pseudo-orthorhombique, que nous venons de décrire et qui est très proche de ce dernier type structural.

Les calculs nécessaires à ce travail ont été effectués aux Centres de Calcul de l'Université de Poitiers (CICUP) et du CNRS (CIRCE).

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The Crystal and Molecular Structure of 2,*trans*-4,*cis*-6,*trans*-8-Tetramethoxy-1,3,5,7-tetramethyl-2,4,6,8-tetraoxocyclotetraphosphazane, [CH₃N.P(O)OCH₃]₄

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The molecular rearrangement of the phosphazene $[NP(OCH_3)_2]_4$ by reaction with methyl iodide gives two isomers of the phosphazane $[CH_3N.P(O)OCH_3]_4$ which have similar ^1H NMR spectra but appreciably different IR spectra. Crystals of the more abundant isomer (the 2,*trans*-4,*cis*-6,*trans*-8 isomer, m.p. 216–218°C) are monoclinic, $a = 17.31$, $b = 7.40$, $c = 15.60$ Å, $\beta = 110.54°$, space group $C2/c$, $Z = 4$. The atomic positions were determined by least-squares refinement from X-ray diffractometer intensities, the final R being 0.053 for 1762 reflexions. The molecule has exact twofold symmetry and a close approximation to symmetry $\bar{4}$, the eight-membered phosphazane ring having a slightly distorted boat conformation. Mean bond lengths are: P—N 1.673, P=O 1.469, P—O 1.579, C—O 1.456, N—C 1.501 Å. The shortness of the P—N bonds and the near coplanarity of the bonds at N atoms indicate partial π-bonding in the phosphazane ring. Mean bond angles in the ring are: N—P—N 106.9 and P—N—P 122.5°.
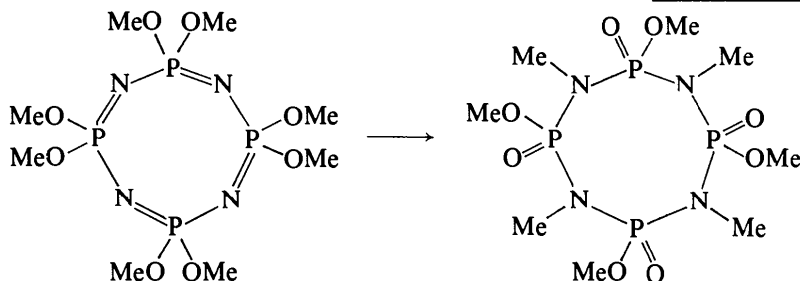
Introduction

Cyclic P,N compounds in which the skeletal structure is based on formally single P—N bonds (phosphazanes) are less common than those with π-bonding within the ring (phosphazenes), but their structures are potentially just as informative. The oxophosphazanes $[RN.P(O)OR]_n$ are especially interesting, because (at least for $n = 3$, 4) they can be made (Fitzsimmons, Hewlett & Shaw, 1964) by rearrangement of the isomeric alkoxyphosphazenes $[NP(OR)_2]_n$, so making it possible to compare the structural effects of exocyclic and endocyclic π-bonding, other molecular changes being kept to a minimum. The structure of the

cyclic triphosphazane [MeN.P(O)OMe]₃* has already been determined (Ansell & Bullen, 1968); the object of the present work is to extend the investigation to the eight-membered ring species.

In principle, four geometrical isomers can be produced in the following rearrangement reaction.

of isomer 1 being the richer in lines, and presumably having the lower symmetry. Typically, in the ν(P=O) region, isomer 2 has two bands, 1265 (νs), 1200 cm⁻¹ (s), and isomer 1 has four at 1288 (s), 1250 (s), 1215 (m), and 1190 cm⁻¹ (m,sh).

The crystals of isomer 2 are monoclinic plates on

We have found two of them. Their ¹H NMR spectra prove their gross structure to be as shown but do not discriminate between the various possible relative positions of the methoxy groups, or between the possible ring conformations. In this paper we report the structure determination of the more abundant isomer. Work is also in progress on the crystal structure of the second isomer.

