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The Crystal and Molecular Structure of 2,2,6,6-Tetrachloro-4,4,8,8-tetraphenylcyclotetraphosphazatetraene, $N_4P_4Cl_4(C_6H_5)_4$

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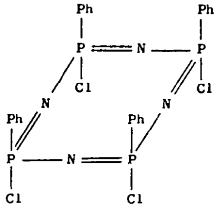
Crystals of 2,2,6,6-$N_4P_4Cl_4(C_6H_5)_4$ are orthorhombic, $a=18{\cdot}36$, $b=16{\cdot}25$, $c=9{\cdot}53$ Å, space group $P2_12_12_1$, $Z=4$. The atomic positions were determined from X-ray diffractometer intensities and refined by full-matrix least-squares calculations to a final R of 0·058 for 2715 reflexions. The eight-membered phosphazene ring has a saddle conformation with approximate symmetry $\bar{4}2m$ (D_{2d}) and P–N–P angles ranging from 128·8° to 135·4°. The symmetry of the whole molecule approaches 222 (D_2) but differences between the orientations of the phenyl groups cause some departure from this ideal symmetry. There are four long and four short P–N bonds in the ring, mean lengths respectively 1·591 and 1·553 Å. Other mean bond lengths are: P–Cl 2·010, P–C 1·806, and C–C 1·39 Å. Differences between the bond lengths in this molecule and in two of its non-geminal isomers are explicable in terms of electron displacements resulting from the different mutual arrangements of the substituent chloro and phenyl groups. The three isomers also have different phosphazene-ring conformations, a major factor governing the conformation probably being steric interaction between neighbouring substituents.

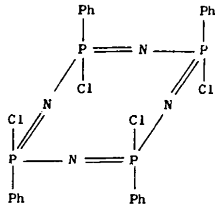
Introduction

Studies of the structures of a number of tetrameric cyclic phosphazene molecules have shown considerable variation in the molecular geometry, in two respects: (i) variation, over a range of *ca.* 0·1 Å, in the lengths of P–N bonds in the ring (surveyed by Wagner, 1971; Bullen & Tucker, 1972*a*) or of exocyclic P–Cl bonds (Bullen & Dann, 1974); and (ii) differences in ring conformation [see for example Marsh & Trotter (1971*a*, *b*), Bullen & Tucker (1972*b*)]. The factors governing these observed differences are most likely to be found by studying isomeric molecules which differ only in the relative placing of the same exocyclic groups.

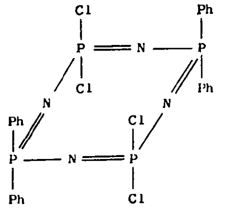
The isomers of a tetra-substituted phosphazene $N_4P_4X_4Y_4$ will be either (*a*) entirely geminal, *i.e.* containing only PX_2 and PY_2 groups – two such isomers are possible, with 2,2,4,4- or 2,2,6,6-structures; (*b*) entirely non-geminal, *i.e.* containing only PXY groups – in this case four *cis–trans* type isomers are possible; or (*c*) partly geminal and partly non-geminal, with again four isomers. The crystal structures of two *cis–trans* isomers of $N_4P_4Cl_4(C_6H_5)_4$ of type (*b*) (I and II, $Ph=C_6H_5$) have already been determined (Bullen & Tucker, 1972*a*; Burr, Carlisle & Bullen, 1974). Their bond lengths are substantially the same but they differ markedly in ring conformation, (I) having an irregular crown form of ring while (II) has a chair. We therefore decided to investigate the crystal structure of a third isomer, the geminal 2,2,6,6-$N_4P_4Cl_4(C_6H_5)_4$ (III), in order to find, by comparison with (I) and (II), what effect the different arrangement of the exocyclic groups has on the bond lengths and ring conformation.



(I)



(II)



(III)

Experimental

Suitable crystals of 2,2,6,6-$N_4P_4Cl_4(C_6H_5)_4$ were grown from a solution in a mixture of n-pentane, n-hexane and dichloromethane at room temperature. The forms developed are the pinacoids {100}, {010}, and {001}. The crystals are needle-shaped, elongated along **c** and having a roughly equidimensional cross-section. The cell dimensions and other data are given in Table 1. X-ray intensities of the 13 layers of reflexions *hk*0–12 were measured at 17–20°C on a Philips Pailred diffractometer with monochromated Mo $K\alpha$ radiation. 2715 reflexions with $I>2\sigma(I)$ were obtained by measuring all reflexions with $\sin\theta/\lambda < 0{\cdot}71$ Å^{-1}. The intensities of the six $00l$ reflexions could not be measured as the crystal was aligned with **c** parallel to the ω axis of the diffractometer. The intensities were corrected for Lorentz and polarization effects but not for absorption.

Table 1. *Crystal data*

2,2,6,6-$N_4P_4Cl_4(C_6H_5)_4$
Orthorhombic
$a = 18{\cdot}36\ (2)$ Å
$b = 16{\cdot}25\ (2)$
$c = 9{\cdot}53\ (2)$
Space group $P2_12_12_1$ (No. 19)
$F(000) = 1280$

$V = 2843$ Å^3
$Z = 4$
$D_m = 1{\cdot}46$ g cm^{-3} (by flotation)
$D_c = 1{\cdot}47$ g cm^{-3}
$\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$ Å
$\mu(\text{Mo } K\alpha) = 6{\cdot}8$ cm^{-1}

Systematic absences: $h00$ when h is odd, $0k0$ when k is odd, $00l$ when l is odd.

The weighted multisolution tangent and least-squares refinements were carried out on the University of Essex PDP-10 computer with programs written by Dr G. M. Sheldrick. The scattering factors were calculated from the analytic function $f = C + \sum_{i=1}^{4} A_i \exp(-B_i \sin^2\theta/\lambda^2)$, the parameters A, B, and C being taken from Cromer & Waber (1965) for Cl, P, N and C, and from Forsyth & Wells (1959) for H (in this case $A_3 = A_4 = 0$).

Structure determination

The phases of the reflexions were determined directly by weighted multisolution tangent refinement (Germain, Main & Woolfson, 1971) applied to the 540 reflexions with $|E| \geq 1{\cdot}3$. The E map calculated after tangent refinement showed the positions of all the chlorine, phosphorus and nitrogen atoms. The carbon atoms were located from a subsequent Fourier synthesis phased on the heavier atoms.

