(CH_2)_2CH_3$ groups for monophosphazenes, and $NEt_2$, $NH(CH_2)_2CH_3$ for phosphinoyl amines. The unexpected geminal phosphazene, $Cl(RRN)_2P{=}N{-}P(O)Cl_2$, {RRN = $N[CH(CH_3)_2]_2$}, was also obtained in moderate yield. The spectral data (IR, $^1H$, $^{13}C$, and $^{31}P$ NMR, and MS) are presented. The structure of 1-(dichlorophosphinyl)-2-chloro-2,2-bis(diisopropylamino)phosphazene (**5**) was determined by X-ray crystallography. The basicities of these and related compounds in nonaqueous nitrobenzene solution were obtained by potentiometric titration.*

## *INTRODUCTION*

During the last decade, *P*-trichloro-*N*-dichlorophosphorylmonophosphazene, $Cl_3P{=}N{-}P(O)Cl_2$, (1) and its derivatives have been of considerable interest for a number of reasons. (1) Thermolysis of compound **1** leads to the elimination of phosphorus oxychloride, $P(O)Cl_3$, and polydichlorophosphazene, $(NPCl_2)_n$ [2]. This is a new route to polydichlorophosphazene based on the polycondensation reaction of **1**. Extensive work has also been done on the polymerization of **1** by De Jaeger and co-workers since 1982 [3]. This area is probably the most significant aspect of **1** chemistry.

$$Cl_3P{=}N{-}P(O)Cl_2 \rightarrow (NPCl_2)_n + P(O)Cl_3$$

(2) Aminolysis of compound **1** with an excess of amines gives, generally, penta-amides, $(RRN)_3P{=}N{-}P(O)(RRN)_2$, and symmetric hydrolysis products, bis(phosphinoyl)amines, $(RRN)_2P(O){-}NH{-}P(O)(RRN)_2$, in lesser yield [1,4]. (3) Reversible silyl group migration (O → O) [5] and irreversible alkyl group migration (O → O and O → N) [6] have been observed for compound **1** derivatives. Compound **1** and its derivatives (which are structurally relatively simple compounds) have also found some applications in preparative chemistry [7–9]. The reactions of compound **1** with amines and alcohols have been reviewed [10,11]. The successful replacement of one chlorine atom by the allyloxy group has been made [12]. Partial aminolysis of compound **1** with methylamine and *t*-butylamine,

Phosphorus–Nitrogen Compounds. Part 2 [1].
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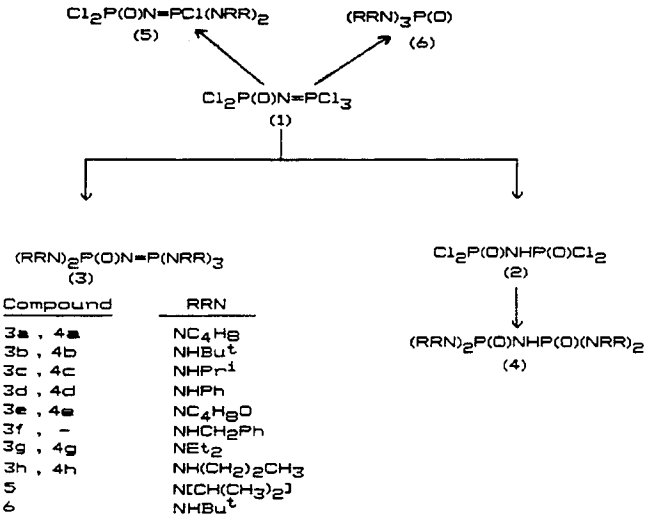


**SCHEME 1**

respectively, has also been described by Bulloch and Keat [13]. The structures of $Cl_3P{=}N{-}P(O)Cl_2$ (**1**) and its penta-amide, $(PhNH)_3P{=}N{-}P(O)(NHPh)_2$, have been determined by X-ray crystallography [14].

## *RESULTS AND DISCUSSION*

Because of the synthetic, spectroscopic, and mechanistic interest concerning amine-linked acyclic phosphazenes, we have previously prepared some derivatives of compound **1** [1,4]. When compound **1** was subjected to reaction in acetonitrile with an excess of primary and secondary amines, two kinds of products were obtained, e.g., fully substituted mono-phosphazenes (penta-amides), $(RRN)_3P{=}N{-}P(O)(NRR)2$ (**3**), as major products, and bis(phosphinoyl)amines (tetra-amides), $[(RRN)_2P(O)]_2NH$ (**4**) (RRN = NHEt, $NHPr^i$, $NHBu^t$, NHPh, pyrrolidino, piperidino, and morpholino), as minor products [1,4] (Scheme 1).

