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Structural Investigations of Ylides. XIII.* Crystal and Molecular Structures of *N*-(Dichlorophosphinoyl)triphenylphosphazene and *N*-(Diphenylphosphinoyl)triphenylphosphazene

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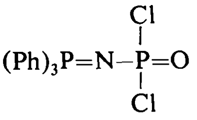
Abstract

The structures of *N*-(dichlorophosphinoyl)triphenylphosphazene (I) and *N*-(diphenylphosphinoyl)triphenylphosphazene (II) have been determined. (I) is monoclinic, space group $P2_1/c$, with $a = 9{\cdot}218$ (1), $b = 10{\cdot}284$ (1), $c = 19{\cdot}456$ (2) Å, $\beta = 91{\cdot}2$ (1)°, $Z = 4$. (II) is orthorhombic, space group $Pna2_1$, with $a = 17{\cdot}755$ (2), $b = 15{\cdot}325$ (2), $c = 8{\cdot}973$ (1) Å, $Z = 4$. (I) was solved by direct methods and refined to a final R of 0·042 for 3012 independent diffractometer data. The heavy-atom technique was used to solve (II), which was refined to a final R of 0·045 for 2274 independent diffractometer data. The analyses reveal significant differences in the dimensions of the P=N–P moieties, and in the conformations of the two molecules, these differences being related to both electronic and steric effects.

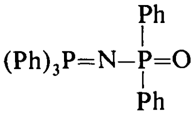
Introduction

The structures of a number of ylides of the type $Ph_3P{=}N.R$ have been described (Table 4 and references therein). Important canonical forms of these compounds are $Ph_3P^+{-}N^-{-}R$ and $Ph_3P{=}N{-}R$, and previous structural data have been interpreted, mainly on the basis of P–N lengths, in terms of significant contributions from the second form, which is generally assumed to be the more important. Although many examples of triphenylphosphazenes containing the P=N–P skeleton are known (Keat, 1978), relatively little information is available on their molecular geometries. We have therefore determined the structures of two representative examples, (I) and (II), which were prepared by literature methods [Appel & Büchler (1963) for (I); Baldwin & Washburn (1961) for (II)].



$$(Ph)_3P{=}N{-}\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{P}}{=}O$$

(I)



$$(Ph)_3P{=}N{-}\overset{\displaystyle Ph}{\underset{\displaystyle Ph}{P}}{=}O$$

(II)

Experimental

Crystal data

N-(Dichlorophosphinoyl)triphenylphosphazene, $C_{18}H_{15}Cl_2NOP_2$, $M_r = 394{\cdot}2$, monoclinic, $a = 9{\cdot}218$ (1), $b = 10{\cdot}284$ (1), $c = 19{\cdot}456$ (2) Å, $\beta = 91{\cdot}2$ (1)°, $U = 1843{\cdot}99$ Å^3, $D_m = 1{\cdot}45$, $Z = 4$, $D_c = 1{\cdot}43$ Mg m^{-3}, $F(000) = 808$, space group $P2_1/c$, Cu $K\alpha$ radiation, $\lambda = 1{\cdot}5418$ Å, $\mu(\mathrm{Cu}\,K) = 4{\cdot}862$ mm^{-1}.

N-(Diphenylphosphinoyl)triphenylphosphazene, $C_{30}H_{25}NOP_2$, $M_r = 477{\cdot}5$, orthorhombic, $a = 17{\cdot}755$ (2), $b = 15{\cdot}325$ (2), $c = 8{\cdot}973$ (1) Å, $U = 2441{\cdot}33$ Å^3, $D_m = 1{\cdot}31$, $Z = 4$, $D_c = 1{\cdot}30$ Mg m^{-3}, $F(000) = 1000$, space group $Pna2_1$, Cu $K\alpha$ radiation, $\lambda = 1{\cdot}5418$ Å, $\mu(\mathrm{Cu}\,K) = 1{\cdot}778$ mm^{-1}.