Experimental

Octamethoxycyclotetraphosphazene (4·0 g, 9·3 mmol) was dissolved in 12 ml methyl iodide, and the solution was heated in an evacuated Carius tube at 100°C for 6 h. The methyl iodide was removed *in vacuo*, and the residue, containing a small amount of tetramethyl-ammonium iodide, was extracted with dichloro-methane. The crude product (~4 g) was precipitated from the extract by adding light petrol (30–60). It was recrystallized from dichloromethane by the slow addition of light petrol. The first crop was of small cube-like crystals of isomer 1, which were separated off as soon as crystals of isomer 2 (long plates) began to appear. The two fractions were again recrystallized in the same way until essentially pure isomer 1 and isomer 2 were obtained in the approximate ratio of 1 : 10. Analysis: calculated for [CH₃N.P(O)OCH₃]₄: C 22·4; H 5·6; N 13·1; OCH₃ 29·0%; found (isomer 1): C 22·5; H 5·8; N 13·1; OCH₃ 28·5%; (isomer 2) C 22·3; H 5·8; N 13·1; OCH₃ 28·5%. ¹H NMR (in CDCl₃, TMS internal reference): isomer 1, two equal bands; OCH₃, δ 3·85 p.p.m., J_{PH} 11·3 Hz; NCH₃, δ 3·04 p.p.m., J_{PH} 10·0 Hz; isomer 2, two equal bands; OCH₃, δ 3·87 p.p.m., J_{PH} 10·7 Hz; NCH₃, δ 3·03 p.p.m., J_{PH} 7·7 Hz; [NP(OMe)₂]₄, one band; OCH₃, δ 3·65 p.p.m., J_{PH} 12·5 Hz. All the spectra showed virtual coupling. The IR spectra of the two isomers differ appreciably, that

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* Me = CH₃.

Table 1. *Crystal data*

[CH₃N.P(O)OCH₃]₄, 2,*trans*-4,*cis*-6,*trans*-8 isomer

M.p. 216–218°C	V = 1871 Å³
Monoclinic	Z = 4
a = 17·31 (2) Å	D_m = 1·526 g cm⁻³
b = 7·40 (1)	D_c = 1·520
c = 15·60 (1)	λ(Mo $K\alpha$) = 0·7107 Å
β = 110·54 (1)°	μ(Mo $K\alpha$) = 4·7 cm⁻¹
Space group $C2/c$	F(000) = 896

Systematic absences: hkl when ($h + k$) is odd, and $h0l$ when l is odd.

{ 100 }, elongated along **b**. Cell dimensions and other data are given in Table 1. X-ray intensities of h,0–10,l were measured at 20–22°C on a Philips Pailred diffractometer with monochromated Mo $K\alpha$ radiation. Measurement of all reflexions with sin θ/λ < 0·70 and of some with 0·70 ≤ sin θ/λ ≤ 0·72 gave 2370 intensities of which 1762 were judged significant with I > 2σ_I. The intensities were corrected for Lorentz and polarization effects but not for absorption.

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 $f = C + \sum\limits_{i}^{4} A_i \exp(-B_i \sin^2\theta/\lambda^2)$, the parameters A, B and C being taken from Cromer & Waber (1965) for P, O, N and C, and from Forsyth & Wells (1959) for H (in which case $A_3 = A_4 = 0$).

Structure determination

The systematic absences indicate space group Cc or $C2/c$. A centrosymmetric structure is suggested by (i) the results of an $N(z)$ test (Howells, Phillips & Rogers, 1950) on the full set of 2370 intensities, and (ii) the normalized structure-factor-amplitude statistics. As $Z = 4$,

the molecules must occupy special positions which may be either centres of symmetry or twofold axes. The structure was solved by the tangent refinement method (Germain, Main & Woolfson, 1971) applied to 594 reflexions with $|E| > 1.3$. The origin was defined by assigning a phase angle of zero to the reflexions 461 and $\overline{13},1,1$. All atoms other than H were located from the E map based on the phases so obtained. The molecules were found to lie on twofold axes.

