

lowered with respect to that found for free carboxylate groups such as in monomeric $[\text{UO}_2(\text{PDC})\text{L}_2]$ (L = PyNO, DMSO) (Degetto *et al.*, 1974) and becomes approximately equal to the value for the bridging carboxylate group.

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X-ray Crystallography of the $\text{Cl}_3[\text{N}(\text{CH}_3)_2]_3\text{P}_3\text{N}_3$ Compounds.

III. *trans* Nongeminal 2,4,6-Trichloro-2,4,6-trisdimethylaminoclotriphosphazatriene*

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trans Nongeminal $\text{Cl}_3[\text{N}(\text{CH}_3)_2]_3\text{P}_3\text{N}_3$ forms monoclinic crystals, $P2_1/a$, with $a=18.118$, $b=7.054$, $c=13.411$ Å, $\beta=99.74^\circ$, and $Z=4$. The structure has been determined by a direct method, and refined by least-squares calculations to $R=0.051$ for the 2027 observed reflexions. The P_3N_3 ring adopts a slight sofa conformation, with one P 0.15 Å out of the mean plane of the other five atoms. The bond formed between this P and the *trans* Cl is 2.068 (2) Å, while the two *cis* P–Cl bonds are 2.034 (2) and 2.049 (2) Å. The exocyclic P–N(CH₃)₂ bonds are of equal lengths, 1.623 ± 0.002 Å. For the PNP segment between the two *cis* Cl atoms, P–N = 1.568 ± 0.002 Å and P–N–P = 121.6 (3)°, while the corresponding values for the other two segments are 1.576 ± 0.005 Å and $120.1 \pm 0.3^\circ$, respectively. The endocyclic N–P–N are 118.9, 119.4 and 118.6 (2)°. The exocyclic Cl–P–N(CH₃)₂ are 104.9, 104.2 and 105.7 (2)°, and the C–N–C are 113.2, 114.1 and 114.3 (5)°.

Introduction

The wide involvement of phosphorus compounds in living processes and industrial applications is a direct result of the high capacity of phosphorus for covalent bond formation (Corbridge, 1974). The crystal structures of some of these compounds provide the essential background to the understanding of their properties and behaviour. The present series examines the effect of conformation on the bonding mechanism in the three isomers of $\text{Cl}_3[\text{N}(\text{CH}_3)_2]_3\text{P}_3\text{N}_3$. In parts I and II Ahmed & Pollard (1972*a,b*) described the structures of the geminal and *cis* nongeminal isomers; this part is concerned with the structure of the *trans* nongeminal isomer.

Suitable crystals for this study were prepared, with difficulty, by Professors R. A. Shaw and R. Keat. The crystals are transparent and colourless flat prisms, with the longest dimension parallel to **b** and the largest face corresponding to the 100 planes. Only thin crystals were found to be single.

Experimental

Crystal data

trans Nongeminal $\text{Cl}_3[\text{N}(\text{CH}_3)_2]_3\text{P}_3\text{N}_3$; M.W. 373.53; monoclinic, $P2_1/a$; $a=18.118$ (4), $b=7.054$ (2), $c=13.411$ (4) Å, $\beta=99.74$ (2)°, $V=1689.28$ Å³; $Z=4$, $D_x=1.468$, $D_m=1.467$ g cm⁻³; $\mu(\text{Cu})=76.3$ cm⁻¹, $\mu(\text{Mo})=8.3$ cm⁻¹.

The X-ray measurements were carried out on an automatic Picker diffractometer (Gabe, Alexander &

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Goodman, 1971), with Mo $K\alpha$ radiation, a graphite monochromator, and single crystals of approximate dimensions $0.2 \times 0.3 \times 0.7$ mm. The cell dimensions were derived from the setting angles of high-order axial reflexions and their Friedel equivalents. The density was measured by flotation in aqueous KI solution at 23°C .

