

***N*-[Bis(2,4,6-trimethylphenoxy)phosphinoyl]-*P,P,P*-tris(2,4,6-trimethylphenoxy)phosphazene**Tuncer Hökelek,^{a*} Nurcan Akduran,^a Saliha Begeç,^b
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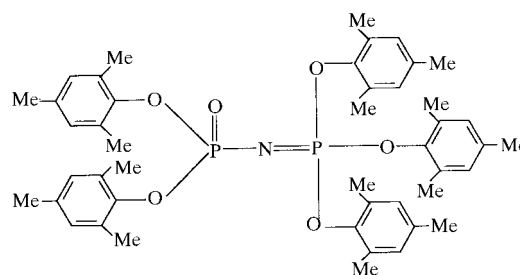
The title compound, C₄₅H₅₅NO₆P₂, consists of an acyclic P=N–P(O) monophosphazene chain and five bulky 2,4,6-trimethylphenoxy side groups which predominantly determine the molecular shape. Although the P–N single [1.586 (3) Å] and P=N double [1.517 (3) Å] bonds are significantly different from each other, both are substantially shorter than the ideal P–N single bond. The P–N–P angle [146.0 (2)°] corresponds to the upper limit reported for acyclic phosphazene derivatives in the literature.

Comment

In the past two decades, 1-(dichlorophosphinoyl)-2,2,2-trichloromonophosphazene, Cl₃P=N–P(O)Cl₂, (I), and its derivatives have been investigated extensively (Hökelek *et al.*, 1998; Kılıç *et al.*, 1989, 1991, 1994, 2000; Bulloch & Keat, 1979). It was observed that thermolysis of (I) leads to the elimination of P(O)Cl₃ and polydichlorophosphazene, (NPCl₂)_n (D'haluin *et al.*, 1992). Polydichlorophosphazene is used to synthesize linear polyorganophosphazenes (Manners, 1996). It has been observed that compound (I) yields partially and fully substituted products as a result of its reactions with primary and secondary amines and alcohols and phenoxides (Kılıç *et al.*, 1989, 1994; Allcock *et al.*, 1985). The reactions of (I) with bulky substituted phenoxides yield partially and fully substituted phenolysis products (Kılıç *et al.*, 2000; Allcock *et al.*, 1992, 1996). The reaction of (I) with 2,4,6-trimethylphenoxy yields the fully substituted monophosphazene (C₆H₃)₂(C₆H₃O-2,4,6-Me)₂P(O)N=P(C₆H₃O-2,4,6-Me)₃, (II). The X-ray crystal structure of some of the bulky phenoxy derivatives of (I) have been determined previously (Kılıç *et al.*, 2000; Allcock *et al.*, 1992, 1996).

The structure determination of the title compound, (II), was undertaken in order to understand the effect of five bulky

2,4,6-trimethylphenoxy groups on the P=N double bond and also to compare the results obtained with the very limited number of reported structures of acyclic phosphazenes in the literature.



(II)

In phosphazene derivatives, the P–N single and double bonds are generally in the ranges 1.628–1.691 and 1.571–1.604 Å, respectively (Allen *et al.*, 1987). In the standard compound, Cl₃P=N–P(O)Cl₂, (I), the P–N bonds show a pronounced character: the P–N ‘double’ and ‘single’ bonds are 1.517 (3)–1.530 (3) and 1.583 (3)–1.593 (3) Å, respectively (Belaj, 1993). In the title compound, (II), the values of the single P–N [P2–N1 1.586 (3) Å] and double P=N [P1–N1 1.517 (3) Å] bonds are significantly different from each other. However, both of them are substantially shorter than the ideal P–N single bond. This deviation possibly depends on resonance between the P=N–P=O atoms. For compound (I), the single and double bonds could not be distinguished by Allcock *et al.* (1985), but it was possible to distinguish between these bonds according to results obtained later for the same compound by Belaj (1993).