The tetra-amides, which are the symmetric aminolysis products of $[Cl_2P(O)]_2NH$ (**2**), were always present in lower yields than the penta-amides. They are easily distinguished by their $^{31}P$ NMR spectra. When $^{31}P$ NMR spectra of the reaction mixtures are recorded, penta- and tetra-amides give AX and $A_2$ type spectra, respectively [1,4]. In order to gain more knowledge of bulky steric effects, compound **1** was subjected to reaction in acetonitrile with an excess of amine, and, except for the use of diisopropylamine, the expected penta-amide (**3**) was obtained. The unexpected partially substituted geminal product, $Cl_2P(O){-}N{=}P(NRR)_2Cl$ (**5**), was obtained only from the reaction of compound **1** with an excess of diisopropylamine. The reason for this is probably that steric effects hinder complete substitution. The structure of compound **5** was determined by X-ray crystallography. In contrast

**TABLE 1** pKa' Values and Half-Neutralization Potentials (Hnp) of Some Phosphazene and Phosphinoylamine Derivatives Titrated Potentiometrically with Perchloric Acid in Nitrobenzene Solvent[a,b]

| *Compound* | *pKa'* | *Hnp (mV)* |
|---|---|---|
| **3a**[c] | 5.88 | 42 |
| **3b** | 2.71 | 229 |
| **3c** | 1.24 | 316 |
| **3f** | 1.19 | 319 |
| **3g** | −1.37 | 470 |
| **3h** | 1.00 | 330 |
| **4a**[c] | 2.36 | 249 |
| **4b** | −0.69 | 430 |
| **4g** | not titrated | |
| **5** | not titrated | |
| **6** | −1.66 | 487 |

[a]For all compounds, the end points occur at one and equivalents of acid.
[b]Potentials have been recorded against a buffer solution, whose potentiometer readings are −17 mV and 7 pH.
[c]Taken from Ref. [1].

to observations by Bulloch and Keat for the reactions of compound **1** with methylamine and *t*-butylamine [13], where methylamine follows geminal and *t*-butylamine follows a nongeminal substitution pattern, the structure of compound 5 was found to be geminal. Hence, as in our previous studies [1,4], we repeated the reactions of compound **1** with primary and secondary amines in acetonitrile and always isolated penta-amides as major products and tetra-amides, which are a hydrolysis product of compound **2**, as minor products. The partially substituted products could not be isolated from the reaction mixtures for comparison to compound **5**, but the mono-amide, $(RRN)_3P(O)$ (**6**), was obtained from the reaction mixture of compound **1** with *t*-butylamine. In the literature [8], the reaction of **1** with $HN(CH_2CH_2Cl)_2$ is reported to give only mono and fully substituted products, which shows that the mechanism of the substitutions (geminal or nongeminal) in these reactions is still not well understood. As a further entry to this problem, thiols give only geminal substitution products, $Cl_2P(O)N{=}PR_nCl_{3-n}$ ($n$ = 1–3) [9], when they react with **1**. Although the reaction of diisopropylamine with **1** is regio-selective (geminal) and difficult to induce to go beyond the bis stage of substitution, further work with bulky subtituents is required to establish the mechanism firmly. The data for the potentiometric titrations of monophosphazene and the phosphinoylamine derivatives with perchloric acid in nonaqueous nitrobenzene are presented in Table 1. The acyclic phosphazenes (**3**) are, in general, stronger bases than the bis(phosphinoyl)amines (**4**) but weaker than the monocyclic phosphazenes, $N_3P_3(NRR)_6$, and the bicyclic phosphazenes, $N_4P_4(NR)(NHR)(NRR)_5$ [1].

Interestingly, the pKa values of monophosphazenes (**3**) are ca. 3.45 pKa units larger than the values of bis(phosphinoyl)amines (**4**) containing the same substituents. It is assumed that the presence of electron-withdrawing–P=O groups in tetra-amides (**4**) may decrease their basicity. On the other hand, compounds **4g** and **5** cannot be titrated with perchloric acid in nonaqueous nitrobenzene because of the fact that they are weak bases, as can be seen from their structures.

## *SPECTROSCOPIC STUDIES*

The IR spectra of the penta-amides and tetra-amides show the PNHR vibration at 3230–3360 $cm^{-1}$ and that of PNHP at 3400–3490 $cm^{-1}$, respectively. The characteristic band in the IR spectra of penta-amides is that attributed to a degenerate stretching frequency, P=N, which occurs at 1160–1230 $cm^{-1}$. This band decreases with the increasing degree of chlorine replacement by amino groups, e.g., 1300 $cm^{-1}$ for **1**, 1230 $cm^{-1}$ for **5**, and 1160 $cm^{-1}$ for **3a**. These acyclic phosphazenes and bis(phosphinoyl)amines show ions in their MS spectra in excess of the molecular weights of the molecules (**3**, **4**, and **5**) of the respective amines. These observations, which are not unprecedented [15–17], could arise from a possible decomposition, followed by rearrangement, of these compounds during the MS analysis. In view of this finding, assignments made by mass analysis must be regarded as tentative assignments only. On the other hand, other spectral data clearly support these proposed structures. The $^{31}P$ NMR chemical shifts of the compounds are listed in Table 2. The tetra-amides give chemical shifts in the same region as the tetrameric, $N_4P_4Cl_8$, derivatives rather than those of the trimeric, $N_3P_3Cl_6$, derivatives [18,19]. Chemical shifts reflect the structural features, and all of the two bond-coupling constants, $^2J_{PNP}$, for aminophosphazenes, are between ca. 32–50 Hz. The original compound **5**, derived from the reaction of the penta-chloride **1** with diisopropylamine, may have two possible structures, e.g., geminal or non-geminal. The $^1H$-$^{31}P$ NMR coupled spectrum of compound **5** gives evidence of the presence of two different environments, namely, phosphazenyl and phosphinyl. The phosphazenyl part of the spectrum is seen to be broadened. This proves that compound **5** has the geminal structure. The solid-state structure of compound **5** was also determined by X-ray crystallography, and the geminal structure was confirmed. The $^1H$ NMR data are presented in Table 3. In the penta-amides (**3**), the $P(NRR)_3$ environments are more deshielded than those of the $P(O)(NRR)_2$ compounds and can be distinguished in some cases, e.g., $\delta P(NHCH_2Ph)_3$ = 4.1 and $\delta P(O)(NHCH_2Ph)_2$ = 3.9 for **3f**. Under certain conditions, it is also possible to distinguish the P(O)NH and N=PNH signals. The $^{13}C$ NMR data