The atomic positions were refined by full-matrix least-squares cycles with isotropic temperature factors until R had dropped to 0·12. At this stage the hydrogen atoms were inserted as a fixed contribution to the structure factors, their positions being calculated from the formula $x_H = x_0 + 1{\cdot}776\ (x_C - x_0)$, where x_H and x_C represent positional coordinates of bonded hydrogen and carbon atoms, and x_0 the coordinate of the centre of the benzene ring. With the hydrogen atoms inserted and assigned isotropic thermal parameters $(\bar{u^2})$ 0·013 Å^2 greater than those of the attached carbon atom, the temperature factors of all the other atoms were allowed to become anisotropic. Limitations on computer store prevented all parameters from being refined simultaneously. They were therefore divided into two blocks, one of which contained the 12 chlorine, phosphorus, and nitrogen atoms, and the other the 24 carbon and 2 phosphorus atoms in the two $P(C_6H_5)_2$ groups. The weighting scheme $w = (8{\cdot}0 - 0{\cdot}236|F_o| + 0{\cdot}002|F_o|^2)^{-1}$ was used to make the average values of $w\Delta^2$ (where $\Delta = |F_o| - |F_c|$) for groups of reflexions fairly uniform over the whole range of $|F_o|$. The two blocks were refined alternately, each for a total of seven cycles. The final R is 0·058 for 2715 reflexions and R' $[=(\sum w\Delta^2/\sum w|F_o|^2)^{1/2}]$ is 0·044. In the last cycle of refinement all parameter shifts were less than $0{\cdot}06\sigma$.

The final atomic coordinates and thermal parameters are listed in Tables 2–4.* The molecular shape and the numbering of the atoms are shown in Fig. 1. Bond lengths are shown in Fig. 2 and Table 5, and bond angles in Fig. 3.

Table 2. *Fractional atomic coordinates* (× 10^4) *with estimated standard deviations*

	x/a	y/b	z/c
Cl(1)	3803 (1)	−582 (1)	977 (2)
Cl(2)	5167 (1)	−542 (1)	−929 (2)
Cl(3)	4853 (1)	3417 (1)	−967 (3)
Cl(4)	4460 (1)	3471 (1)	2191 (2)
P(1)	4524 (1)	223 (1)	166 (2)
P(2)	5510 (1)	1306 (1)	1617 (2)
P(3)	4623 (1)	2657 (1)	633 (2)
P(4)	3610 (1)	1549 (1)	−676 (2)
N(1)	4950 (3)	563 (3)	1450 (5)
N(2)	5325 (3)	2168 (3)	928 (6)
N(3)	3869 (3)	2239 (3)	391 (6)
N(4)	4149 (3)	791 (3)	−935 (5)
C(11)†	5617 (4)	1410 (4)	3482 (7)
C(12)	5471 (4)	763 (5)	4368 (7)
C(13)	5570 (5)	853 (6)	5795 (9)
C(14)	5800 (5)	1583 (7)	6350 (10)
C(15)	5958 (6)	2225 (7)	5460 (10)
C(16)	5860 (5)	2143 (5)	4035 (10)
C(21)	6382 (4)	1029 (4)	926 (7)
C(22)	6721 (4)	310 (5)	1358 (9)
C(23)	7403 (5)	96 (6)	863 (12)
C(24)	7734 (5)	578 (7)	−120 (11)
C(25)	7402 (5)	1283 (6)	−621 (11)
C(26)	6729 (4)	1511 (5)	−69 (8)
C(31)	3449 (4)	1977 (4)	−2398 (7)
C(32)	3773 (5)	1686 (6)	−3545 (9)
C(33)	3670 (7)	2057 (7)	−4820 (11)
C(34)	3224 (5)	2714 (7)	−4968 (11)
C(35)	2898 (6)	3005 (7)	−3845 (12)
C(36)	3012 (6)	2644 (6)	−2543 (10)
C(41)	2756 (4)	1209 (5)	19 (8)
C(42)	2286 (4)	764 (6)	−806 (11)
C(43)	1657 (6)	440 (8)	−220 (12)
C(44)	1502 (6)	570 (7)	1184 (14)
C(45)	1983 (6)	988 (6)	2002 (11)
C(46)	2609 (5)	1316 (5)	1425 (9)

† Atoms C(11)–C(16) constitute phenyl group (1) *etc.*

The amplitudes of vibration corresponding to the thermal parameters listed in Table 3 are given in Table 6. As some of the carbon atoms are clearly undergoing very large vibrations, rigid-body libration analyses were attempted for various parts of the molecule by the method of Schomaker & Trueblood (1968), which treats the molecular vibrations in terms of three tensors: **T** for translation, **L** for libration, and **S** for cor-

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* The table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30583 (15 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

relations of translation and libration. It was thought unlikely that the whole molecule would behave as a rigid body, and indeed it was not possible to find three tensors which would adequately describe the motion of all the atoms in the molecule.

Table 3. *Components of thermal vibration tensors* (Å^2, $\times 10^3$) *and their estimated standard deviations*