The twinning in these crystals occurs through reflexion of the unit cell across the (ab) plane. This

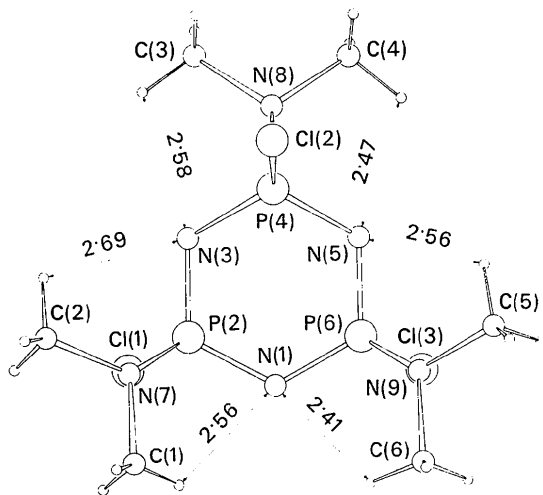


Fig. 1. A view of the *trans* nongeminal isomer down the normal to the five coplanar atoms of the ring. The short intramolecular contacts are in Å.

results in approximate overlap of the hkl and $h\bar{k}l$ reflexions when $h=4n$, and intermediate spots for the other values of h , because $|8c \cos \beta| = 18.153 \text{ \AA}$, which is approximately equal to a .

Intensity data

The intensities were measured by the θ - 2θ scan method, at 4° take-off angle, and a scan rate of 2° min^{-1} . The scan range was calculated from the expression $2\theta = 2.0 + 0.7 \tan \theta$, and the background was measured at the beginning and end of each scan. Three reference reflexions were monitored after every 50 measurements, and their intensities were found to drop steadily at approximately the same rate during the data collection. As a result, two crystals were used for the full data set, and the intensities were scaled from the reference measurements. Of the 2763 unique reflexions in the range $2\theta \leq 50^\circ$, 2027 (73.4%) had $I(\text{net}) \geq 1.2\sigma(I)$ and were classified as observed. This gave 8.7 observations per parameter. L_p corrections were applied to the net counts, but absorption corrections were considered to be negligible.

Structure determination

The structure was solved by symbolic addition. All the non-hydrogen atoms were located from an E map which was computed with the 541 reflexions with $|E| \geq 1.30$. Refinement of this model by four cycles of block-diagonal least-squares calculations reduced R to 0.07. The H atoms were then located from a difference map

Table 1. Fractional coordinates and anisotropic thermal parameters (\AA^2) for the expression

$$T = \exp[-2\pi^2(U_{11}a^*h^2 + \dots + 2U_{23}b^*c^*kl + \dots)]$$

All quantities $\times 10^4$. The isotropic B values are in \AA^2 .