Crystallographic measurements and structure determinations

Small crystals of both compounds were exposed to Ni-filtered Cu radiation on a Hilger & Watts Y290 diffractometer, and intensity measurements were made with the θ,ω-scan technique in the 2θ range 0–136°, yielding 3012 independent reflexions [$I \geq 2\sigma_I$, $\sigma_I = (I + B_1 + B_2)^{1/2}$] for (I), and 2274 independent reflexions ($I \geq 2\sigma_I$) for (II). Both sets of intensities were corrected for Lorentz and polarization factors, but not for absorption.

(I) was solved by direct methods with programs incorporated in XRAY 72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). Solution of (II) by the heavy-atom method was complicated by the presence of pseudosymmetry. However, careful choice of atomic positions during structure factor and electron-density calculations yielded the complete structure. The structures were refined by least-squares calculations in which, because of computational limitations, both molecules were divided into two groups of atoms. These groups were refined in alternate cycles by full-matrix calculations, while the other groups were included as fixed contributors. The refinement of (I) converged when R was 0·042 and R' ($= \sum w\Delta^2/\sum w|F_o|^2$) was 0·004; for (II) the final values of R and R' were 0·045

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[*] Part XII: Cameron, Duncanson & Morris (1976).

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and 0·003 respectively. Both sets of data were weighted according to $w = xy$ [$x = 1$ if $\sin\theta \geq 0{\cdot}60$, else $x = (\sin\theta)/0{\cdot}60$; $y = 1$ if $|F_o| \leq 10{\cdot}0$, else $y = 10{\cdot}0/|F_o|$]. Positions were calculated for the H atoms of both molecules, and these atoms were included as fixed contributors.

Final coordinates for both compounds are presented in Tables 1 and 2;* Table 3 contains details of the geometries of the two molecules. Figs. 1 and 2 show views of (I) and (II) and define the atomic numbering.

Table 1. *Fractional coordinates* (× 10^5 *for* P, Cl; × 10^4 *for other atoms*) *for* (I)

	x	y	z
P(1)	67681 (6)	28504 (6)	8953 (3)
P(2)	67082 (7)	51012 (6)	18314 (4)
Cl(1)	64863 (11)	40044 (9)	26876 (4)
Cl(2)	46370 (9)	56988 (9)	16679 (5)
N(1)	7170 (3)	4212 (2)	1226 (1)
O(1)	7615 (3)	6228 (2)	1991 (1)
C(1)	7716 (5)	2768 (5)	97 (2)
C(2)	8243 (6)	3894 (5)	−188 (3)
C(3)	9034 (7)	3821 (6)	−796 (3)
C(4)	9276 (6)	2645 (6)	−1100 (3)
C(5)	8751 (7)	1522 (6)	−820 (3)
C(6)	7953 (6)	1571 (6)	−216 (3)
C(7)	4860 (5)	2594 (5)	725 (2)
C(8)	3971 (5)	2317 (6)	1279 (3)
C(9)	2488 (5)	2149 (6)	1161 (3)
C(10)	1926 (5)	2262 (7)	505 (4)
C(11)	2796 (6)	2553 (7)	−47 (3)
C(12)	4284 (5)	2720 (6)	66 (3)
C(13)	7383 (5)	1509 (5)	1409 (2)
C(14)	6729 (5)	305 (5)	1383 (3)
C(15)	7254 (7)	−734 (6)	1765 (3)
C(16)	8482 (7)	−556 (7)	2180 (3)
C(17)	9171 (6)	643 (7)	2203 (3)
C(18)	8641 (5)	1678 (6)	1823 (3)

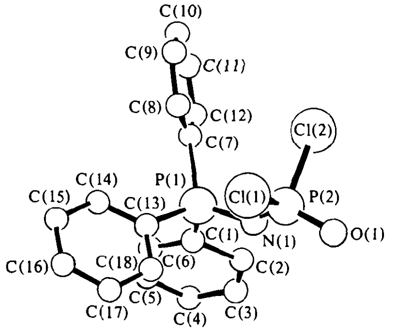

Fig. 1. A view of one molecule of (I) defining the atomic numbering.