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl(1)	68 (1)	53 (1)	65 (1)	12 (1)	−6 (1)	−24 (1)
Cl(2)	87 (2)	68 (1)	53 (1)	−12 (1)	4 (1)	36 (1)
Cl(3)	104 (2)	82 (2)	87 (2)	52 (1)	−2 (1)	−8 (1)
Cl(4)	96 (2)	62 (1)	81 (2)	−32 (1)	−14 (1)	7 (1)
P(1)	39 (1)	34 (1)	33 (1)	−2 (1)	−3 (1)	1 (1)
P(2)	40 (1)	37 (1)	42 (1)	2 (1)	−10 (1)	−1 (1)
P(3)	53 (1)	33 (1)	43 (1)	6 (1)	−8 (1)	2 (1)
P(4)	41 (1)	42 (1)	33 (1)	−1 (1)	−3 (1)	4 (1)
N(1)	48 (3)	38 (3)	42 (3)	4 (3)	−6 (3)	−4 (3)
N(2)	55 (4)	37 (3)	63 (4)	7 (3)	−13 (3)	−5 (3)
N(3)	49 (3)	49 (3)	56 (4)	−3 (3)	−6 (3)	9 (3)
N(4)	48 (3)	41 (3)	40 (3)	−1 (3)	0 (3)	3 (3)
C(11)	54 (4)	38 (4)	52 (4)	−3 (3)	−13 (4)	6 (4)
C(12)	77 (5)	56 (4)	45 (4)	1 (4)	1 (5)	8 (4)
C(13)	97 (7)	106 (7)	39 (4)	8 (5)	−2 (5)	8 (6)
C(14)	109 (8)	120 (9)	59 (6)	−37 (7)	−31 (6)	16 (7)
C(15)	181 (12)	87 (7)	56 (6)	−19 (5)	−35 (7)	−39 (8)
C(16)	140 (9)	55 (5)	65 (6)	−8 (5)	−30 (6)	−19 (6)
C(21)	41 (4)	55 (4)	40 (4)	−10 (4)	−6 (4)	−4 (3)
C(22)	58 (5)	53 (4)	84 (6)	9 (5)	11 (5)	15 (4)
C(23)	62 (6)	84 (6)	106 (8)	2 (7)	11 (6)	11 (5)
C(24)	52 (5)	104 (8)	95 (8)	−29 (7)	14 (6)	−8 (6)
C(25)	65 (6)	94 (7)	69 (6)	−4 (6)	6 (5)	−15 (6)
C(26)	58 (5)	76 (5)	40 (4)	3 (5)	0 (4)	−8 (5)
C(31)	46 (4)	54 (4)	38 (4)	12 (4)	1 (3)	3 (4)
C(32)	119 (8)	99 (7)	63 (6)	29 (6)	20 (6)	63 (7)
C(33)	181 (12)	150 (11)	62 (7)	28 (7)	38 (8)	89 (10)
C(34)	99 (8)	114 (9)	59 (6)	37 (7)	4 (6)	37 (7)
C(35)	128 (9)	118 (9)	96 (9)	50 (7)	13 (8)	65 (8)
C(36)	130 (9)	130 (9)	55 (6)	27 (6)	20 (6)	84 (8)
C(41)	49 (4)	60 (5)	38 (4)	7 (4)	1 (4)	12 (4)
C(42)	53 (5)	114 (8)	69 (6)	−2 (6)	3 (5)	−24 (5)
C(43)	85 (8)	144 (11)	95 (9)	16 (8)	−4 (7)	−43 (7)
C(44)	74 (7)	114 (9)	114 (10)	31 (8)	31 (7)	1 (7)
C(45)	103 (8)	87 (7)	59 (6)	10 (5)	33 (6)	15 (6)
C(46)	81 (6)	59 (5)	58 (6)	7 (5)	15 (5)	1 (5)

Table 4. *Fractional coordinates* ($\times 10^3$) *and mean-square amplitude of thermal vibration* (Å^2, $\times 10^3$) *assigned to hydrogen atoms* (*numbered according to the carbon atom to which they are attached*)

	x/a	y/b	z/c	$\overline{u^2}$
H(12)	528	19	394	69
H(13)	546	35	648	93
H(14)	587	165	746	90
H(15)	615	279	588	111
H(16)	597	264	335	95
H(22)	646	−7	211	74
H(23)	767	−45	123	93
H(24)	826	41	−52	92
H(25)	767	166	−141	86
H(26)	647	206	−42	68
H(32)	411	117	−344	100
H(33)	393	183	−570	117
H(34)	314	300	−596	96
H(35)	256	352	−397	126
H(36)	276	287	−166	112
H(42)	240	67	−190	86
H(43)	129	10	−86	103
H(44)	101	33	164	105
H(45)	187	107	309	84
H(46)	298	165	206	83

Analyses of the individual P–C_6H_5 groups did however give sensible results, although some of the tensor components have large estimated standard deviations. The **T**, **L**, and **S** tensors were first calculated by reference to the crystallographic axes (Table 7*a*). Then, in order that the librations could be better appreciated in terms of molecular motion, each **L** tensor was transformed to axes taken parallel to the inertial axes of the P–C_6H_5 group, defined as follows: for phenyl group (*n*) the *x* axis is parallel to the bisector of the angle C(*n*2)–P–C(*n*6), *z* is normal to the plane of these three

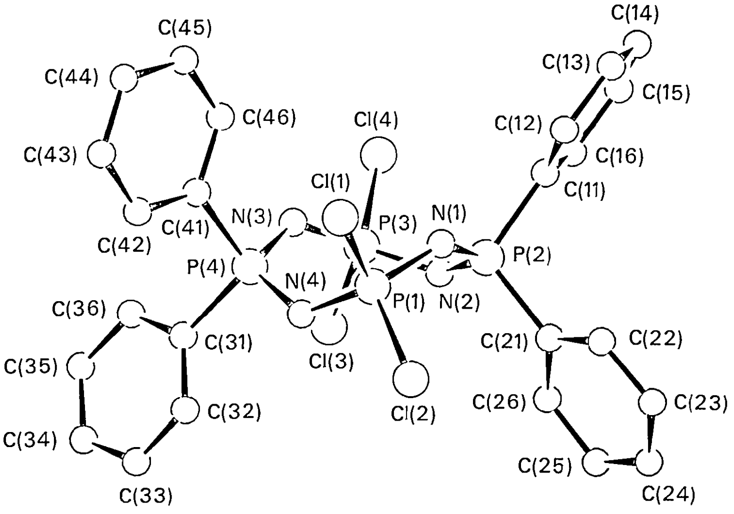
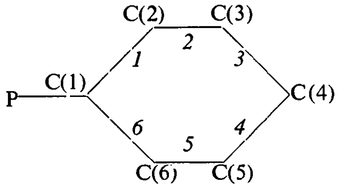


Fig. 1. Molecular shape and numbering of the atoms.