In the literature, the single P–N [1.653 (13) Å] and double P=N [1.480 (12) Å] bonds in monocyclic phosphazene derivatives can only be distinguished in the diisopropylamino derivative, Cl[NCH(CH₃)₂]₂P=N–P(O)Cl₂ (Kılıç *et al.*, 1994), since the two geminal diisopropylamino groups withdraw the N-atom electrons by increasing the P=N double-bond character. This effect is not predominant when neither one diisopropylamino group nor two 2,4,6-tri-*tert*-butylphenoxy groups (Kılıç *et al.*, 2000) are present.

The P=O bond distance [P2–O1 1.457 (2) Å] is similar to those found for other phosphorylphosphazenes (Allcock *et al.*, 1985; Belaj, 1993; Kılıç *et al.*, 1994; Hökelek *et al.*, 1998). The average values of the P–O single-bond lengths are 1.568 (2) and 1.594 (2) Å for the O atoms bonded to the phosphazenylyl and phosphoryl phosphorous, respectively. The average values of the O–C bond lengths and P–O–C bond angles are 1.407 (4) Å, 123.1 (2)° and 1.428 (4) Å, 126.1 (2)°, for the phosphoryl and phosphazenylyl parts of the molecule, respectively, which may probably reflect the influences of the steric hinderances between the phenoxy groups. On the other hand, several interatomic distances ranging between 2.367 [O1···H7C(C7)] and 2.880 Å [O2···H7C(C7)] indicate the close contacts which may affect the overall molecular geometry. The steric influences of the side groups are especially interesting and probably more striking effects might be expected when the side groups are larger (Kılıç *et al.*, 1994;

Hökelek *et al.*, 1998). The P1···P2 distance is 2.967 (2) Å, which can be compared with the corresponding values [2.856 (3) and 3.005 (3) Å] in Cl₂P(O)N=PCl{N[CH(CH₃)₂]₂}₂, (III) (Hökelek *et al.*, 1998), and Cl₂PON=PCl(OC₆H₂Bu^t-2,4,6)₂, (IV) (Kılıç *et al.*, 2000), which are the expected values for cyclophosphazenes and linear short-chain phosphazenes.

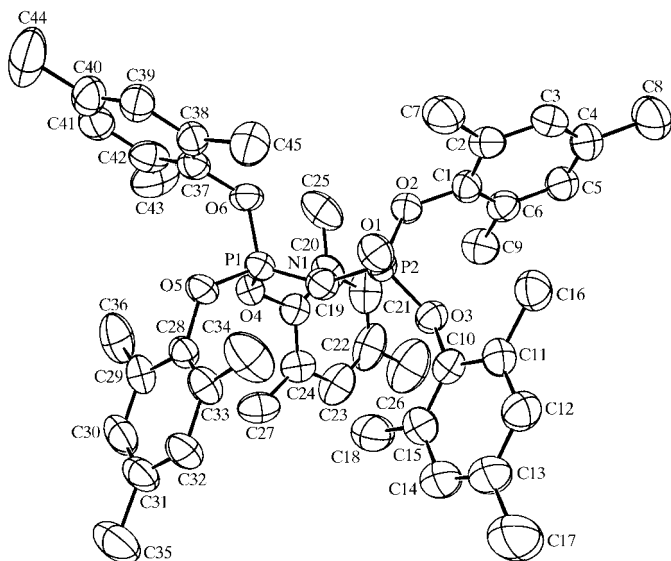


Figure 1

An ORTEPII (Johnson, 1976) drawing of the title molecule with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level.

The P1–N1–P2 angle [146.0 (2)°] is larger than in compound (III) [134.0 (2)°] but smaller than in compounds (IV) [158.0 (3)°] and (I) [144.5 (6) and 148.0 (1)° (Allcock *et al.*, 1985) and 137.8 (2)–144.1 (2)° (Belaj, 1993)]. The range of values is much wider than has been found in the past for cyclotriphosphazenes (118.4–124.6°; Fincham *et al.*, 1986), but is similar to the angle observed in cyclotetraphosphazenes (131.0–146.7°; Allcock, 1972; Hökelek & Kılıç, 1990; Hökelek *et al.*, 1996).

