

Data collection

Nonius CAD-4 diffractometer	$R_{\text{int}} = 0.059$
ω - 2θ scans	$\theta_{\text{max}} = 74.91^\circ$
Absorption correction: none	$h = -4 \rightarrow 6$
3143 measured reflections	$k = -5 \rightarrow 9$
2862 independent reflections	$l = -37 \rightarrow 63$
2281 reflections with $I > 2\sigma(I)$	3 standard reflections
	frequency: 60 min
	intensity decay: 5%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} = -0.004$
$R[F^2 > 2\sigma(F^2)] = 0.060$	$\Delta\rho_{\text{max}} = 0.390 \text{ e } \text{\AA}^{-3}$
$wR(F^2) = 0.175$	$\Delta\rho_{\text{min}} = -0.338 \text{ e } \text{\AA}^{-3}$
$S = 1.044$	Extinction correction: none
2860 reflections	Scattering factors from
282 parameters	<i>International Tables for</i>
Only H-atom U 's refined	<i>Crystallography</i> (Vol. C)
$w = 1/[\sigma^2(F_o^2) + (0.1106P)^2 + 0.4663P]$	Absolute structure:
where $P = (F_o^2 + 2F_c^2)/3$	Flack (1983)
	Flack parameter = 0.01 (4)

Table 1. Selected torsion angles ($^\circ$)

C10—C5—C6—C7	-21.5 (6)	C11—C12—C13—C14	45.9 (5)
C5—C6—C7—C8	50.2 (5)	C12—C13—C14—C8	-45.4 (5)
C6—C7—C8—C9	-63.9 (5)	C17—C13—C14—C15	-40.5 (4)
C7—C8—C9—C10	47.4 (5)	C9—C8—C14—C13	52.3 (4)
C14—C8—C9—C11	-60.8 (5)	C13—C14—C15—C16	27.8 (6)
C6—C5—C10—C9	5.9 (6)	C14—C15—C16—C17	-4.5 (7)
C8—C9—C10—C5	-19.2 (6)	C14—C13—C17—C16	38.6 (5)
C8—C9—C11—C12	60.8 (5)	C15—C16—C17—C13	-21.0 (6)
C9—C11—C12—C13	-53.0 (5)		

Since μ_x had a value of 0.29, an absorption correction was not considered necessary. H atoms were located from difference Fourier syntheses and refined with a riding model (including free rotation about O—C).

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CELSIUS* (Svenson, 1974). Data reduction: *CORINC* (Dräger & Gattow, 1971). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991). Software used to prepare material for publication: *SHELXL93* and *PARST95* (Nardelli, 1995).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1312). Services for accessing these data are described at the back of the journal.

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***P,P*-Dichloro-*N*-(dichlorophosphinoyl)-*P*-(diisopropylamino)monophosphazene**

TUNCER HÖKELEK,^{a*} ZEYNEL KILIÇ^b AND HAKAN DAL^b

^aHacettepe University, Department of Physics, 06532 Beytepe, Ankara, Turkey, and ^bAnkara University, Department of Chemistry, 06100 Tandoğan, Ankara, Turkey. E-mail: merzifon@eti.cc.hun.edu.tr

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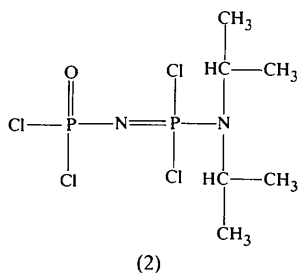
Abstract

The title compound, $\text{C}_6\text{H}_{14}\text{Cl}_4\text{N}_2\text{OP}_2$, has an acyclic monophosphazene skeleton and a bulky diisopropylamino side group. The bulky substituent is instrumental in determining the molecular geometry. The P—N bonds have neither single- nor double-bond character and are substantially shorter than the ideal P—N single bond. The P—N—P angle [$134.0(2)^\circ$] is similar to the angle found in cyclotetraphosphazenes, but wider than that in cyclotriphosphazenes.

Comment

Over the past decade, the reactions of *P,P,P*-trichloro-*N*-(dichlorophosphinoyl)monophosphazene, $\text{Cl}_2\text{P}(\text{O})\text{N}=\text{P}-\text{Cl}_3$, (1), with amines have been investigated extensively (Kiliç *et al.*, 1989, 1991, 1994; Bulloch & Keat, 1979). Thermolysis of compound (1) leads to the elimination of phosphorus oxychloride, $\text{P}(\text{O})\text{Cl}_3$, and polydichlorophosphazene, $(\text{NPCl}_2)_n$ (D'halluin *et al.*, 1992). Polydichlorophosphazene is used to obtain linear polyorganophosphazenes. The reaction of (1) with bulky diisopropylamine yield partial aminolysis products $\text{Cl}_2\text{P}(\text{O})\text{N}=\text{P}-\text{Cl}_2\{\text{N}[\text{CH}(\text{CH}_3)_2]_2\}$, (2), and $\text{Cl}_2\text{P}(\text{O})\text{N}=\text{P}-\text{Cl}\{\text{N}[\text{CH}(\text{CH}_3)_2]_2\}_2$, (3). The X-ray crystal structure of (3) has been determined previously, confirming the geminal structure (Kiliç *et al.*, 1994). The structure determination of compound (2) was undertaken in order to understand the effect of a single bulky diisopropylamino group on the P=N double bond and also to compare the obtained results with those of compounds

(1) (Belaj, 1993) and (3) (Kılıç *et al.*, 1994), and also with the very limited number of reported structures of acyclic phosphazene derivatives in the literature.