Table 2. *Fractional coordinates* (× 10^5 *for* P; × 10^4 *for other atoms*) *for* (II)

	x	y	z
P(1)	22725 (3)	5094 (4)	48578 (11)
P(2)	8537 (3)	15967 (4)	50000 (–)
N(1)	1571 (1)	1014 (2)	5440 (3)
O(1)	858 (1)	2117 (2)	3599 (3)
C(1)	2812 (2)	156 (3)	6467 (5)
C(2)	2879 (3)	729 (3)	7654 (6)
C(3)	3290 (3)	481 (4)	8908 (7)
C(4)	3615 (3)	−336 (4)	8967 (6)
C(5)	3546 (3)	−914 (3)	7808 (6)
C(6)	3141 (2)	−672 (3)	6534 (6)
C(7)	2914 (2)	1152 (3)	3715 (5)
C(8)	2623 (3)	1791 (3)	2810 (6)
C(9)	3105 (3)	2262 (3)	1868 (7)
C(10)	3870 (3)	2078 (4)	1857 (7)
C(11)	4161 (3)	1447 (4)	2771 (6)
C(12)	3687 (2)	978 (4)	3711 (6)
C(13)	2075 (2)	−467 (3)	3780 (5)
C(14)	2587 (3)	−791 (3)	2723 (6)
C(15)	2410 (3)	−1533 (4)	1915 (7)
C(16)	1710 (4)	−1943 (3)	2156 (7)
C(17)	1211 (3)	−1636 (3)	3206 (7)
C(18)	1393 (2)	−892 (3)	4027 (6)
C(19)	709 (2)	2312 (2)	6597 (4)
C(20)	317 (2)	3086 (2)	6374 (5)
C(21)	160 (2)	3632 (2)	7585 (6)
C(22)	389 (3)	3408 (3)	9002 (6)
C(23)	781 (2)	2626 (3)	9231 (5)
C(24)	939 (2)	2090 (2)	8028 (4)
C(25)	32 (1)	901 (2)	5051 (4)
C(26)	−32 (2)	216 (2)	6063 (4)
C(27)	−681 (2)	−297 (2)	6106 (4)
C(28)	−1266 (2)	−112 (2)	5148 (5)
C(29)	−1219 (2)	574 (3)	4157 (5)
C(30)	−569 (2)	1081 (2)	4102 (4)

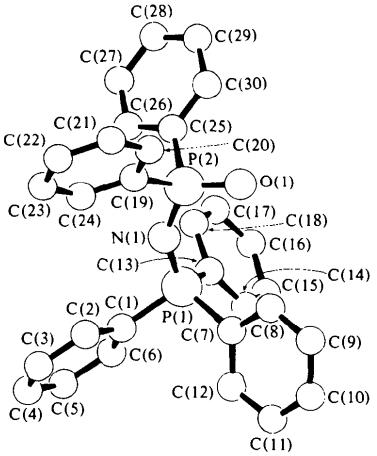

Fig. 2. A view of one molecule of (II) defining the atomic numbering.

Discussion

Relevant features of the geometries of (I) and (II) are compared with those of related structures in Table 4.