	x	y	z	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{13}$	$2U_{12}$
N(1)	779 (2)	1092 (6)	1496 (3)	594 (26)	793 (29)	745 (27)	-680 (47)	311 (41)	-160 (45)
P(2)	1601 (1)	1680 (2)	1959 (1)	527 (8)	551 (7)	528 (6)	-224 (11)	366 (11)	-14 (11)
N(3)	1734 (2)	3059 (6)	2902 (3)	491 (24)	759 (28)	671 (24)	-419 (44)	228 (36)	-112 (42)
P(4)	1055 (1)	3668 (2)	3421 (1)	457 (6)	436 (6)	497 (6)	-202 (10)	191 (10)	-36 (11)
N(5)	233 (2)	3234 (6)	2876 (3)	468 (23)	636 (24)	666 (24)	-408 (40)	182 (35)	-13 (39)
P(6)	89 (1)	1852 (2)	1940 (1)	485 (6)	498 (7)	503 (6)	-184 (11)	140 (10)	-116 (11)
N(7)	2119 (2)	-196 (6)	2185 (3)	675 (27)	637 (26)	730 (27)	-85 (43)	346 (43)	191 (43)
N(8)	1137 (2)	5884 (5)	3752 (3)	666 (27)	442 (21)	690 (24)	-206 (37)	282 (39)	-102 (38)
N(9)	-424 (2)	74 (6)	2173 (3)	792 (29)	575 (24)	629 (25)	-159 (40)	294 (42)	-380 (43)
Cl(1)	2027 (1)	3092 (2)	847 (1)	956 (11)	853 (10)	661 (8)	140 (15)	524 (14)	-267 (17)
Cl(2)	1184 (1)	2215 (2)	4779 (1)	804 (10)	663 (8)	661 (7)	248 (13)	267 (13)	150 (14)
Cl(3)	-551 (1)	3347 (2)	815 (1)	958 (11)	797 (9)	647 (8)	220 (15)	2 (14)	153 (17)
C(1)	1980 (4)	-1834 (9)	1505 (5)	1365 (60)	761 (41)	1002 (48)	-407 (73)	477 (85)	519 (82)
C(2)	2901 (4)	21 (9)	2636 (5)	853 (44)	859 (43)	1100 (49)	43 (75)	429 (72)	450 (71)
C(3)	1878 (3)	6575 (8)	4210 (4)	863 (40)	673 (35)	905 (40)	-334 (61)	317 (63)	-585 (63)
C(4)	516 (3)	6789 (8)	4146 (5)	888 (42)	545 (32)	1172 (49)	-374 (66)	450 (71)	141 (61)
C(5)	-1015 (3)	326 (9)	2762 (5)	745 (40)	808 (40)	1050 (45)	101 (69)	586 (68)	-301 (63)
C(6)	-564 (5)	-1429 (11)	1414 (6)	1779 (78)	968 (52)	1255 (59)	-874 (91)	1210 (111)	-1487 (107)

	x	y	z	B		x	y	z	B
H(1,1)	1544 (37)	-1832 (96)	1178 (51)	9.5 (1.7)	H(4,1)	560 (32)	6451 (91)	4933 (45)	8.4 (1.5)
H(1,2)	2160 (32)	-3091 (86)	1932 (44)	10.0 (1.8)	H(4,2)	6 (30)	6190 (80)	3770 (41)	8.1 (0.5)
H(1,3)	2188 (31)	-1348 (92)	891 (45)	8.8 (1.6)	H(4,3)	500 (33)	7920 (91)	3858 (47)	9.9 (1.8)
H(2,1)	3120 (37)	-1067 (109)	3040 (50)	10.1 (1.8)	H(5,1)	-1137 (37)	-826 (113)	3046 (51)	10.0 (1.8)
H(2,2)	3120 (31)	162 (82)	2072 (43)	8.8 (1.6)	H(5,2)	-1462 (29)	710 (88)	2369 (41)	9.5 (1.7)
H(2,3)	2996 (26)	973 (76)	3144 (37)	7.2 (1.3)	H(5,3)	-850 (29)	1237 (85)	3315 (41)	7.2 (1.3)
H(3,1)	1948 (26)	6247 (75)	4970 (37)	6.9 (1.3)	H(6,1)	-142 (35)	-1350 (97)	1035 (50)	11.2 (2.0)
H(3,2)	2284 (39)	6048 (110)	3864 (53)	11.4 (2.0)	H(6,2)	-570 (30)	-2462 (84)	1755 (40)	7.5 (1.4)
H(3,3)	1881 (29)	7660 (80)	4134 (40)	7.0 (1.3)	H(6,3)	-1000 (43)	-1102 (124)	1000 (61)	14.7 (2.6)

and included in the refinement. In the last three cycles, eight very strong reflexions showing high discrepancies were given zero weights.

The quantity minimized was $\sum w(\Delta F)^2$, where $w = 1/\{1 + [(|F_o| - 26)/22]^4\}$ and $4.2 \leq |F_o| \leq 189.6$. The F curves were those of Hanson, Herman, Lea & Skillman (1964) for C, N, P, Cl; and of Stewart, Davidson & Simpson (1965) for H.

At the final cycle, R and R_w for the observed reflexions were 0.051 and 0.057, respectively, and the average and maximum shifts were 0.2σ and 0.8σ .* The residual electron density in the final difference map was randomly distributed within $\pm 0.3 \text{ e } \text{Å}^{-3}$.