Table 5. C–C *and* P–C *bond lengths* (Å) *before and after correction for phenyl-group libration*



(*a*) Uncorrected

Bond	Phenyl group: (1)	(2)	(3)	(4)
1	1·375 (9)*	1·386 (9)	1·332 (10)	1·373 (10)
2	1·379 (10)	1·383 (11)	1·369 (12)	1·387 (12)
3	1·365 (11)	1·364 (13)	1·352 (12)	1·384 (14)
4	1·375 (12)	1·382 (12)	1·315 (13)	1·360 (13)
5	1·376 (12)	1·394 (10)	1·389 (12)	1·381 (11)
6	1·376 (9)	1·385 (9)	1·355 (10)	1·378 (10)
P–C	1·797 (7)	1·788 (7)	1·807 (7)	1·789 (7)

(*b*) Corrected

1	1·397	1·399	1·390	1·392
2	1·386	1·388	1·375	1·393
3	1·392	1·378	1·391	1·400
4	1·397	1·396	1·373	1·378
5	1·382	1·399	1·395	1·387
6	1·403	1·399	1·394	1·394
Mean	1·393 (7)†	1·393 (8)	1·386 (9)	1·391 (7)
P–C	1·805	1·794	1·816	1·798

* Standard deviations obtained from least-squares refinement.

† Standard deviations calculated from the deviations of individual values from the mean.

Table 6. *Ranges of root-mean-square amplitudes* (Å) *of thermal vibration along the principal axes of the vibration ellipsoids found for the various types of atom*

	Minor	Medium	Major
Cl	0·18–0·19	0·25–0·32	0·30–0·37
P	0·17–0·18	0·18–0·21	0·20–0·24
N	0·19–0·20	0·20–0·23	0·22–0·27
C	0·17–0·25	0·20–0·31	0·24–0·52

atoms, and y is orthogonal to x and z, *i.e.* almost parallel to the C(n2)–C(n6) direction* (Table 7*b*).

The transformed **L** tensors (Table 7*b*) show that all the phenyl groups have a much larger libration about the group x axis (the P–C bond) than about y or z and the smallest libration is that about y. L_{11} is particularly large for ring (3) and corresponds to an r.m.s. amplitude of libration of 17°. The same libration pattern $L_{11} > L_{33} > L_{22}$ was found for the phenyl groups in *cis*-$N_4P_4Cl_4(C_6H_5)_4$ (I) (Bullen & Tucker, 1972*a*). It can be explained in terms of the effect of atomic displacements on the bonding. Rotation about the P–C bond (the group x axis) reduces only the (weak) π overlap between carbon and phosphorus, while rotation about z reduces σ overlap, and rotation about y reduces both. Alternatively it may be that rotation about x occurs most easily because the moment of inertia of the phenyl group is smallest about this direction.

C–C and P–C bond lengths corrected for the effect of these phenyl group librations are shown in Table 5. Many of the corrections are substantial. This is particularly so for phenyl group (3), where the correction raises the apparently very low bond lengths (1·315, 1·332 Å) by 0·06 Å so bringing them into line with the C–C lengths in the other rings. No other parts of the molecule were successfully analysed for rigid-body li-

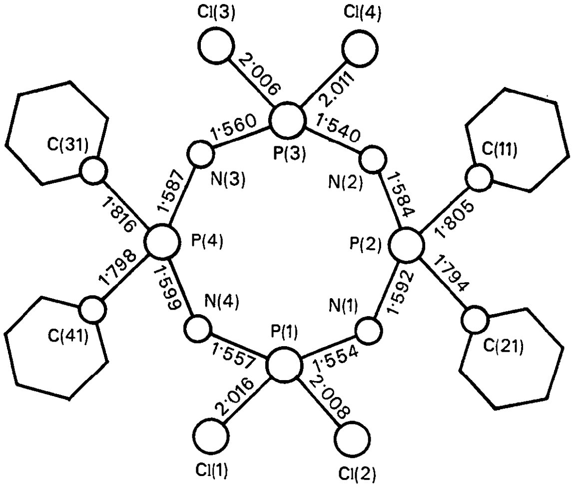


Fig. 2. Bond lengths (Å). Estimated standard deviations are: P–Cl 0·003, P–N 0·005, and P–C 0·007 Å. The P–C lengths are corrected for libration.

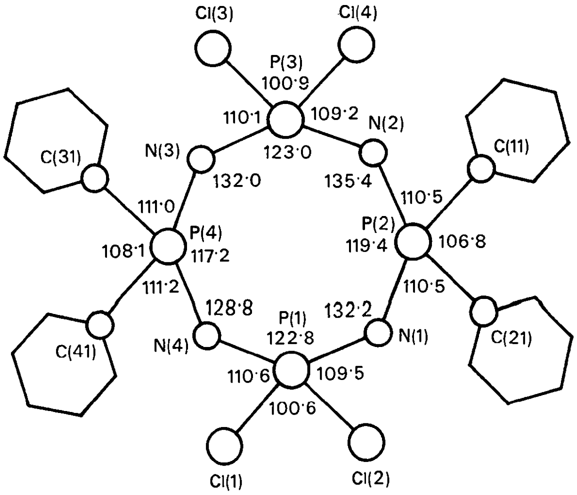


Fig. 3. Bond angles (°). The following are not shown: Cl(1)–P(1)–N(1) 105·0, Cl(2)–P(1)–N(4) 106·1, C(31)–P(4)–N(4) 105·0, C(41)–P(4)–N(3) 104·1, Cl(3)–P(3)–N(2) 106·3, Cl(4)–P(3)–N(3) 105·3, C(11)–P(2)–N(1) 103·9, C(21)–P(2)–N(2) 105·2. Estimated standard deviations are: Cl–P–Cl 0·1°, Cl–P–N 0·2°, all other angles 0·3°.

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* This definition is approximately equivalent to placing the x axis along the P–C bond and z normal to the phenyl ring. The two axes cannot be placed exactly along these directions because the directions are not truly orthogonal in all the P–C_6H_5 groups (see Table 9).

bration and it was therefore not possible to correct the P–Cl and P–N bond lengths for this effect.

Discussion

The geminal isomer (III) of $N_4P_4Cl_4(C_6H_5)_4$ differs from the non-geminal (I) and (II) both in its bond lengths and in the phosphazene ring conformation (Table 8).