The atomic positions were refined by full-matrix least-squares with anisotropic temperature factors for P, O and N atoms until R had dropped to 0.08. A difference synthesis calculated at this stage revealed the positions of the H atoms, which were adjusted slightly to make C—H = 1.05 Å and to produce O—C—H and H—C—H bond angles close to 109°. The refinement was then continued with H atoms included in the calculations (with the coordinates listed in Table 4 and isotropic temperature factors $\overline{u^2} = 0.060$ Å^2). Their positions were not refined. The weighting scheme $w = (8 - 0.2|F_o| + 0.003|F_o|^2)^{-1}$ 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 final R is 0.053 for 1762 reflexions and $R'[= (\Sigma \, w\Delta^2/\Sigma \, w|F_o|^2)^{1/2}]$ is 0.063. In the last cycle all parameter shifts were less than 0.08σ.

Table 4. *Fractional coordinates* ($\times 10^3$) *assigned to hydrogen atoms*

	x	y	z
H(11)	189	619	200
H(12)	179	413	147
H(13)	134	602	85
H(21)	115	−46	498
H(22)	174	139	498
H(23)	206	−71	478
H(31)	154	−28	196
H(32)	72	−118	218
H(33)	59	−31	112
H(41)	161	553	401
H(42)	79	602	434
H(43)	74	647	325

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 given in Table 5 and bond angles in Table 6.

The amplitudes of vibration corresponding to the thermal parameters listed in Table 3 are given in Table

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

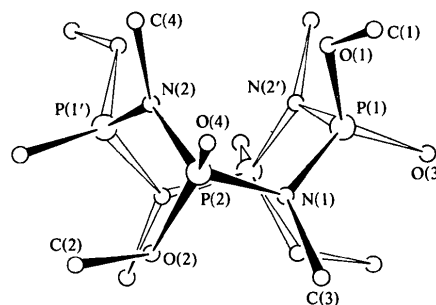|	x	y	z
P(1)	264.5 (5)	3203.2 (13)	1345.9 (6)
P(2)	1203.4 (5)	2204.2 (13)	3234.7 (6)
N(1)	724 (2)	1661 (4)	2134 (2)
N(2)	623 (2)	3729 (4)	3507 (2)
O(1)	750 (2)	5016 (4)	1685 (2)
O(2)	1096 (2)	378 (4)	3699 (2)
O(3)	192 (2)	2608 (4)	426 (2)
O(4)	2053 (2)	2849 (4)	3476 (2)
C(1)	1495 (3)	5360 (7)	1487 (4)
C(2)	1541 (3)	126 (7)	4674 (3)
C(3)	901 (3)	−159 (6)	1824 (3)
C(4)	966 (3)	5571 (6)	3802 (3)

Fig. 1. Molecular shape and numbering of the atoms. A primed atom is related to the corresponding unprimed atom by rotation about the diad axis of 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}
P(1)	26.2 (4)	31.3 (4)	26.0 (4)	0.8 (4)	12.8 (3)	−1.5 (3)
P(2)	21.7 (4)	32.5 (4)	29.7 (4)	−2.8 (4)	7.7 (3)	4.5 (3)
N(1)	30 (1)	29 (1)	28 (1)	−1 (1)	13 (1)	5 (1)
N(2)	26 (1)	28 (1)	31 (1)	−5 (1)	12 (1)	0 (1)
O(1)	33 (1)	36 (1)	48 (2)	0 (1)	21 (1)	−7 (1)
O(2)	47 (2)	35 (1)	31 (1)	3 (1)	6 (1)	7 (1)
O(3)	54 (2)	53 (2)	29 (1)	−1 (1)	20 (1)	0 (1)
O(4)	22 (1)	60 (2)	52 (2)	−11 (1)	9 (1)	3 (1)
C(1)	40 (2)	63 (3)	75 (3)	2 (3)	35 (2)	−14 (2)
C(2)	63 (3)	67 (3)	31 (2)	8 (2)	3 (2)	10 (2)
C(3)	69 (3)	35 (2)	42 (2)	−5 (2)	20 (2)	20 (2)
C(4)	44 (2)	35 (2)	60 (3)	−21 (2)	24 (2)	−11 (2)