**TABLE 2** $^{31}P$ NMR Data of Derivatives[a]

| *Compound* | $\delta P(O)(NRR')_2$[b] | $\delta P(NRR')_3$[b] | $^2J(PP)$[b] |
|---|---|---|---|
| **1** | −10.6(−12.0) | −2.6(−4.1) | 21.3(19.5) |
| **3a** | 3.3 | 7.5 | 45.8 |
| **3b** | −0.3 | 4.4 | 32.6 |
| **3c** | 8.7 | 9.1 | 36.6 |
| **3d** | −11.1(−10.0) | −7.1(−7.8) | 45.9(50.7) |
| **3e** | 7.6 | 15.9 | 43.3 |
| **3f** | 9.9 | 12.6 | 36.7 |
| **3g** | −4.7 | −0.2 | 37.8 |
| **3h** | 10.4 | 14.1 | 35.5 |
| **4a** | 8.9 | | |
| **4b** | 5.0 | | |
| **4c** | 7.0 | | |
| **4d**[d] | −5.7 | | |
| **4e** | 6.0 | | |
| **4g** | 0.3 | | |
| **4h**[d] | 12.6 | | |
| **5** | −16.4 | 2.8 | 43.0 |

[a]In $CDCl_3$ at room temperature at 24.15 and 161.903 MHz.
[b]In parts per million.
[c]In hertz.
[d]Not isolated but detected by $^{31}P$ NMR spectroscopy in reaction mixture.
Values in parentheses are taken from Ref. [12].
Values of compounds **3a**, **3b**, **3c**, **3e**, **4a**, **4b**, **4c**, and **4e** taken from Refs. [1] and [3] for comparison.

are listed in Table 4. As expected, two environments are observed for the penta-amides and one environment is observed for the tetra-amides and for compound **5**. As mentioned previously, the non-geminal structure was expected for compound **5**. But, according to the results of X-ray structure analysis, it was observed that two diisopropylamino groups are substituted by two chlorine atoms bonded to the phosphorus atom at the P2 position to give a geminal structure (Figure 1). Within the unit cell, the molecules are aligned parallel to the *c*-axis of the cell, while, in the *b* direction, the molecules are packed in staggered layers (Figure 2). The methods employed to solve the structure and other related parameters and procedures are given in Table 5. Non-H atoms were included with anisotropic thermal parameters. Difference syntheses did not show clearly the electron density for H atoms. Therefore, H atoms were geometrically positioned 1.08 Å from C atoms with coordinates and isotropic temperature-factor coefficients ($U$ = 0.05 $Å^2$) fixed in the refinement process. The final atomic coordinates and isotropic displacement parameters are given in Table 6. A view of the molecule and the atomic numbering is shown in Figure 1, and selected bond distances and angles with torsion angles are given in Table 7. As can be seen from Table 7, P1–N1 [1.653(13)], P2–N2 [1.623(10)], and P2–N3 [1.644(12)] Å have single bond character, while P2–N1 [1.480(12)] Å has a double bond character. In the literature, the single and double

**TABLE 3** $^{1}H$ NMR Data of Derivatives[a,b]

| Compound | | δα-CH | δβ-CH | δσ-CH | δph-CH | δP(O)NH | δN=PNH |
|---|---|---|---|---|---|---|---|
| **3b** | $P(NRR')_3$ | | 1.33 | | | | 3.09 |
| | $P(O)(NRR')_2$ | | 1.32 | | | 1.30 | 2.09 |
| **3f**[c] | $P(NRR')_3$ | 4.10 | | | 7.10–7.35 | | 3.43 |
| | $P(O)(NRR')_2$ | 3.90 | | | 7.10–7.35 | 3.52 | |
| **3g** | $P(NRR')_3$ | 3.12 | 1.15 | | | | |
| | $P(O)(NRR')_2$ | 3.08 | 1.01 | | | | |
| **3h** | $P(NRR')_3$ | 2.75 | 1.21 | 1.02 | | | 2.85 |
| | $P(O)(NRR')_2$ | 2.71 | 1.19 | 0.98 | | 1.90 | |
| **4b** | | | 1.32 | | | 4.47 | 3.12 |
| **4g** | | 3.08 | 1.03 | | | 2.28 | |
| **5**[d] | $P(NRR')_2Cl$ | 3.50–3.70 | 1.37, 1.25 | | | | |
| | $P(O)Cl_2$ | | | | | | |

[a] In $CDCl_3$ (room temperature) at 199.5 MHz.
[b] δvalues in parts per million and $J_{P-H}$ in hertz
[c] $^{3}J_{(PNCH_2)}$ 15.7 Hz, $^{3}J_{(P(O)NCH_2)}$ 17.5 Hz, $^{2}J_{PNH}$ 16.0 Hz.
[d] $^{3}J_{H-H}$ 7.9 Hz.