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* Lists of structure factors and anisotropic thermal parameters for (I) and (II) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34247 (46 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

As expected, the P—N bonds are all shorter than that in sodium phosphoramide [1·77 (2) Å] (Cruickshank, 1964). Multiple bonding is an important factor in determining these dimensions, although other influences, for example electrostatic attraction implicit in canonical forms such as $Ph_3P^+{-}N^-{-}P(O)X_2$, and also steric effects, should be taken into account (Glidewell, 1973). In (I) the formal P=N double bond [1·582 (2) Å] is longer than the formal P—N single bond [1·558 (2) Å], the latter being one of the shortest known formal P—N single bonds, more typical values being 1·67 (4) Å in $Cl_2P(O)NMe_2$ (Vilkov & Khaikin, 1975), 1·681 (6) Å in $Ph_2P(O)NMe_2$ (Ul-Haque & Caughlan, 1976) and 1·62–1·69 Å in dimethylaminophosphazenes (*e.g.* Bullen & Dann, 1974), although high e.s.d.'s render some of the above comparisons of doubtful significance. Shorter P—N bonds are found in the symmetrical cation $[Ph_3P{\cdots}N{\cdots}PPh_3]^+$, which can assume a range of P—N lengths and P—N—P angles (*e.g.* Wilson & Bau, 1974). ESCA studies indicate that the latter cationic species are best formulated as $[Ph_3P^+{-}N^-{-}P^+Ph_3]$ (Swartz, Ruff & Hercules, 1972). However, comparison of the dimensions of (I) and (II) suggests that replacement of the Cl atoms of (I) by the phenyl groups of (II) strengthens the formal P=N double bond in (II) relative to that in (I). Such changes in the lengths of the formal P=N double bonds are reasonable when the σ-inductive withdrawing ability of Cl atoms relative to phenyl groups is considered together with the ability of phosphinoyl groups to compete with the ylidic P atom for the p_π electrons on N.

The shortness of the P—N bonds within the *N*-phosphinoyl groups of (I) and (II) in comparison with those in $Cl_2P(O)NMe_2$ and $Ph_2P(O)NMe_2$ suggests that

Table 3. *Interatomic distances* (Å) *and angles* (°)

(*a*) Bond distances

	(I)	(II)		(I)	(II)		(II)
P(2)—Cl(1)	2·025 (1)	–	C(4)—C(5)	1·369 (9)	1·371 (8)	C(19)—C(20)	1·390 (5)
P(2)—Cl(2)	2·025 (1)	–	C(5)—C(6)	1·399 (8)	1·400 (7)	C(19)—C(24)	1·390 (5)
P(1)—N(1)	1·582 (2)	1·556 (2)	C(7)—C(8)	1·396 (7)	1·373 (7)	C(20)—C(21)	1·399 (6)
P(1)—C(1)	1·799 (4)	1·815 (4)	C(7)—C(12)	1·384 (7)	1·398 (5)	C(21)—C(22)	1·378 (7)
P(1)—C(7)	1·803 (5)	1·822 (4)	C(8)—C(9)	1·393 (7)	1·403 (8)	C(22)—C(23)	1·401 (6)
P(1)—C(13)	1·789 (5)	1·816 (5)	C(9)—C(10)	1·373 (9)	1·387 (8)	C(23)—C(24)	1·385 (6)
P(2)—N(1)	1·557 (2)	1·605 (2)	C(10)—C(11)	1·385 (9)	1·369 (8)	C(25)—C(26)	1·393 (5)
P(2)—O(1)	1·459 (2)	1·489 (3)	C(11)—C(12)	1·396 (7)	1·391 (8)	C(25)—C(30)	1·393 (4)
P(2)—C(19)	–	1·822 (3)	C(13)—C(14)	1·378 (7)	1·404 (7)	C(26)—C(27)	1·395 (5)
P(2)—C(25)	–	1·808 (2)	C(13)—C(18)	1·410 (7)	1·393 (5)	C(27)—C(28)	1·378 (5)
C(1)—C(2)	1·377 (7)	1·385 (7)	C(14)—C(15)	1·384 (8)	1·385 (8)	C(28)—C(29)	1·379 (6)
C(1)—C(6)	1·393 (8)	1·398 (6)	C(15)—C(16)	1·390 (9)	1·409 (9)	C(29)—C(30)	1·392 (5)
C(2)—C(3)	1·404 (8)	1·394 (8)	C(16)—C(17)	1·387 (10)	1·376 (9)		
C(3)—C(4)	1·367 (9)	1·380 (8)	C(17)—C(18)	1·380 (9)	1·395 (7)		