Results

The refined atomic parameters are listed in Table 1. A view of the molecule along the normal to the mean plane of N(1), P(2), N(3), N(5) and P(6) is shown in Fig. 1. The bond lengths and angles, without correction for thermal vibration, are presented in Fig. 2. The C-H lengths are in the range 0.77–1.08 Å, mean = 0.96 Å.

Discussion

Description of the molecule

In this molecule, Cl(2) is *trans* to Cl(1) and Cl(3), as shown in Fig. 1. The phosphazene ring has a slight sofa conformation, where N(1), P(2), N(3), N(5) and P(6) are coplanar and within $\pm 0.003 \text{ Å}$ of their mean plane; $\chi^2 = 8.16$ and $0.05 > P > 0.01$. The sixth atom, P(4) which is bonded to Cl(2), is 0.146 Å from the mean plane of the other five atoms and on the same side as Cl(2). This represents a bending in the ring by 10.6° at the line N(3)···N(5).

The planes of the three pairs of ligands Cl(1)–P(2)–N(7), Cl(2)–P(4)–N(8) and Cl(3)–P(6)–N(9) make dihedral angles of 89.1 , 89.7 and 89.3° , respectively, with the mean plane of the five coplanar atoms of the ring, and $120.0 \pm 0.3^\circ$ with each other. The plane of the

ligands at P(4) is nearly perpendicular to the plane of its local CNC group. The angle between these two planes is 88.7° , whereas the corresponding angles at P(2) and P(6) are 84.1 and 86.2° , respectively. In the *cis* nongeminal structure the corresponding angles are 89.1 , 84.9 , 86.8° for molecule I, and 88.4 , 84.5 and 88.0° for molecule II, which show the same pattern.

Interatomic distances

The mean bond lengths are $1.573 (2) \text{ Å}$ for the six *endo* P–N, $1.623 (2) \text{ Å}$ for the three P–NMe₂, and $1.459 (3) \text{ Å}$ for the six N–C. For each of these types, the observed variations in the bond lengths are not significant. There is some indication, however, of slight contraction of P(2)–N(1) and P(6)–N(1) which connect the two *cis* Cl atoms. The mean for these two bonds is $1.568 (3) \text{ Å}$, while the mean for the other four P–N bonds of the ring is $1.576 (2) \text{ Å}$.

The P–Cl are of lengths $2.034 (2)$, $2.049 (2)$, and $2.068 (2) \text{ Å}$, which are significantly different from each other. The longest is P(4)–Cl(2), which is *trans* to the other two bonds, as predicted by the *cis* effect postulated by Keat & Shaw (1966). The ^{35}Cl n.q.r. data of Faucher, Labarre & Shaw (1975) suggest the presence of only two different P–Cl lengths: 2.051 and 2.064 Å as calculated from the expression $y = 2.355 - 0.0128x$ by Keat, Port, Tong & Shaw (1972), where y = bond length in Å and x = n.q.r. frequency in MHz. The two *cis* P–Cl bonds are chemically equivalent and, presumably, should be of equal lengths. However, such significant variations in the lengths of chemically equivalent P–Cl have been observed in the following structures: (a) geminal $\text{Cl}_4\text{Ph}_2\text{P}_3\text{N}_3$ (Mani, Ahmed & Barnes, 1965); (b) geminal $\text{Cl}_2\text{Ph}_4\text{P}_3\text{N}_3$ (Mani, Ahmed & Barnes, 1966); and (c) $\text{N}_3\text{P}_3\text{Cl}_4\text{Ph}(\text{NPPH}_3)$ (Biddlestone, Bullen, Dann & Shaw, 1974). In each of these structures, the P–Cl ligands which share the same P atom are different in length by significant amounts of 0.012 – $0.034 (3) \text{ Å}$, as shown in Table 2.