**TABLE 4** $^{13}C$ NMR Data of Derivatives[a,b]

| Compound | | δα-C | δβ-C | δσ-C | δδ-C | δph-$CH_2$ | $^{2}J(PC)$ | $^{3}J(PC)$ |
|---|---|---|---|---|---|---|---|---|
| **3a** | $P(NRR')_3$ | 47.01 | 26.58 | | | | 4.30 | 8.33 |
| | $P(O)(NRR')_2$ | 46.69 | 24.41 | | | | 4.57 | 8.86 |
| **3b** | $P(NRR')_3$ | 50.80 | 31.86 | | | | 2.76 | 4.56 |
| | $P(O)(NRR')_2$ | 49.98 | 31.93 | | | | 1.10 | 4.47 |
| **3c** | $P(NRR')_3$ | 43.06 | 26.03 | | | | | 6.23 |
| | $P(O)(NRR')_2$ | 43.03 | 25.94 | | | | | 5.31 |
| | | 43.02 | 25.94 | | | | | 4.73 |
| **3d** | $P(NRR')_3$ | 142.99 | 116.76 | 128.08 | 118.40 | | | 7.32 |
| | $P(O)(NRR')_2$ | 140.42 | 117.96 | 128.66 | 120.69 | | | 7.33 |
| **3e** | $P(NRR')_3$ | 45.46 | 67.49 | | | | 0.37 | 7.56 |
| | $P(O)(NRR')_2$ | 45.39 | 66.89 | | | | 0.73 | 6.47 |
| **3f** | $P(NRR')_3$ | 141.45 | 128.46 | 127.32 | 127.00 | 45.52 | 5.00 | 6.40 |
| | $P(O)(NRR')_2$ | 139.84 | 128.21 | 127.10 | 126.80 | 44.71 | 5.10 | 6.44 |
| **3g** | $P(NRR')_3$ | 39.70 | 14.83 | | | | 6.40 | 4.55 |
| | $P(O)(NRR')_2$ | 39.21 | 14.62 | | | | 5.63 | 4.03 |
| **3h** | $P(NRR')_3$ | 37.32 | 24.33 | 15.48 | | | | 7.13 |
| | $P(O)(NRR')_2$ | 36.75 | 24.12 | 15.30 | | | | 7.32 |
| **4a** | | 46.39 | 26.58 | | | | 5.23 | 10.68 |
| **4b** | | 51.06 | 31.62 | | | | | 5.01 |
| **4c** | | 43.32 | 25.71 | | | | | 5.18 |
| | | | 25.63 | | | | | 6.30 |
| **4g** | | 39.15 | 13.60 | | | | 6.10 | 4.58 |
| **5** | | 47.97 | 22.09 | | | | | 5.60 |
| | | 47.87 | 21.61 | | | | | 5.35 |
| **6** | | 50.69 | 31.64 | | | | | 3.42 |

[a] In $CDCl_3$ (room temperature) at 50.10 and 100.577 MHz.
[b] δValues in parts per million and $J_{PC}$ values in hertz.
Values of compounds **3b**, **3c**, **3d**, **3e**, **4b**, and **4c** taken from Ref. [3].

P–N bonds cannot be distinguished in $Cl_2P(O)NPCl_3$ (**1**) derivatives [14]. The reason for the observed P–N double bond can be the electron-withdrawing influence of diisopropylamino groups increasing the $d\pi$-$p\pi$ overlap character. The P=O bond distance [P1–O1 = 1.438(11) Å] is similar to values found for other phosphorylphosphazenes [14]. The average values of P–Cl and N–C bond lengths are 2.005(6) and 1.504(17) Å, respectively. The P–Cl bond distances are of two types. In the P1 bonded chlorine atoms, the average P–Cl distance is 1.993(6) Å. In the P2 bonded chlorine atom, the P–Cl distance is 2.027(5) Å. The P1 . . . P2 distance is 2.917(4) Å, and this is typical of cyclophosphazenes and other