(*b*) Bond angles

	(I)	(II)		(I)	(II)		(I)	(II)
C(1)—P(1)—N(1)	106·2 (2)	107·7 (2)	C(6)—C(1)—C(2)	120·5 (4)	120·4 (4)	C(17)—C(16)—C(15)	120·2 (6)	121·4 (5)
C(7)—P(1)—N(1)	115·1 (2)	114·9 (2)	C(3)—C(2)—C(1)	119·2 (5)	119·5 (5)	C(18)—C(17)—C(16)	120·7 (5)	119·5 (5)
C(13)—P(1)—N(1)	112·7 (2)	115·7 (2)	C(4)—C(3)—C(2)	120·3 (5)	119·8 (5)	C(17)—C(18)—C(13)	119·3 (5)	120·0 (4)
C(7)—P(1)—C(1)	108·8 (2)	106·2 (2)	C(5)—C(4)—C(3)	120·8 (6)	121·3 (5)	C(20)—C(19)—P(2)	–	118·1 (3)
C(13)—P(1)—C(1)	107·0 (2)	106·2 (2)	C(6)—C(5)—C(4)	120·0 (6)	119·6 (5)	C(24)—C(19)—P(2)	–	122·5 (2)
C(13)—P(1)—C(7)	106·7 (2)	105·5 (2)	C(5)—C(6)—C(1)	119·3 (5)	119·3 (4)	C(24)—C(19)—C(20)	–	119·3 (3)
P(1)—N(1)—P(2)	139·7 (2)	146·0 (2)	C(8)—C(7)—P(1)	118·2 (3)	118·9 (3)	C(21)—C(20)—C(19)	–	119·9 (4)
O(1)—P(2)—N(1)	117·6 (1)	120·1 (1)	C(12)—C(7)—P(1)	120·8 (3)	120·8 (4)	C(22)—C(21)—C(20)	–	120·6 (3)
Cl(1)—P(2)—N(1)	109·2 (1)	–	C(12)—C(7)—C(8)	120·9 (4)	120·3 (4)	C(23)—C(22)—C(21)	–	119·7 (4)
Cl(1)—P(2)—Cl(2)	100·9 (1)	–	C(9)—C(8)—C(7)	119·2 (5)	119·6 (5)	C(24)—C(23)—C(22)	–	119·6 (4)
Cl(1)—P(2)—O(1)	109·5 (1)	–	C(10)—C(9)—C(8)	119·6 (5)	119·8 (5)	C(23)—C(24)—C(19)	–	121·0 (3)
Cl(2)—P(2)—N(1)	109·3 (1)	–	C(11)—C(10)—C(9)	121·7 (5)	120·6 (5)	C(26)—C(25)—P(2)	–	121·8 (2)
Cl(2)—P(2)—O(1)	109·1 (1)	–	C(12)—C(11)—C(10)	119·1 (5)	120·0 (5)	C(30)—C(25)—P(2)	–	119·1 (2)
C(19)—P(2)—N(1)	–	104·7 (1)	C(11)—C(12)—C(7)	119·5 (5)	119·8 (5)	C(30)—C(25)—C(26)	–	119·0 (3)
C(25)—P(2)—N(1)	–	107·8 (1)	C(14)—C(13)—P(1)	122·6 (4)	121·7 (3)	C(27)—C(26)—C(25)	–	120·7 (3)
C(19)—P(2)—O(1)	–	110·0 (2)	C(18)—C(13)—P(1)	118·2 (4)	117·9 (3)	C(28)—C(27)—C(26)	–	119·3 (3)
C(25)—P(2)—O(1)	–	110·0 (1)	C(18)—C(13)—C(14)	119·1 (5)	120·3 (4)	C(29)—C(28)—C(27)	–	120·9 (3)
C(25)—P(2)—C(19)	–	102·8 (2)	C(15)—C(14)—C(13)	121·7 (5)	119·8 (5)	C(30)—C(29)—C(28)	–	119·9 (4)
C(2)—C(1)—P(1)	119·3 (4)	117·9 (3)	C(16)—C(15)—C(14)	118·9 (6)	119·1 (5)	C(29)—C(30)—C(25)	–	120·2 (3)
C(6)—C(1)—P(1)	120·2 (4)	121·7 (4)						