Bond lengths and bond angles

Comparison of the bond lengths provides evidence for the operation of two effects: (*A*) In the geminal isomer chlorine atoms withdraw electrons from

Table 7. *Rigid-body libration analyses for the* $P–C_6H_5$ *groups*

(*a*) Tensors **T** (Å², × 10³), **L** (deg²), and **S** (deg Å, × 10) referred to the crystallographic axes. The origin specified for each group is that which makes **S** symmetric

Group (1). Origin (0·556, 0·118, 0·218)

$$\mathbf{T}=\begin{bmatrix} 40\ (7) & 1\ (6) & -7\ (6) \\ & 33\ (6) & 0\ (5) \\ & & 43\ (4) \end{bmatrix} \qquad \mathbf{L}=\begin{bmatrix} 19\ (5) & 1\ (5) & 5\ (11) \\ & 10\ (6) & 1\ (8) \\ & & 129\ (20) \end{bmatrix}$$

$$\mathbf{S}=\begin{bmatrix} -3\ (2) & 1\ (2) & 1\ (4) \\ & -1\ (2) & 0\ (5) \\ & & 4\ (2) \end{bmatrix}$$

Group (2). Origin (0·573, 0·167, 0·190)

$$\mathbf{T}=\begin{bmatrix} 45\ (5) & -2\ (4) & -15\ (5) \\ & 35\ (5) & 7\ (6) \\ & & 30\ (7) \end{bmatrix} \qquad \mathbf{L}=\begin{bmatrix} 49\ (11) & -16\ (5) & -23\ (6) \\ & 22\ (5) & 12\ (3) \\ & & 20\ (5) \end{bmatrix}$$

$$\mathbf{S}=\begin{bmatrix} -2\ (2) & 1\ (3) & -1\ (3) \\ & 1\ (1) & 1\ (1) \\ & & 1\ (2) \end{bmatrix}$$

Group (3). Origin (0·395, 0·080, 0·023)

$$\mathbf{T}=\begin{bmatrix} 9\ (30) & -38\ (21) & -25(\ 16) \\ & 29\ (20) & 2\ (13) \\ & & 49\ (11) \end{bmatrix} \qquad \mathbf{L}=\begin{bmatrix} 29\ (6) & -36\ (7) & 61\ (10) \\ & 100\ (11) & -135\ (11) \\ & & 198\ (22) \end{bmatrix}$$

$$\mathbf{S}=\begin{bmatrix} 5\ (4) & -1\ (4) & -1\ (8) \\ & -4\ (4) & -5\ (7) \\ & & -1\ (5) \end{bmatrix}$$

Group (4). Origin (0·352, 0·164, −0·061)

$$\mathbf{T}=\begin{bmatrix} 43\ (6) & 11\ (6) & -8\ (6) \\ & 46\ (7) & 1\ (7) \\ & & 35\ (7) \end{bmatrix} \qquad \mathbf{L}=\begin{bmatrix} 49\ (16) & 22\ (10) & -27\ (9) \\ & 30\ (8) & -21\ (6) \\ & & 31\ (10) \end{bmatrix}$$

$$\mathbf{S}=\begin{bmatrix} 0\ (3) & 3\ (4) & 0\ (4) \\ & 0\ (2) & -1\ (3) \\ & & 0\ (3) \end{bmatrix}$$

(*b*) Libration tensors (deg²) referred to individual group axes as defined in the text

Group (1)

$$\mathbf{L}=\begin{bmatrix} 128 & -11 & -4 \\ & 12 & 4 \\ & & 18 \end{bmatrix}$$

Group (2)

$$\mathbf{L}=\begin{bmatrix} 68 & -3 & -10 \\ & 10 & 5 \\ & & 13 \end{bmatrix}$$

Group (3)

$$\mathbf{L}=\begin{bmatrix} 296 & -63 & -12 \\ & 15 & 2 \\ & & 15 \end{bmatrix}$$

Group (4)

$$\mathbf{L}=\begin{bmatrix} 80 & -9 & 16 \\ & 10 & -4 \\ & & 20 \end{bmatrix}$$

Table 8. *Mean lengths* (Å) *of groups of chemically equivalent bonds in the three isomers of* $N_4P_4Cl_4(C_6H_5)_4$ *and in* $N_4P_4Cl_8$

				P–N	P–Cl	P–C	Ring shape	Reference
$N_4P_4Cl_4(C_6H_5)_4$	non-geminal	*cis-*	(I)	1·570	2·041	1·783	crown	Bullen & Tucker (1972*a*)
		β-trans	(II)	1·572	2·044	1·796	chair	Burr *et al.* (1974)
	geminal		(III)	1·553, 1·591	2·010	1·803	saddle	This work
$N_4P_4Cl_8$	*T*-form			1·56	1·992	–	chair	Wagner & Vos (1968)
	K-form			1·57	1·989	–	boat	Hazekamp, Migchelsen & Vos (1962)

phosphorus and the deficiency is made up by transfer of electrons from neighbouring nitrogen atoms, so increasing the π-character of the Cl_2P–N bonds in the phosphazene ring and decreasing that of the $(C_6H_5)_2P$–N bonds. This effect is assisted by the tendency of the phenyl groups to be electron-donating. (*B*) In the two non-geminal isomers electron withdrawal by chlorine and electron donation by the phenyl group occur cooperatively at the same $>PCl(C_6H_5)$ centre, producing electron transfer in a direction perpendicular to the phosphazene ring instead of along it.

The difference in π-character of the P–N bonds resulting from effect (*A*) is shown by the occurrence of four short and four long bonds in (III) (mean lengths respectively 1·553 and 1·591 Å, see Fig. 2 and Table 8). A similar arrangement of short and long bonds was found in 2,2,6,6-$N_4P_4F_4(CH_3)_4$ (Marsh & Trotter, 1971*a*). In the non-geminal molecules where effect (*A*) cannot operate because all the phosphorus atoms carry identical pairs of substituents, the P–N bonds do not differ greatly in length and their means (1·570 or 1·572 Å) lie midway between the short and long P–N bonds of the geminal isomer. The longer P–Cl bonds in (III) as compared to $N_4P_4Cl_8$ (Table 8) and the reduction of the mean Cl–P–Cl angle from 103° in $N_4P_4Cl_8$ to 100·8° (Fig. 3) also indicate a weakening of the P–Cl bond owing to effect (*A*).