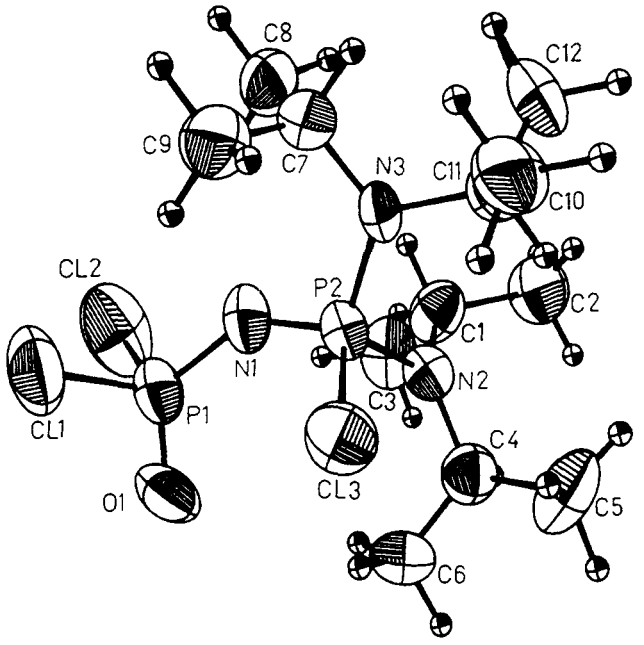


**FIGURE 1** An ORTEP [30] drawing of the title molecule with the atom numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.

linear, short-chain phosphazenes. The phosphazene skeleton P1–N1–P2 is not planar. The distances between C11 ... O1, C11 ... C12, C12 ... O1, C11 ... N1, C12 ... N1, C13 ... N1, C13 ... N2, C13 ... N3, O1 ... N1, N1 ... N2, N1 ... N3, and N2 ... N3 are 2.794(13), 3.086(8), 2.782(12), 2.965(14), 2.902(14), 2.900(12), 2.916(10), 2.984(12), 2.737(15), 2.659(16), 2.510(17), and 2.634(15) Å, respectively. The given twistings of bonds in Table 7 have reduced the distances between the side groups nonbonding atoms and N1 ... (side groups

**TABLE 5** Experimental Details

| | |
|---|---|
| *Crystal data* | |
| C12H28N3OCL3P2 | CU $K_\alpha$ radiation |
| Mr = 398.68 | $\lambda$ = 1.54180 Å |
| Orthorhombic | cell parameters from 25 reflections |
| *Pc2₁n* | $\theta$ = 6–14° |
| *a* = 10.333(1) Å | $\mu$ = 5.72 $mm^{-1}$ |
| *b* = 10.826(2) Å | *T* = 293 K |
| *c* = 18.158(4) $Å_3$ | irregular |
| *V* = 2031.3(7) Å | 0.20 × 0.25 × 0.50 mm |
| *Z* = 4 | colorless |
| *Dx* = 1.304 Mg $m^{-3}$ | crystal source: synthesized in laboratory, see manuscript |
| *Data collection* | |
| Enraf–Nonius CAD-4 diffractometer | $\theta_{max}$ = 75° |
| $w/2\theta$ scans | *h* = 0 → 12 |
| Absorption correction: | *k* = 0 → 13 |
| semiempirical [26] | *l* = 0 → 22 |
| $T_{min}$ = 2.69, $T_{max}$ = 3.49 | three standard reflections |
| 2104 unique measured reflections | frequency: 180 minutes |
| 1417 observed reflections [$F \geq 3\sigma(F)$] | intensity variation: 1% |
| $R_{int}$ = 0 | |
| (since the symmetry related reflections are eliminated) | |
| Refinement | |
| Refinement on *F* | $(\Delta/\sigma)_{max}$ = 0.101 |
| Final *R* = 0.063 | $\rho_{max}$ = +0.9 $eÅ^{-3}$ |
| *wR* = 0.063 | $\rho_{min}$ = −0.3 $eÅ^{-3}$ |
| 1417 reflections | atomic scattering factors from *International Tables for X-ray* |
| 190 parameters | |
| H-atom parameters not refined | *Crystallography* [27] |

The programs used were SHELX76 [28], SHELXS86 [29], and ORTEP [30].

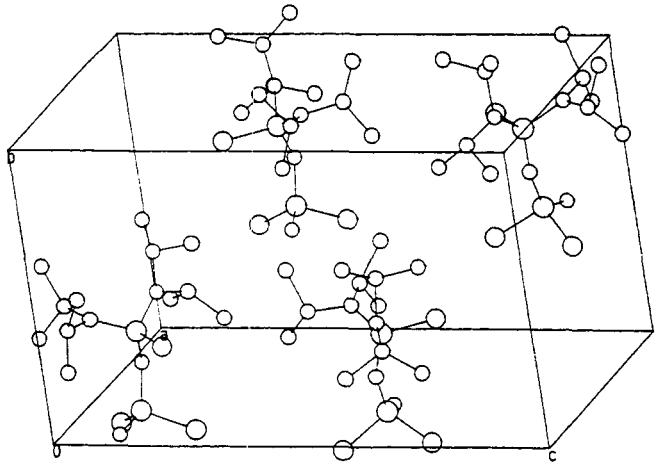

**FIGURE 2** The perspective view of the crystal packing.

carbon atoms) and presumably generated repulsions. Nearly all the atoms in the molecule have unusually large thermal parameters, leading to the aforementioned repulsive interactions. Therefore, the steric influences of the side groups are especially interesting, and probably more striking effects might be expected when the side groups are larger. The P1–N1–P2 angle [137.2(7)]° is much wider than has been assumed in the past for this angle in phosphazene high polymers [14] and cyclotriphosphazenes (118.4–124.6°) [20] but is similar to the angle found in cyclotetraphosphazenes (131.0–146.7°) [21,22]. The P–N–P angles in the short-chain species vary widely over the range 128.7–146°, and the value mentioned above may be in response to side-group electronic or chain packing variations. The N1–P2–N2, N1–P2–N3, and N2–P2–N3 bond angles [117.8(6), 106.8(6), and 107.5(5), respectively] are narrower than the en-