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 compound (1), 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, and the P—Cl bonds of the P(O)Cl₂ groups [1.998 (2)–2.018 (2) Å] are longer than the P—Cl bonds of the NPCl₃ groups [1.956 (2)–1.978 (2) Å] (Belaj, 1993). However, in the title compound, (2), the P—N bonds P1—N1 [1.564 (3) Å], P2—N1 [1.537 (3) Å] and P2—N2 [1.596 (2) Å] have neither single- nor double-bond character, and the P—Cl bonds of the P(O)Cl₂ groups [1.987 (1)–1.989 (1) Å] are shorter than the P—Cl bonds of the NPCl₂{N[CH(CH₃)₂]₂} group [1.991 (1)–2.012 (1) Å]. Small influences of the diisopropylamino group on the phosphazene skeleton have been seen to affect the bond distances and angles. The single and double bonds could not be distinguished in compound (1) by Allcock *et al.* (1985), contrary to the results obtained for the same compound by Belaj (1993). But in compound (3) (Kılıç *et al.*, 1994), the single and double bonds are easily distinguished since the two geminal diisopropylamino groups are withdrawing the N-atom electrons by increasing the P=N double-bond character. This effect is not dominant when only one diisopropyl group is present. The P=O bond distance [P1—O1 1.449 (2) Å] is similar to those found for other phosphinoylphosphazenes (Allcock *et al.*, 1985; Belaj, 1993; Kılıç *et al.*, 1994). The average values of the P—Cl and P—N bond lengths are 1.995 (1) and 1.566 (3) Å, respectively. The P1···P2 distance is 2.856 (3) Å, which is typical of cyclophosphazenes and linear short-chain polyphosphazenes.

As can be observed in other acyclic and linear short-chain polyphosphazene derivatives, the phosphazene skeleton, including the N2 atom, is non-planar [P1—N1—P2—N2 torsion angle $-170.2(2)^\circ$]. The P1—N1—P2 angle [134.0(2) $^\circ$] is smaller than in compounds (1) [144.5(6) and 148.0(1) $^\circ$] (Allcock *et al.*, 1985); 137.8(2)–144.1(2) $^\circ$ (Belaj, 1993)] and (3) [137.2(7) $^\circ$; Kılıç *et al.*, 1994]. The range of val-

ues is much wider than has been assumed in the past for phosphazene high polymers (Allcock *et al.*, 1985) and cyclotriphosphazenes (118.4–124.6 $^\circ$; Fincham *et al.*, 1986), but is similar to the angle found in cyclotetraphosphazenes (131.0–146.7 $^\circ$; Allcock, 1972; Hökelek & Kılıç, 1990; Hökelek *et al.*, 1996).

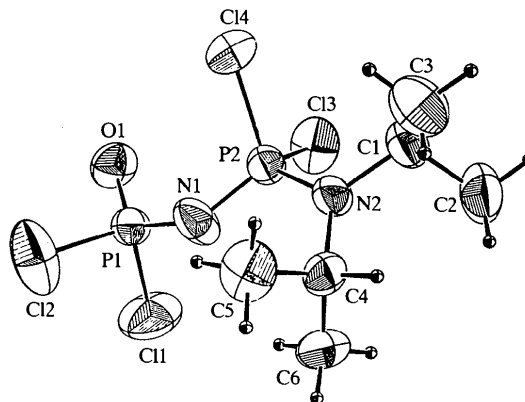


Fig. 1. An ORTEP (Johnson, 1976) drawing of the title molecule with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level.

Experimental

To a stirred solution of compound (1) (7.4 mmol) in acetonitrile (80 ml), a solution of diisopropylamine (113.0 mmol) in acetonitrile (40 ml) was added dropwise at 253 K over a period of 1 h. After refluxing the mixture for 2 h using a condenser fitted with a CaCl₂ drying tube and cooling to room temperature, the precipitated salts were filtered off and the solvent removed by rotary evaporation. The residue was dried *in vacuo* and chromatographed on silica gel (THF—CH₂Cl₂ 1:1) to give compound (2), which was recrystallized from THF—CH₂Cl₂ (1:2); *R_f* 0.75 (THF—CH₂Cl₂ 1:1), m.p. 345 K.