Despite these differences there seem to be two common features in all these phosphazene compounds. These features can be seen clearly in Fig. 3, which shows the three projections normal to the Cl–P–NMe₂ planes of the ligands of the present structure. The first feature is that the Cl···NMe₂ distances are the same for the three pairs of substituents. They are $2.920 (5)$, $2.926 (4)$, and $2.925 (4) \text{ Å}$, mean = $2.924 (3) \text{ Å}$. The

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30780 (12pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Geometry of the pairs of PCl₂ ligands in different phosphazene compounds

		P–Cl _a	P–Cl _b	Cl _a –P–Cl _b	Cl _a ···Cl _b	Direction*
(a) Cl ₄ Ph ₂ P ₃ N ₃	At P(4)	2.002 (2) Å	1.990 (2) Å	100.4	3.067 (2) Å	88.3°
	At P(6)	1.989 (2)	2.010 (2)	100.3	3.069 (2)	88.7
	Mol. I	2.008 (5)	2.030 (5)	98.3	3.053 (5)	88.9
(b) Cl ₂ Ph ₄ P ₃ N ₃	Mol. II	2.005 (5)	2.024 (5)	98.6	3.055 (5)	88.6
	At P(1)	2.036	2.002	99.0	3.071†	
(c) N ₃ P ₃ Cl ₄ Ph(NPPH ₃)	At P(2)	2.017	1.992	99.2	3.053†	

* Angle between the Cl···Cl vector and the local NPN segment of ring.

† Structure is not fully refined; final parameters are not available.

second is that, within the accuracy of the analysis, the $\text{Cl}\cdots\text{NMe}_2$ vector is always normal to the plane of the local NPN segment of the phosphazene ring. The corresponding angles are 89.0° for the substituents at P(2) and P(6), and 89.6° at P(4), see Fig. 3. The same features occur also in the geminal and *cis* nongeminal isomers. The $\text{Cl}\cdots\text{NMe}_2$ distances are 2.922 (4) Å in