**TABLE 6** Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^4$) with Esd's in Parentheses[a]

| Atom | x | y | z | $U_{eq}$ |
|---|---|---|---|---|
| CL1 | 2990(5) | −648(6) | 2168(3) | 1128(20) |
| CL2 | 3586(6) | −694(6) | 503(3) | 1418(25) |
| CL3 | 1237(3) | 2887(6) | 2199(2) | 782(12) |
| P1 | 2493(5) | 197(4) | 1228(2) | 744(15) |
| P2 | 2552(4) | 2880 | 1371(2) | 533(10) |
| O1 | 1166(10) | −114(9) | 1078(7) | 1043(49) |
| N1 | 3069(10) | 1620(12) | 1254(6) | 700(40) |
| N2 | 1843(10) | 3554(10) | 682(5) | 545(33) |
| N3 | 3781(11) | 3751(10) | 1617(6) | 578(37) |
| C1 | 2645(16) | 3656(15) | 2(8) | 791(54) |
| C2 | 2565(18) | 4977(15) | 342(8) | 931(63) |
| C3 | 2377(17) | 2674(16) | 557(7) | 877(63) |
| C4 | 426(14) | 3756(14) | 556(7) | 675(45) |
| C5 | −95(17) | 4919(17) | 972(9) | 1018(73) |
| C6 | −428(13) | 2679(17) | 638(9) | 871(66) |
| C7 | 4983(13) | 3277(12) | 1940(7) | 657(49) |
| C8 | 5884(13) | 2688(15) | 1366(8) | 798(55) |
| C9 | 4795(14) | 2467(15) | 2604(8) | 837(61) |
| C10 | 3597(14) | 5175(14) | 1707(8) | 692(51) |
| C11 | 3442(16) | 5533(14) | 2518(9) | 874(61) |
| C12 | 4601(16) | 5871(12) | 1311(9) | 844(66) |

[a] $U_{eq}$ is the mean of the principal axes of the thermal ellipsoid.

docyclic angle observed in cyclotetraphosphazenes [22].

## EXPERIMENTAL

Melting points were taken in capillary tubes in a Thomas–Hoover melting point apparatus and are uncorrected. IR spectra were recorded with a Perkin–Elmer 377 spectrophotometer in KBr discs and are reported in $cm^{-1}$ units. Proton (200 MHz) NMR spectra were obtained with a Bruker AC-200 FT-NMR spectrometer ($Me_4Si$ as internal standard); $^{13}C$ (50 MHz) NMR were also obtained with the Bruker instrument, referring to the center signal of $CDCl_3$ (77.0 ppm). $^{31}P$ (80.984 MHz) NMR spectra (in $CDCl_3$ solution, 85% $H_3PO_4$ as external standard) were recorded on Varian XL 200-FT and Bruker WH 400-FT (162-MHz) spectrometers. Chemical shifts are expressed on the $\delta$ scale with low frequency shifts being negative. MS spectra were obtained at 70 eV on a VG 7070 spectrometer operating with a Finnigan data system. Microanalyses were carried out by the microanalytical service of TÜBİTAK-MAE, Gebze–Kocaeli (Turkey). The pKa′ values of the compounds were determined with an Orion Model 1801-A digital pH meter equipped with glass and calomel electrodes, according to the method given in the literature [23,24]. For this purpose, solutions ($1.0 \times 10^{-3}$ M in nitrobenzene) of the compounds were titrated with a solution ($3.4 \times 10^{-3}$ M in nitrobenzene) of perchloric acid in a glass titration cell. Silica gel used for column chromatography was 70–230 mesh (Merck), and all reactions were monitored by using Kieselgel 60 F254 (silica gel) precoated TLC plates. Standard procedures were employed in drying solvents. Amines (Fluka Ltd.) were distilled from Zn (dust)/KOH, and other chemicals were used as supplied. The starting compound, $Cl_2P(O)N{=}PCl_3$ (**1**), was prepared by the literature method [25] and purified by vacuum distillation. The amino derivatives of **1** were obtained by the reactions of **1** with primary and secondary amines. The compounds **3a–3e** and **4a–4e** were prepared by the known literature procedures [1,4], and the new compounds **3f**, **3h**, **4g**, **5**, and **6** were synthesized in this study. The compound **5** was recrystallized from $CH_2Cl_2$/*n*-heptane (3:2) by slow evaporation during 2 weeks, in order to prepare X-ray quality crystals. Analytical data of the new compounds are given in Table 8.