(*c*) Selected torsion angles

	(I)	(II)		(I)	(II)
C(1)—P(1)—N(1)—P(2)	170·3 (3)	173·0 (3)	Cl(1)—P(2)—N(1)—P(1)	44·5 (3)	–
C(7)—P(1)—N(1)—P(2)	49·8 (3)	54·9 (4)	Cl(2)—P(2)—N(1)—P(1)	−64·9 (3)	–
C(13)—P(1)—N(1)—P(2)	−72·9 (3)	−68·4 (4)	C(19)—P(2)—N(1)—P(1)	–	−149·4 (3)
N(1)—P(1)—C(1)—C(2)	−17·4 (4)	−39·9 (4)	C(25)—P(2)—N(1)—P(1)	–	101·7 (3)
N(1)—P(1)—C(7)—C(8)	−75·7 (4)	−33·8 (4)	C(20)—C(19)—P(2)—N(1)	–	157·5 (3)
N(1)—P(1)—C(13)—C(14)	154·5 (4)	154·6 (4)	C(26)—C(25)—P(2)—N(1)	–	33·3 (3)
O(1)—P(2)—N(1)—P(1)	170·1 (2)	−25·3 (4)			

Table 3 (*cont.*)

(*d*) Selected intramolecular non-bonded distances for (I) and (II)

Compound (I)		Compound (II)	
P(1)···Cl(1)	3·70 (1)	P(1)···O(1)	3·69 (1)
P(1)···Cl(2)	3·85 (1)	N(1)···C(24)	3·06 (1)
N(1)···C(2)	2·96 (1)	N(1)···C(26)	3·15 (1)
N(1)···C(8)	3·54 (1)	N(1)···C(2)	3·09 (1)
N(1)···C(18)	3·15 (1)	N(1)···C(8)	3·24 (1)
Cl(1)···C(8)	3·96 (1)	N(1)···C(18)	3·20 (1)
Cl(1)···C(13)	3·68 (1)	O(1)···C(21)	3·05 (1)
Cl(1)···C(18)	3·55 (1)	O(1)···C(30)	3·02 (1)
Cl(2)···C(7)	3·69 (1)		
Cl(2)···C(8)	3·61 (1)		

(*e*) Intermolecular distances <3·8 Å for (I)

O(1)···C(15^{I})	3·17 (1)	O(1)···C(9^{IV})	3·72 (1)
O(1)···C(16^{II})	3·42 (1)	Cl(1)···C(14^{IV})	3·75 (1)
Cl(1)···C(5^{II})	3·58 (1)	Cl(1)···C(15^{IV})	3·64 (1)
Cl(17)···C(4^{II})	3·74 (1)	Cl(2)···Cl(1^{IV})	3·78 (1)
Cl(2)···C(3^{III})	3·79 (1)		

Roman numerals as superscripts refer to the following operations, which should be applied to the coordinates of the second atom:

(I)	x,	$1+y$,	z	(III)	$1-x$,	$1-y$,	$-z$
(II)	x,	$\frac{1}{2}-y$,	$\frac{1}{2}+z$	(IV)	$1-x$,	$\frac{1}{2}+y$,	$\frac{1}{2}-z$.