Experimental

2,4,6-Trimethylphenol (5.00 g, 0.037 mol) in dioxane (20 ml) was added slowly over a period of 30 min to small pieces of Na (0.90 g, 0.039 mol) in dioxane (20 ml) with stirring at 298 K, with argon passed over the reaction mixture. Excess Na was removed by filtration and the solution obtained was cooled. To this mixture, Cl₂PONCl₃, (I) (9.89 g, 0.037 mol), in dioxane (40 ml) was added slowly and the resulting solution allowed to reach ambient temperature with constant stirring. After the mixture had been vigorously stirred for 72 h at room temperature, the precipitated salt (NaCl) was filtered off and the solvent removed *in vacuo*. The residue was dissolved in *n*-hexane and set aside to crystallize (m.p. 482 K).

Crystal data

C₄₅H₅₅NO₆P₂
M_r = 767.89
 Triclinic, P1̄
a = 11.704 (1) Å
b = 11.751 (2) Å
c = 15.640 (2) Å
 α = 91.75 (1)°
 β = 92.18 (1)°
 γ = 90.55 (1)°
V = 2148.3 (5) Å³

Z = 2
D_x = 1.187 Mg m⁻³
 Cu K α radiation
 Cell parameters from 25 reflections
 θ = 19–42°
 μ = 1.29 mm⁻¹
T = 298 K
 Block-like, colourless
 0.30 × 0.25 × 0.20 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ scan (MolEN; Fair, 1990)
 T_{\min} = 0.646, T_{\max} = 0.774
 9238 measured reflections
 8754 independent reflections
 5311 reflections with $F > 4\sigma(F)$

R_{int} = 0.060
 θ_{max} = 74.35°
 h = 0 → 14
 k = -14 → 14
 l = -19 → 19
 3 standard reflections
 frequency: 120 min
 intensity decay: 1%

Refinement

Refinement on F^2
 R = 0.068
 wR = 0.199
 S = 1.002
 8754 reflections
 502 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0938P)^2 + 1.2262P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}}$ = 0.04
 $\Delta\rho_{\text{max}}$ = 0.48 e Å⁻³
 $\Delta\rho_{\text{min}}$ = -0.62 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

P1–N1	1.517 (3)	P2–O1	1.457 (2)
P1–O6	1.560 (2)	P2–N1	1.586 (3)
P1–O5	1.573 (2)	P2–O2	1.591 (2)
P1–O4	1.572 (2)	P2–O3	1.596 (2)
N1–P1–O6	115.44 (14)	O1–P2–O3	111.61 (14)
N1–P1–O5	118.44 (14)	N1–P2–O3	105.92 (14)
O6–P1–O5	100.78 (13)	O2–P2–O3	101.84 (13)
N1–P1–O4	109.95 (14)	C1–O2–P2	124.2 (2)
O6–P1–O4	106.55 (12)	C10–O3–P2	121.9 (2)
O5–P1–O4	104.45 (12)	C19–O4–P1	123.80 (19)
O1–P2–N1	117.95 (15)	C28–O5–P1	127.3 (2)
O1–P2–O2	114.68 (14)	C37–O6–P1	127.2 (2)
N1–P2–O2	103.20 (13)	P1–N1–P2	146.0 (2)
O6–P1–N1–P2	27.1 (4)	O1–P2–N1–P1	58.5 (4)
O5–P1–N1–P2	–92.5 (4)	O2–P2–N1–P1	–69.1 (4)
O4–P1–N1–P2	147.6 (3)	O3–P2–N1–P1	–175.7 (3)

H atoms were positioned geometrically at distances of 0.96 and 0.93 Å for CH₃ and CH bonds, respectively, from the corresponding C atom and a riding model was used during the refinement process.

Data collection: MolEN (Fair, 1990); cell refinement: MolEN; data reduction: MolEN; program(s) used to solve structure: SHELXS86 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEPII (Johnson, 1976); software used to prepare material for publication: SHELXL97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1021). Services for accessing these data are described at the back of the journal.

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