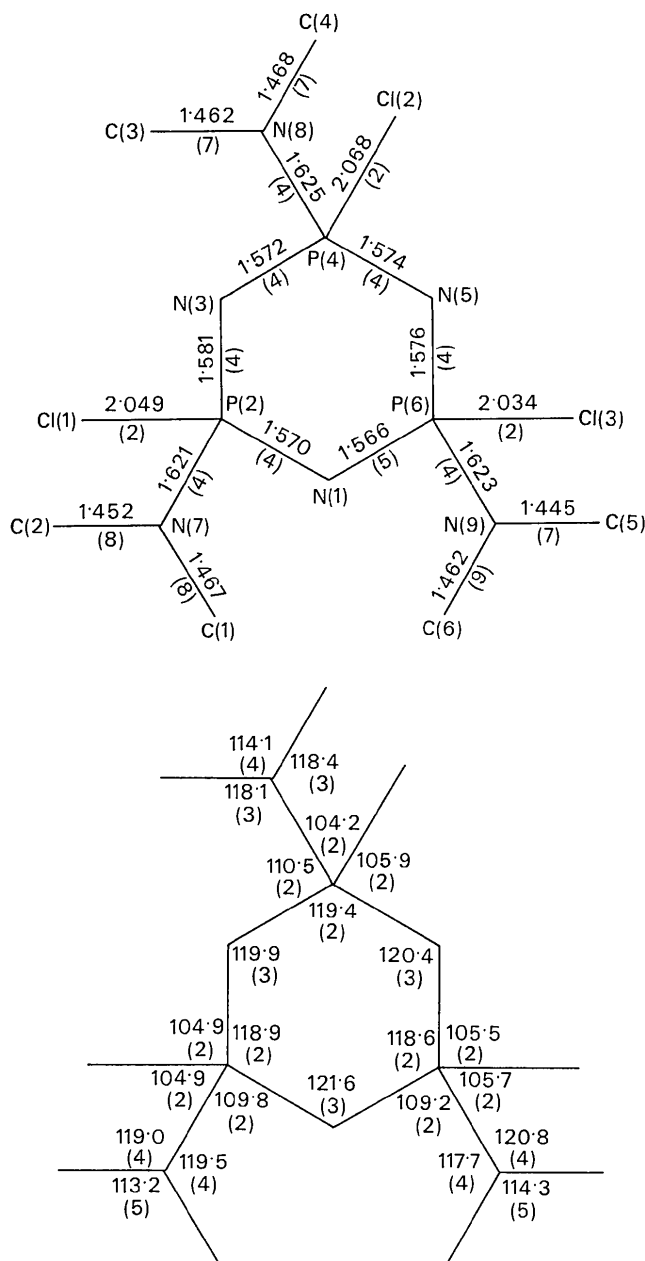


Fig. 2. Bond lengths (Å), valency angles ($^\circ$), with their estimated standard deviations in parentheses. Angles not shown on the diagram are $\text{N}(1)\text{--P}(2)\text{--Cl}(1) = 106.8$ (2), $\text{N}(3)\text{--P}(2)\text{--N}(7) = 110.3$ (2), $\text{N}(5)\text{--P}(4)\text{--Cl}(2) = 105.7$ (2), $\text{N}(3)\text{--P}(4)\text{--N}(8) = 109.9$ (2), $\text{N}(1)\text{--P}(6)\text{--Cl}(3) = 106.7$ (2), and $\text{N}(5)\text{--P}(6)\text{--N}(9) = 110.3$ (2) $^\circ$.

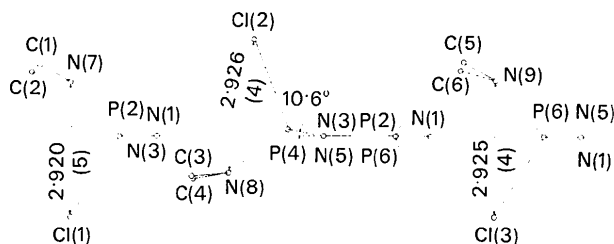


Fig. 3. Views normal to the planes of the $\text{Cl}\text{--P}\text{--NMe}_2$ ligands at P(2), P(4) and P(6). Despite the significant differences in the $\text{P}\text{--Cl}$ lengths, the $\text{Cl}\cdots\text{NMe}_2$ vectors are of nearly equal lengths and always normal (89.0 , 89.6 , and 89.0° , respectively) to the corresponding local NPN segments of the ring.

the geminal molecule, and 2.926, 2.929, 2.928, 2.922, 2.926 and 2.901 (6) Å (mean = 2.922 Å) in the two molecules of the *cis* nongeminal structure. Each $\text{Cl}\cdots\text{NMe}_2$ vector is also nearly normal ($87.5\text{--}88.3^\circ$) to the plane of the local NPN segment of the ring.

Similarly, as summarized in Table 2, the $\text{Cl}\cdots\text{Cl}$ vectors are 3.068 ± 0.001 Å* for compound (a) and 3.054 ± 0.001 Å for compound (b). The corresponding distances of compound (c) are slightly different from each other, but this may be because the parameters have not been fully refined. In the structure of $\text{Cl}_6\text{P}_3\text{N}_3$ (Bullen, 1971), where the six $\text{P}\text{--Cl}$ bonds are of equal lengths, the $\text{Cl}\cdots\text{Cl}$ separations are 3.072 ± 0.001 Å. In (a) and (b), the $\text{Cl}\cdots\text{Cl}$ vectors make angles of 88.5 ± 0.2 and $88.6 \pm 0.3^\circ$, respectively, with the planes of the corresponding local NPN segments of the ring. In the geminal isomer of the present compound, the two Cl atoms which are substituted at P(2) are not chemically equivalent, and their $\text{P}\text{--Cl}$ lengths are 2.014 (2) and 1.992 (2) Å. The $\text{Cl}\cdots\text{Cl}$ vector in this case is 3.062 (2) Å and is at 89.4° to its local NPN plane.

In the present structure, there are no intermolecular distances shorter than normal van der Waals separations. However, there are six intramolecular distances of the type $\text{H}\cdots\text{N}(\text{ring})$ which are shorter than the corresponding van der Waals contact of 2.7 Å. These distances are marked in Fig. 1, and are in the range 2.41–2.69 Å. This general pattern is also found in the structures of the geminal and *cis* nongeminal isomers.