(*f*) Intermolecular distances ≤3·6 Å for (II)

C(26)···C(30^{I})	3·54 (1)	C(28)···C(15^{I})	3·60 (1)
C(26)···C(17^{I})	3·58 (1)	C(29)···C(15^{I})	3·57 (1)
C(27)···O(1^{I})	3·59 (1)	C(29)···C(16^{I})	3·52 (1)
C(27)···C(18^{I})	3·43 (1)	O(1)···C(5^{II})	3·28 (1)
C(28)···C(14^{I})	3·57 (1)		

Roman numerals as superscripts refer to the following operations, which should be applied to the coordinates of the second atom:

(I) $-x$, $-y$, $\frac{1}{2}+x$ (II) $\frac{1}{2}-x$, $\frac{1}{2}+y$, $-\frac{1}{2}+z$.

Table 4. *Structural data for selected triphenylphosphazenyl derivatives,* $Ph_3P{=}N{-}R$

R	P=N (Å)	N–P (Å)	∠P=N–*R* (°)	Reference
$-P(O)Cl_2$	1·582 (2)	1·558 (2)	139·7 (2)	This work
$-P(O)Ph_2$	1·557 (2)	1·604 (2)	146·0 (2)	This work
$-N_3P_3Cl_5$	1·597 (8)	1·614 (8)	–	(*a*)
$-N_3P_3Cl_4Ph$ (geminal)	1·578 (7)	1·585 (7)	131·7 (4)	(*b*)
$-N_4P_4Cl_7$	1·587 (9)	1·566 (9)	–	(*c*)
$-P^+Ph_3$*	1·539 (2)	1·539 (2)	180	(*d*)
$-C_6H_4$-*p*-Br	1·567 (6)	–	124·2 (5)	(*e*)
$-C_3N_3ClNMe_2$	1·622 (5)	–	121	(*f*)
$-C_5(CN)_7$	1·615 (2)	–	130·0 (1)	(*g*)
$-SO_2C_6H_4$-*p*-Me	1·579 (4)	–	126·4 (2)	(*h*)
$-S_3N_3$	1·645 (10)	–	121·0 (6)	(*i*)
$-C_6(NO_2)_3(N{=}PPh)_2$	1·54–1·58	–	mean 137	(*j*)
	1·630 (5)	–	129	(*k*)

References: (*a*) Babu *et al.* (1976); (*b*) Biddlestone *et al.* (1974); (*c*) Babu, Manohar, Cameron & Shaw (1978); (*d*) Wilson & Bau (1974); (*e*) Hewlins (1971); (*f*) Cameron, Mannan, Biddlestone & Shaw (1975); (*g*) Butterfield, Tebby & King (1978); (*h*) Cameron *et al.* (1974); (*i*) Holt & Holt (1974); (*j*) Cameron & Prout (1969*a*); (*k*) Cameron & Prout (1969*b*).

* The $[Ph_3P\overset{\cdot\cdot}{-}N\overset{\cdot\cdot}{-}PPh_3]^+$ cation displays a wide range of dimensions (see text).

the relevant P atoms in (I) and (II) might be electron-rich relative to those in analogous dialkylaminophosphinoyl compounds. However, this is not reflected in the P=O length of (I) [1·459 (2) Å], which is not significantly different from those in Cl_3PO [1·448 (5) Å] (Moritani, Kuchitsu & Morino, 1971), $Cl_2P(O)NPhP(S)Cl_2$ [1·449 (6) Å] (Ghouse *et al.*, 1972) and $Cl_2P(O)CH_2P(O)Cl_2$ [1·463 (4) Å] (Sheldrick, 1975). Moreover, the P=O bond of (II) [1·489 (3) Å] is close to the values in Ph_3PO [1·483 (2) Å] (Ruban & Zabel, 1976) and $Ph_2P(O)NMe_2$ [1·482 (5) Å].