The evidence for effect (*B*) is the considerable further lengthening of the P–Cl bonds in the two non-geminal isomers (to 2·04 Å) which has already been discussed by Bullen & Tucker (1972*a*). The close proximity of the electron-donating phenyl group to the electron-withdrawing chlorine atom produces more bond lengthening, and therefore weakening, than when effect (*A*) operates, and moreover in the non-geminal molecules the effect does not have to be shared between two P–Cl bonds. We have found even longer P–Cl bonds (up to 2·10 Å) in phosphazenes containing $>PCl[N(CH_3)_2]$, the dimethylamino-group being a good electron donor (Bullen & Dann, 1973, 1974). Evidence for effect (*B*) is also provided by other studies: (i) magneto-optic rotations are larger for phosphazenes containing non-geminal $>PCl[N(CH_3)_2]$ groups than for those geminally substituted (Bruniquel, Faucher, Labarre, Hasan, Krishnamurthy, Shaw & Woods, 1973) and (ii) ^{35}Cl n.q.r. frequencies are lower for non-geminal compounds than for geminal compounds (Keat, Porte, Tong & Shaw, 1972).

The cooperative nature of effect (*B*) should lead to shorter P–C bonds in a $>PCl(C_6H_5)$ group than in a $>P(C_6H_5)_2$ group. The data in Table 8 agree with this but the differences in length between the three isomers are hardly significant when standard deviations are taken into account. The mean P–C length in (III) is almost the same as in $N_3P_3(C_6H_5)_6$ (1·804 Å) (Ahmed, Singh & Barnes, 1969). No data are available for $N_4P_4(C_6H_5)_8$.

Effect (*A*) also produces longer P–Cl bonds in *gem*-$N_3P_3Cl_4(C_6H_5)_2$ (Mani, Ahmed & Barnes, 1965) and *gem*-$N_3P_3Cl_2(C_6H_5)_4$ (Mani, Ahmed & Barnes, 1967) than in $N_3P_3Cl_6$ (Bullen, 1971), but a curious feature of these trimeric geminally substituted molecules is that there are significantly different P–Cl bond lengths within the same molecule: $N_3P_3Cl_4(C_6H_5)_2$ 2·006 and 1·990 Å, $N_3P_3Cl_2(C_6H_5)_4$ 2·027 and 2·007 Å. This defies explanation.

The four P–N–P angles in (III) differ from each other by up to 7° (Fig. 3). Such a variation is common in eight-membered phosphazene rings but the angles are usually larger than 130°. The value 128·8°, found here for P(1)–N(4)–P(4), is one of the smallest known.

At both P(1) and P(3), two of the Cl–P–N angles are in the region of 106° while the other two are near 110° (Fig. 3). This indicates that the Cl–P–Cl plane is not exactly perpendicular to the N–P–N plane. A similar slight twist occurs between the C–P–C and N–P–N planes at P(2) and P(4). In both cases it probably arises from repulsion between the chlorine atoms and neighbouring phenyl groups (discussed below).

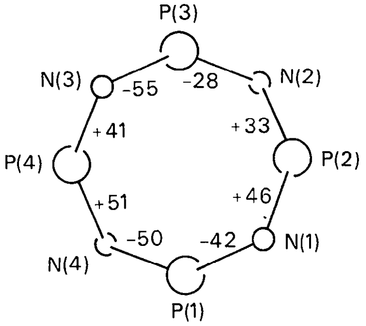

Fig. 4. Torsion angles (°) in the phosphazene ring.

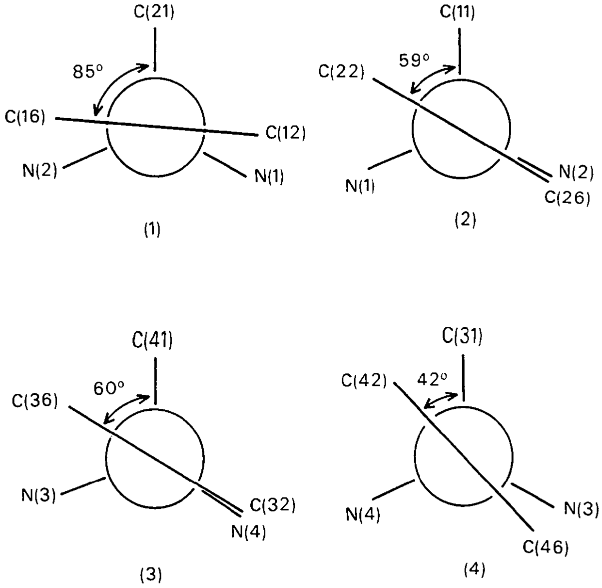

Fig. 5. Newman projections down carbon–phosphorus bonds showing the orientation of phenyl groups (1)–(4) relative to neighbouring atoms.

Ring conformation

In (III) the phosphazene ring has the saddle conformation. The four phosphorus atoms are very nearly coplanar (deviations from their mean plane, δ_P, are only $\pm 0{\cdot}04$ Å, see Table 9) with the nitrogen atoms alternately above or below their plane, but by amounts (δ_N) ranging from 0·43 to 0·61 Å. The variation in δ_N introduces some irregularity into the saddle shape which is evident also from the different torsion angles (τ) around the ring (ranging from 28° to 55°, see Fig. 4). The signs of the torsion angles satisfy $\bar{4}2m$ (D_{2d}) symmetry but their magnitudes do not. The phosphazene rings in $N_4P_4F_4(CH_3)_4$ and $N_4P_4F_6(CH_3)_2$ (Marsh & Trotter, 1971*a*, *b*) have saddle conformations with exact $\bar{4}2m$ symmetry, in both cases one diad axis of the point group being required crystallographically. A saddle conformation also occurs in $N_4P_4(OCH_3)_8$ (Ansell & Bullen, 1971) which shows about the same departure from $\bar{4}2m$ symmetry as (III) ($|\tau|$, 30° to 55°). Here, however, the failure to achieve $\bar{4}2m$ symmetry results more from lack of coplanarity of the four phosphorus atoms ($\delta_P = \pm 0{\cdot}1$ Å) since the δ_N values are more uniform (0·50–0·55 Å) than in (III). The mean $|\tau|$ for the various rings are: 2,2,6,6-$N_4P_4Cl_4(C_6H_5)_4$ 43·1°, $N_4P_4(OCH_3)_8$ 42·6°, $N_4P_4F_4(CH_3)_4$ 40·2°, $N_4P_4F_6(CH_3)_2$ 15·5°.