From these observations it could be concluded that the conformation of the phosphazene ring and the orientation of its substituents are fixed by the electronic effects and intramolecular steric interactions, while the $\text{P}\text{--Cl}$ lengths and the valency angles they make with their neighbouring bonds can be slightly varied in order to equalize the $\text{Cl}\cdots\text{NMe}_2$ (or $\text{Cl}\cdots\text{Cl}$) distances of the molecule, and to keep them in a direction almost normal to the π cloud of the local NPN segment of the ring. This directional feature is

* In this discussion, \pm refer to the limits of observed deviations from the mean values, and () are used for the estimated standard deviations.

particularly striking in the $\equiv\text{PCINMe}_2$ groups, where the exocyclic N and Cl atoms are always very nearly eclipsed despite the large difference between the P–Cl and P–NMe₂ bond lengths.

Valency angles

The pattern of the endocyclic angles is consistent with the expected mirror symmetry of the ring across the N(1)···P(4) diagonal. Thus, the angles are $118.8 \pm 0.2^\circ$ at P(2) and P(6) and $119.4 (2)^\circ$ at P(4); $120.1 \pm 0.3^\circ$ at N(3) and N(5) and $121.6 (3)^\circ$ at N(1). The three exocyclic Cl–P–NMe₂ angles which are 104.9 , 104.2 and $105.7 (2)^\circ$ are significantly different from each other, presumably for the reasons stated previously in the discussion of bond lengths. The two Me groups at N(7) and those at N(8) are symmetrical about their respective P–N bonds, but those at N(9) are not symmetrical about P(6)–N(9). The angles P(6)–N(9)–C(5) and P(6)–N(9)–C(6) are $120.8 (4)$ and $117.7 (4)^\circ$, respectively. Despite this considerable asymmetry, the mean angles at the three exocyclic N atoms are nearly equal (117.2 , 116.9 and 117.6°).

The authors are grateful to Professors R. A. Shaw and R. Keat for supplying the crystals, to Professor Shaw for commenting on the results, and to Mrs M. E. Pippy for assistance with the computations. All calculations were carried out with programs by Ahmed, Hall, Pippy & Huber (1973).

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The Crystal Structure of Sodium Chlorite Trihydrate, $\text{NaClO}_2 \cdot 3\text{H}_2\text{O}$

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$\text{NaClO}_2 \cdot 3\text{H}_2\text{O}$ is triclinic, with $a = 6.960 (2)$, $b = 8.842 (3)$, $c = 5.504 (2) \text{ \AA}$, $\alpha = 92.36 (7)$, $\beta = 119.09 (7)$, $\gamma = 104.73 (7)^\circ$, space group $P\bar{1}$, $Z = 2$. The structure was solved by Patterson methods and refined to an R_w of 4.0% by full-matrix least-squares methods based on 2227 independent counter reflexions. Only one oxygen of ClO_2^- is coordinated to Na^+ ; the other shares a hydrogen bond. Chains of edge-sharing irregular Na octahedra run along c ; connexion between the chains is achieved by a system of hydrogen bonds in which all the hydrogens are involved. Cl–O distances: 1.557 (3) and 1.570 (3) \AA ; O–Cl–O angle: $108.37 (8)^\circ$; Na–O distances range between 2.367 (3) and 2.496 (3) \AA .

Introduction

The title compound is of some importance in the textile industry and of growing interest in water

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deposition. In crystal chemistry it stands out as a gap in the systematics of the simplest compounds. Moreover, as the crystal structures of only a few chlorites have been determined, *i.e.* of ammonium chlorite (Gillespie, Sparks & Trueblood, 1959), silver chlorite (Cooper & Marsh, 1961) and lanthanum chlorite trihydrate (Coda, Giuseppetti & Tadini, 1965), a new contribution to the crystal chemistry of these compounds seemed useful.