The P–Cl bonds of (I) [both 2·025 (1) Å] do not differ significantly from the value [2·033 (8) Å] in the electron-diffraction study of $Cl_2P(O)NMe_2$. The same conclusion may be drawn from ^{35}Cl NQR data (Dalgleish, Keat, Porte & Shaw, 1977), which show that the P–Cl lengths in (I) fit a correlation between ^{35}Cl NQR frequencies and P–Cl lengths.

Although the opening of the P–N–P interbond angles in (I) [139·7 (2)°] and (II) [146·0 (2)°] relative to the values observed in many other triphenylphosphazenyl derivatives might be expected to optimize the degree of multiple bonding between N and P (or other hetero atom), it seems more likely that this angle is determined largely by steric effects. Thus the phenyl groups in (II), being more bulky than the Cl atoms in (I), are associated with the larger angle. No other trends in this angle have been recognized; the foregoing results and the variable P–N–P angle in the $[Ph_3P\overset{\cdot\cdot}{-}N\overset{\cdot\cdot}{-}PPh_3]^+$ cation indicate that the variations in this angle [134·6–180°] are the result of a subtle combination of steric and electronic effects.

Particular interest has centred on the conformation adopted about the bond to the triphenylphosphazenyl group in *N*-sulphonyl and *N*-cyclophosphazenyl derivatives (Cameron, Hair & Morris, 1974; Shaw, 1975). The relevant torsion angles in Table 3 reveal that whereas a value of 170·1 (2)° is observed for O(1)–P(2)–N(1)–P(1) in (I), giving an approximate *transoid* arrangement of O(1) and P(1), the value in (II) is −25·3 (4)°, giving an approximate *cisoid* arrangement of the same atoms. This difference may be partly attributed to differing non-bonded interactions. Thus, in (I) the conformation about P(2)–N(1) may be understood in terms both of electrostatic interactions between the Cl atoms and P(1) and also of possible steric interactions, whereas in (II) the *cisoid* arrangement of P(1) and O(1) may represent the minimization of steric interactions between the phenyl groups at either end of the molecule. In this context we have already noted the relative enlargement of P(1)–N(1)–P(2) in (II). Whilst comparisons between the conformations in $N_3P_3Cl_5(N{=}PPh_3)$ (Babu, Cameron, Krishnamurthy, Manohar & Shaw, 1976) and geminal $N_3P_3Cl_4Ph(N{=}PPh_3)$ (Biddlestone, Shaw, Bullen & Dann, 1974), and the present conformations are difficult, it may be noted that the conformations of (I) and (II) are such that the formal P=N double bond lies approximately parallel to the P=O bond. This may be compared with $N_3P_3Cl_5$-(N=PPh_3), where the exocyclic P=N bond lies parallel to the phosphazene ring with its multiple-bonded P–N system, but contrasts with geminal $N_3P_3Cl_4Ph$-(N=PPh_3), in which the exocyclic P=N bond lies perpendicular to the phosphazene ring.

In both (I) and (II), the Ph_3P=N groups exhibit the familiar propeller conformation, in which the interplanar angles are 81·7, 96·2 and 117·6° in (I), and 85·8, 98·1 and 79·9° in (II). The absence of short intermolecular contacts in the crystal structures of both compounds suggests that the packing is dominated by van der Waals forces.

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Geometry of the Bicyclo[2.2.2]octatriene System: Crystal Structure of 2,3-(Tetrafluorobenzo)bicyclo[2.2.2]octatriene

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Abstract

$C_{12}H_6F_4$ is monoclinic, space group $C2/c$, with a = 16·10 (1), b = 8·17 (1), c = 14·95 (1) Å, β = 104·71 (5)°, Z = 8. The structure was refined to R = 4·62% for 1173 observed counter amplitudes. E.s.d.'s average 0·004 Å for bond lengths and 0·25° for bond angles not involving H atoms. The bicyclo[2.2.2]-octatriene skeleton deviates to a small but significant extent from its idealized geometry, but maintains *mm*2 symmetry consistent with the overall geometry of the molecule.

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