The phosphazene rings in the three isomers of $N_4P_4Cl_4(C_6H_5)_4$ so far examined all have different conformations (Table 8). In comparing the two nongeminal isomers Bullen & Tucker (1972*a*) concluded that their ring conformations are determined mainly by the need for the bulky phenyl groups on adjacent phosphorus atoms to avoid each other. Thus in (I) the crown conformation adopted allows all four phenyl groups to occupy equatorial positions which are less sterically crowded than the axial positions occupied by the chlorine atoms. In (III) this factor is of no im-

Table 9. *Equations of mean planes through sets of atoms and distances* (Å) *of atoms from the plane* (*in square brackets*)

Coordinates in Å are referred to the crystallographic axes.

Plane (i)
P(1), P(2), P(3), P(4)
$0{\cdot}535X + 0{\cdot}070Y - 0{\cdot}842Z = 4{\cdot}303$
[P(1) and P(3) 0·036, P(2) and P(4) −0·036, N(1) −0·537, N(2) 0·433, N(3) −0·559, N(4) 0·614]

Plane (ii)
C(11)–C(16)
$0{\cdot}945X - 0{\cdot}314Y - 0{\cdot}087Z = 8{\cdot}747$
[C(11) −0·003, C(12) 0·000, C(13) 0·008, C(14) −0·012, C(15) 0·009, C(16) −0·001, P(2) 0·018]

Plane (iii)
C(21)–C(26)
$0{\cdot}445X + 0{\cdot}520Y + 0{\cdot}729Z = 6{\cdot}717$
[C(21) 0·009, C(22) −0·020, C(23) 0·012, C(24) 0·006, C(25) −0·017, C(26) 0·009, P(2) 0·011]

Plane (iv)
C(31)–C(36)
$0{\cdot}778X + 0{\cdot}606Y + 0{\cdot}166Z = 6{\cdot}496$
[C(31) −0·002, C(32) −0·007, C(33) 0·009, C(34) −0·003 C(35) −0·006, C(36) 0·008, P(4) 0·078]

Plane (v)
C(41)–C(46)
$0{\cdot}489X - 0{\cdot}845Y + 0{\cdot}218Z = 0{\cdot}829$
[C(41) −0·011, C(42) 0·005, C(43) 0·008, C(44) −0·017, C(45) 0·012, C(46) 0·002, P(4) 0·145]

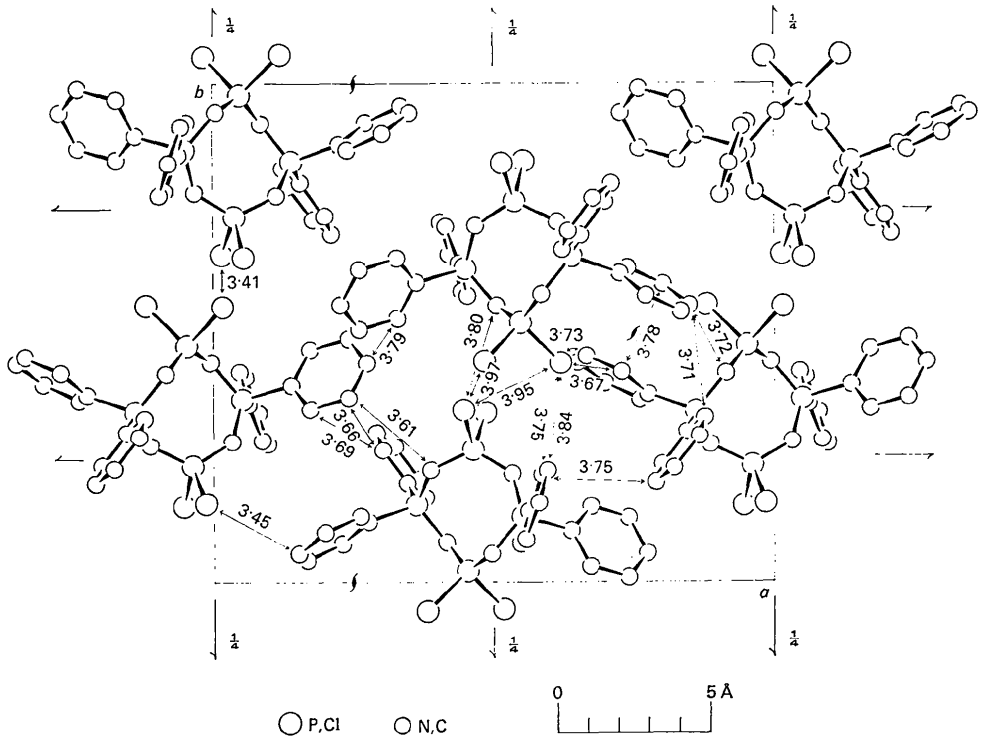

Fig. 6. Projection of the structure down the *c* axis with intermolecular distances (Å).

portance because the phenyl groups are attached in pairs to phosphorus atoms on opposite sides of the molecule and are therefore well separated (Fig. 1). While a saddle conformation is ideally suited to π-orbital overlap, particularly of the π_a type, it can be unfavourable from a steric point of view because it involves closer contact between substituents on adjacent phosphorus atoms than do the boat or chair conformations (Paddock, 1964). Consequently it has been found only where at least some of the substituent atoms are small (F, or O in methoxy groups) or in the present case where the larger substituents will be well separated irrespective of the conformation. From this it might be argued that the saddle is the favoured conformation provided that steric overcrowding does not preclude it, but this argument is weakened by the failure of this conformation to occur for $N_4P_4Cl_8$. In the observed forms of the latter the shortest non-bonded Cl···Cl distances are: chair form 3·78 Å, boat form 4·23 Å (Wagner & Vos, 1968). Since non-bonded Cl···Cl contacts can be as short as 3·4 Å (see below) steric arguments alone would not seem to prevent $N_4P_4Cl_8$ also having the saddle conformation.