### *Synthetic Procedures*

*1-Bis(benzylaminophosphinyl)-2,2,2-tris(benzylamino)phosphazene* (**3f**). Benzylamine (12.6 g, 119.0 mmol) in acetonitrile (40 $cm^3$) was added dropwise to a stirred solution of compound **1** (1.8 g, 7.5 mmol) in acetonitrile (60 $cm^3$) at −20°C for over 1.0 hour. After the mixture had been allowed to come to ambient temperature, it was boiled under reflux (3.0 hours) using a condenser fitted with a $CaCl_2$ drying tube. The precipitated benzylamine hydrochloride was filtered off and the solvent removed by rotary evaporation. The crude product was passed through a short column of silica gel (50 g) with the aid of methylene chloride to remove traces of salts. The compound **3f** was recrystallized from *n*-heptane-methylene chloride (1:2), 0.66 g (15%), mp 148°C.

*1-(Dichlorophosphinyl)-2-chloro-2,2-bis(diisopropylamino)phosphazene* (**5**). Diisopropylamine (14.8 g, 146 mmol) in acetonitrile (50 $cm^3$) and compound **1** (3.5 g, 12.9 mmol) in acetonitrile (100 $cm^3$) were allowed to react and worked up as in the preparation of compound **3f**. The precipitated diisopropylamine hydrochloride was filtered off and the solvent and excess of amine removed in vacuo. The crude product was dissolved in boiling *n*-heptane-methylene chloride (1:2) and set aside for crystallization of compound **5**, 1.47 g (29%), mp 130°C.

*1-Bis(t-butylaminophosphinyl)-2,2,2-tris(t-butylamino)phosphazene* (**3b**), *Bis[di(t-butylaminophosphinoyl)]amine* (**4b**), *and Phosphorus Oxytri(t-butylamine)* (**6**). Compound **1** (4.0 g, 16.7 mmol) and an excess of *t*-butylamine (17.4 g, 238.0 mmol) were allowed to react at −20°C and worked up as in the literature [4]. The oily mixture, after filtration on a short column of silica gel to remove traces of salts,

**TABLE 7** Bond Lengths (Å) and Angles with the Selected Torsion Angles (°) (Esd's in Parentheses)

| | | | |
|---|---|---|---|
| P1–CL1 | 2.003(6) | C7–N3 | 1.466(17) |
| P1–CL2 | 1.984(6) | C10–N3 | 1.562(15) |
| P2–CL3 | 2.027(5) | C1–C2 | 1.563(19) |
| O1–P1 | 1.438(11) | C1–C3 | 1.495(20) |
| N1–P1 | 1.653(13) | C4–C5 | 1.564(21) |
| N1–P2 | 1.480(12) | C4–C6 | 1.470(21) |
| N2–P2 | 1.623(10) | C7–C8 | 1.535(18) |
| N3–P2 | 1.644(12) | C7–C9 | 1.504(17) |
| C1–N2 | 1.491(17) | C10–C11 | 1.531(19) |
| C4–N2 | 1.498(17) | C10–C12 | 1.470(19) |
| CL2–P1–CL1 | 101.4(3) | C7–N3–P2 | 124.2(8) |
| O1–P1–CL1 | 107.4(6) | C10–N3–P2 | 120.0(1.0) |
| O1–P1–CL2 | 107.7(6) | C10–N3–C7 | 114.0(1.1) |
| N1–P1–CL1 | 108.0(5) | C2–C1–C3 | 111.8(1.2) |
| N1–P1–CL2 | 105.5(5) | C2–C1–N2 | 111.6(1.3) |
| N1–P1–O1 | 124.5(6) | C3–C1–N2 | 113.9(1.3) |
| N1–P2–N2 | 117.8(6) | C5–C4–N2 | 112.4(1.3) |
| N1–P2–N3 | 106.8(6) | C5–C4–C6 | 112.1(1.3) |
| N1–P2–CL3 | 110.6(5) | C6–C4–N2 | 117.1(1.2) |
| N2–P2–CL3 | 105.6(4) | C8–C7–N3 | 112.9(1.1) |
| N2–P2–N3 | 107.5(5) | C9–C7–N3 | 114.5(1.2) |
| N3–P2–CL3 | 108.3(4) | C9–C7–C8 | 112.4(1.2) |
| P1–N1–P2 | 137.2(7) | C11–C10–N3 | 111.3(1.2) |
| C1–N2–P2 | 114.9(9) | C12–C10–N3 | 111.6(1.2) |
| C4–N2–P2 | 128.6(9) | C9–C7–C8 | 112.4(1.2) |
| C4–N2–C1 | 114.0(1.0) | | |
| CL1–P1–N1–P2 | −104.7(1.1) | P2–N3–C7–C9 | −53.2(1.5) |
| CL2–P1–N1–P2 | 147.5(1.0) | P2–N3–C10–C11 | 100.3(1.2) |
| CL3–P2–N2–C4 | −19.5(1.2) | P2–N3–C10–C12 | −130.3(1.1) |
| CL3–P2–N2–C1 | 179.9(9) | P2–N3–C7–C8 | 77.0(1.4) |
| P2–N2–C1–C3 | 98.0(1.3) | O1–P1–N1–P2 | 22.5(1.5) |
| P2–N2–C1–C2 | −134.1(1.1) | N1–P2–N3–C7 | −22.2(1.2) |
| P2–N2–C4–C6 | −49.6(1.7) | N1–P2–N3–C10 | 173.8(1.0) |
| P2–N2–C4–C5 | 82.6(1.4) | N3–P2–N1–P1 | 159.4(1.0) |
| P1–N1–P2–CL3 | 41.7(1.2) | P1–N1–P2–N2 | −79.7(1.2) |
| P1–N1–P2–N3 | 159.4(1.0) | | |