Crystal data

C₆H₁₄Cl₄N₂OP₂

M_r = 333.949

Monoclinic

*P*2₁/*n*

a = 10.8018 (9) Å

b = 12.5581 (9) Å

c = 10.9691 (9) Å

β = 91.052 (7) $^\circ$

V = 1487.7 (2) Å³

Z = 4

D_x = 1.491 Mg m⁻³

D_m not measured

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 25 reflections

θ = 10–18 $^\circ$

μ = 0.99 mm⁻¹

T = 298 K

Irregular

0.30 × 0.25 × 0.15 mm

Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer

2432 reflections with *F* > σ (*F*)

$\omega/2\theta$ scans
Absorption correction:
empirical via ψ scans
(*MolEN*; Fair, 1990)
 $T_{\min} = 0.792$, $T_{\max} = 0.862$
3335 measured reflections
3022 independent reflections

$R_{\text{int}} = 0.064$
 $\theta_{\max} = 26.3^\circ$
 $h = 0 \rightarrow 13$
 $k = 0 \rightarrow 15$
 $l = -13 \rightarrow 13$
3 standard reflections
every 250 reflections
intensity decay: 1%

Refinement

Refinement on F
 $R = 0.045$
 $wR = 0.063$
 $S = 2.15$
2432 reflections
144 parameters
H atoms riding
 $w = 1/[\sigma(I)^2 + (0.04F^2)^2]^{1/2}$

$(\Delta/\sigma)_{\max} = 0.01$
 $\Delta\rho_{\max} = 0.50 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.16 \text{ e } \text{\AA}^{-3}$
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. Selected geometric parameters (\AA , $^\circ$)

C11—P1	1.987 (1)	P2—N2	1.596 (2)
C12—P1	1.989 (1)	N2—C1	1.489 (4)
C13—P2	2.012 (1)	N2—C4	1.502 (3)
C14—P2	1.991 (1)	C1—C2	1.523 (5)
P1—O1	1.449 (2)	C1—C3	1.517 (5)
P1—N1	1.564 (3)	C4—C5	1.510 (5)
P2—N1	1.537 (3)	C4—C6	1.528 (5)
C11—P1—C12	102.03 (7)	C13—P2—N2	108.4 (1)
C11—P1—O1	110.8 (1)	C14—P2—N1	113.9 (1)
C11—P1—N1	103.8 (1)	C14—P2—N2	109.1 (1)
C12—P1—O1	109.7 (1)	N1—P2—N2	112.2 (1)
C12—P1—N1	106.5 (1)	P1—N1—P2	134.0 (2)
O1—P1—N1	122.1 (2)	C2—C1—C3	111.9 (3)
C13—P2—C14	100.75 (5)	C5—C4—C6	112.6 (3)
C13—P2—N1	111.8 (1)		
C11—P1—N1—P2	-140.2 (3)	N2—P2—N1—P1	-170.2 (2)
C12—P1—N1—P2	112.5 (3)	C13—P2—N2—C1	-56.0 (2)
O1—P1—N1—P2	-14.4 (4)	C13—P2—N2—C4	119.3 (2)
C13—P2—N1—P1	67.8 (3)	C14—P2—N2—C1	52.9 (2)
C14—P2—N1—P1	-45.6 (3)	C14—P2—N2—C4	-131.9 (2)

The title structure was solved by the Patterson method. Atoms H1 and H4 were obtained from the difference synthesis and refined isotropically. The other H-atom positions were calculated geometrically, with $U_{\text{eq}}(\text{H}) = 1.3U_{\text{eq}}(\text{parent atom})$. A riding model was used in the refinement.

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: *MolEN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *MolEN*.

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***p*-Toluidinium 2'-Hydroxy-3'-methoxy-5'-flavonesulfonate Hydrate**

GÉRARD PÈPE,^a JEAN-CLAUDE WALLET,^b AMAR HABSAOUI^b AND EMILE M. GAYDOU^b

^aCentre de Recherche sur les Mécanismes de la Croissance Cristalline, Universités d'Aix-Marseille II et III, Campus de Luminy, Case 913, 13288 Marseille CEDEX 9, France, and ^bLaboratoire de Phytochimie, Case 412, Faculté des Sciences et Techniques de Saint-Jérôme, 13397 Marseille CEDEX 20, France. E-mail: genmol@crmc2.univ-mrs.fr

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Abstract

The title complex, $\text{C}_7\text{H}_{10}\text{N}^+ \cdot \text{C}_{16}\text{H}_{11}\text{O}_7\text{S}^- \cdot \text{H}_2\text{O}$, is a *p*-toluidinium hydrated salt of 2'-hydroxy-3'-methoxy-5'-flavonesulfonic acid [systematic name: 4-hydroxy-5-methoxy-3-(4-oxo-4*H*-[2]benzopyran-2-yl)benzenesulfonic acid]. The N atom of *p*-toluidine is protonated to give the cation. The self-assembly of the ionic counterparts is mediated by a water molecule of hydration.

Comment

The X-ray structure determination of the title compound, (I), was carried out as a preliminary study of interactions