Orientation of phenyl groups

In (III) the orientation of the phenyl groups will be influenced to a considerable extent by repulsive forces exerted by chlorine atoms on adjacent phosphorus atoms. Since all the phenyl groups are similarly situated, each having one nearest-neighbour chlorine atom, *e.g.* phenyl group (2)···Cl(2), one might have expected a uniform orientation of phenyl groups with respect to neighbouring atoms. The Newman projections in Fig. 5 show that there is a general similarity between their orientations but differences in detail, the C–C–P–C torsion angles being 85°, 59°, 60°, and 42° for phenyl groups (1)–(4) respectively. A torsion angle near 60°, causing the phenyl group to be eclipsed with a neighbouring nitrogen atom is expected if repulsion by the neighbouring chlorine atom is the predominant influence, since markedly short Cl···C contacts are thereby avoided. Phenyl group (1), with a torsion angle of 85°, deviates most from this ideal situation. It is staggered with respect to the two neighbouring nitrogen atoms and as a result its nearest-neighbour chlorine atom, Cl(4), is much closer to one edge of the phenyl ring than to the other (Fig. 1). This less symmetric orientation may be caused by crystal forces. With a saddle conformation for the phosphazene ring the symmetry of the whole molecule is potentially 222 (D_2) but the differences between the phenyl-ring orientations cause a small but significant departure from this symmetry.

Intermolecular distances

The arrangement of the molecules in the cell and the intermolecular distances are shown in Fig. 6. Only those Cl···Cl distances less than 4·0 Å and other distances less than 3·85 Å are given. The following contacts between molecules related by the c translation have had to be omitted from the diagram: Cl(4)···C(34) $(x,y,1+z)$ 3·74, C(13)···C(32) $(x,y,1+z)$ 3·62, C(14)···C(32) $(x,y,1+z)$ 3·73, and C(14)···C(26) $(x,y,1+z)$ 3·82 Å. The shortest Cl···Cl distance in this structure is 3·41 Å, as compared to 3·38 Å in (I) and 3·51 Å in (II). Closest contacts of other types are Cl···N 3·80, Cl···CH 3·45, N···CH 3·61, and CH···CH 3·62 Å.

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3,6-Dimethyl-5-thioformylpyrrolo[2,1-*b*]thiazole

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$C_9H_9NS_2$, triclinic, space group $P\bar{1}$, a = 8·360 (3), b = 9·113 (3), c = 7·772 (3) Å, α = 102·36 (5), β = 106·90 (5), γ = 119·09 (5)°, Z = 2, R = 0·028, 824 reflexions. Although the expected position for the thioformyl group of all thioformylpyrrolo[2,1-*b*]thiazoles is a *syn* configuration due to the polarized sulphur and nitrogen atoms, in this molecule it is *anti*, with C–C = 1·394 (4) and C–S = 1·656 (2) Å. The bond lengths of the thioformyl group and the pyrrolo ring suggest a significant contribution from the ionic as well as the covalent from.

Introduction

The compound was synthesized and crystals grown by Webster (1972). The crystals are dark red needles elongated along [001]. Preliminary cell parameters were obtained from zero-layer Weissenberg photographs. A Delaunay (1933) reduction was used to obtain the reduced triclinic primitive cell. The final cell parameters were obtained from the best orientation matrix on a Siemens four-circle diffractometer.

The crystal data are:

Formula $C_9H_9NS_2$
a = 8·360 (3); b = 9·113 (3); c = 7·772 (3) Å
α = 102·36 (5); β = 106·90 (5); γ = 119·09 (5)°.
V = 447·96 Å^3; D_c = 1·447 (2) g cm^{-3}.
Space group $P\bar{1}$; Z = 2; μ(Mo $K\alpha$) = 5·15 cm^{-1}.

A crystal 0·2 × 0·3 × 0·3 mm was chosen to obtain the intensities of 824 independent reflexions on the diffractometer with Mo $K\alpha$ radiation and a zirconium β-filter. The five-point measuring cycle was employed and most of the intensities were measured with an accuracy of between 2 and 6%. However, 40 of the intensities were measured within a counting statistics of 6 to 13%. As a check on electronic and crystal stability, three standard reflexions were measured before every 20 reflexions and no statistically significant changes were observed. Appropriate time scale and attenuator factors were applied to put the integrated intensities on the same scale, the attenuator factors being determined by a separate experiment. The intensities were corrected for Lorentz and polarization factors but not for absorption.

The coordinates of the two sulphur atoms were obtained from a Patterson synthesis calculated with 237 reflexions ($0 < 2\theta < 30°$). A Fourier map phased on the two sulphur atoms yielded the positions of all the non-hydrogen atoms. Five cycles of full-matrix least-squares refinement with isotropic temperature factors and all observed data gave an R of 0·077 where

$$R = \frac{\sum||F_o| - |F_c||}{\sum|F_o|}.$$

Two further cycles with anisotropic temperature factors reduced R to 0·047. At this stage a difference synthesis clearly revealed the positions of the nine hydrogen atoms. The parameters of the hydrogen atoms were not refined and the isotropic temperature factor for each was assumed to be that of its attached carbon. Three more cycles reduced R to 0·029. Absolute weights (Killean & Lawrence, 1969) were assigned with the values $c^2 = 0{\cdot}0002$ and $k^2 = 0{\cdot}0008$. Two more cycles of refinement gave a final R of 0·028 and

$$\frac{\sum \omega\Delta^2}{m-n} = 1{\cdot}04.^*$$

Table 1. *Atomic coordinates and standard deviations*

	x/a	y/b	z/c
S(1)	0·2173 (2)	0·0378 (2)	0·2082 (2)
S(2)	0·7629 (2)	−0·2949 (2)	0·2884 (2)
N	0·4753 (4)	−0·0428 (4)	0·2516 (4)
C(1)	0·2823 (5)	−0·1109 (5)	0·2309 (5)
C(2)	0·1919 (5)	−0·2857 (5)	0·2259 (6)
C(3)	0·3326 (5)	−0·3271 (5)	0·2432 (5)
C(4)	0·5132 (5)	−0·1774 (5)	0·2599 (5)
C(5)	0·2948 (6)	−0·5057 (5)	0·2432 (7)
C(6)	0·6992 (5)	−0·1493 (5)	0·2833 (5)
C(7)	0·5759 (6)	0·1315 (5)	0·2495 (5)
C(8)	0·4562 (7)	0·1909 (6)	0·2249 (6)
C(9)	0·7890 (7)	0·2342 (6)	0·2719 (7)
H(1)	0·310	−0·583	0·128
H(2)	0·180	−0·585	0·260
H(3)	0·400	−0·480	0·360
H(4)	0·038	−0·375	0·210
H(5)	0·805	−0·015	0·295
H(6)	0·470	0·305	0·210
H(7)	0·800	0·158	0·168
H(8)	0·813	0·340	0·270
H(9)	0·890	0·260	0·413

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30527 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.