**TABLE 8** Analytical Data of Derivatives

| *Compound* | *Formula* | *MS Found (Required)* | *Elemental Analyses (pct) Found (Calculated)* C | H | N |
|---|---|---|---|---|---|
| **3f** | $C_{36}H_{40}N_5P_2O$ | 622 (622) | 67.69 (67.51 | 6.70 6.46 | 9.84 9.94) |
| **3g** | $C_{20}H_{50}N_6P_2O$ | 452 (452) | 53.03 (53.08 | 11.06 11.06 | 18.58 18.58) |
| **3h** | $C_{15}H_{40}N_6P_2O$ | 382 (382) | 46.98 (47.11 | 10.54 10.54 | 21.99 21.97) |
| **4g** | $C_{16}H_{41}N_5P_2O_2$ | 397 (397) | 48.33 (48.35 | 10.21 10.40 | 17.49 17.62) |
| **5** | $C_{12}H_{28}N_3P_2Cl_3O$ | 397 (397) | 36.10 (35.92 | 7.02 6.81 | 10.53 10.39) |
| **6** | $C_{12}H_{30}N_3PO$ | 263 | 54.75 (54.94 | 12.54 12.26 | 15.96 16.11) |

was chromatographed (silica gel: 100 g; eluent: THF-$CH_2Cl_2$, 1:2) to give the components in the following order, these being recrystallized as follows: **3b**, Rf = 0.87 (THF-$CH_2Cl_2$, 1:2), 1.67 g (25%), and mp 120°C (*n*-heptane-$CH_2Cl_2$, 1:2, Ref. [3], mp 120°C); and **4b**, Rf = 0.70 (THF-$CH_2Cl_2$, 1:2), 0.29 g (5%), and mp 181°C (*n*-hexane-$CH_2Cl_2$, 1:2, Ref. [3], mp 180°C). On the other hand, the higher molecular weight product, $(Bu^tNH)_2P(O)-NH-P(NHBu^t)_2=N-P(NHBu^t)_2=N-P(O)(NHBu^t)_2$, reported in our previous article [4] could not be observed, but phosphorus oxytri(*t*-butylamine), $(Bu^tNH)_3PO$ (**6**), was isolated as follows: the precipitate [*t*-butylamine hydrochloride and (**6**)] was extracted with $CH_2Cl_2$ (2 × 30 $cm^3$), and the solvent was removed under aspirator pressure. The residue was dissolved in $CH_2Cl_2$ (8 $cm^3$) and chromatographed (neutral alumina: 75 g; eluent: $CH_2Cl_2$), and the compound **6** was separated and crystallized from *n*-heptane-$CH_2Cl_2$ (2:1), 0.11 g (11%), mp 246°C.

*1-Bis(diethylaminophosphinyl)-2,2,2-tris(diethylamino)phosphazene* **3g** *and Bis[di(diethylaminophosphinoyl)]amine* **4g**. To a stirred solution of compound **1** (6.5 g, 24.1 mmol) and triethylamine (18.3 g, 180.9 mmol) in acetonitrile (40 $cm^3$) was added dropwise a solution of diethylamine (8.8 g, 120.6 mmol) in acetonitrile (20 $cm^3$) at −95°C over 0.5 hours. After the mixture had been allowed to come to ambient temperature, it was boiled under reflux (2.0 hours) using a condenser fitted with a $CaCl_2$ drying tube. After the mixture had been cooled to room temperature, the precipitated salts were filtered off and the solvent and the excess of amines removed by rotary evaporation. The residue was dried under vacuo and chromatographed (silicagel: 100 g; eluent: THF-$CH_2Cl_2$, 1:2) to give the components in the following order, and these being recrystallized as follows: **3g**, $R_f$ = 0.82 (THF-$CH_2Cl_2$, 1:2), 4.5 g (42%), and mp 221°C ($CHCl_3$), and **4g** $R_f$ = 0.67 (THF-$CH_2Cl_2$, 1:2), 2.48 g (26%), mp 196°C ($CH_2Cl_2$).

*1-Bis(n-propylaminophosphinyl)-2,2,2-tris(n-propylamino)phosphazene* **3h**. Triethylamine (18.4 g, 182.5 mmol) and compound **1** (4.0 g, 14.8 mmol) in acetonitrile (50 $cm^3$) and n-propylamine (5.3 g, 89.0 mmol) were allowed to react and worked up as in the preparation of compound **3g**. The precipitated salts were filtered off and the solvent and excess of amines removed in vacuo. The crude product was chromatographed (silica gel: 100 g; eluent: THF-$CH_2Cl_2$, 1:2) and the oily compound **3h** was isolated. $R_f$ = 0.73 (THF-$CH_2Cl_2$, 1:2), 5.7 g (22%).

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