7. A rigid-body libration analysis of the molecule, in which the molecular vibrations are treated in terms of three tensors: T for translation, L for libration, and S for correlations of translation and libration (Schomaker & Trueblood, 1968), gave the results shown in Table 8. As the molecule possesses a twofold axis parallel to **b**, all three tensors have a principal axis coincident with **b** and hence components such as L_{12} and L_{23} are equal to zero. Since L_{13} is also not significantly different from

Table 5. *Bond lengths* (Å) *with estimated standard deviations*

(a) Bond lengths from the least-squares refinement

P(1)—N(1)	1·661	P(1)—O(1)	1·573
P(1)—N(2')	1·677	P(2)—O(2)	1·575
P(2)—N(1)	1·673	σ	0·003
P(2)—N(2)	1·662		
σ	0·003	P(1)—O(3)	1·464
		P(2)—O(4)	1·465
N(1)—C(3)	1·498	σ	0·003
N(2)—C(4)	1·493		
σ	0·005	C(1)—O(1)	1·449
		C(2)—O(2)	1·456
		σ	0·005

(b) Corrected for molecular oscillations

P(1)—N(1)	1·666	P(1)—O(1)	1·578
P(1)—N(2')	1·682	P(2)—O(2)	1·580
P(2)—N(1)	1·678	Mean	1·579 (3)*
P(2)—N(2)	1·667		
Mean	1·673 (2)*	P(1)—O(3)	1·468
		P(2)—O(4)	1·469
N(1)—C(3)	1·503	Mean	1·469 (3)*
N(2)—C(4)	1·498		
Mean	1·501 (4)*	C(1)—O(1)	1·453
		C(2)—O(2)	1·459
		Mean	1·456 (4)*

* These σ values have been calculated with allowance for error in the unit-cell parameters.

Table 6. *Bond angles* (°)

Estimated standard deviations are 0·2° for all angles at P and N atoms and 0·3° for angles at O atoms.

N(1)—P(1)—N(2')	106·4	N(1)—P(1)—O(1)	106·1
N(1)—P(2)—N(2)	107·4	N(2')—P(1)—O(1)	99·4
		N(1)—P(2)—O(2)	99·8
P(1)—N(1)—P(2)	122·0	N(2)—P(2)—O(2)	106·6
P(1')—N(2)—P(2)	122·9		
		N(1)—P(1)—O(3)	111·9
O(1)—P(1)—O(3)	116·0	N(2')—P(1)—O(3)	115·9
O(2)—P(2)—O(4)	115·6	N(1)—P(2)—O(4)	115·7
		N(2)—P(2)—O(4)	110·9
P(1)—N(1)—C(3)	118·5		
P(2)—N(1)—C(3)	117·6	P(1)—O(1)—C(1)	119·2
P(1')—N(2)—C(4)	117·0	P(2)—O(2)—C(2)	119·1
P(2)—N(2)—C(4)	119·2		

Table 7. *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
P	0·14	0·17	0·18–0·19
O	0·15–0·16	0·19–0·23	0·22–0·27
N	0·15	0·16–0·17	0·18–0·19
C	0·14–0·17	0·20–0·26	0·27–0·28

Table 8. *Molecular vibration tensors referred to orthogonal axes* a', b *and* c

The origin (chosen to make S symmetric) is at (0, 0·283, 0·250).

$$T = \begin{pmatrix} 0.020\,(1) & 0 & 0.002\,(1) \\ & 0.020\,(1) & 0 \\ & & 0.022\,(1) \end{pmatrix} \quad Å^2$$

$$L = \begin{pmatrix} 10.2\,(7) & 0 & 0.3\,(3) \\ & 6.9\,(3) & 0 \\ & & 12.5\,(7) \end{pmatrix} \quad deg^2$$

$$S = \begin{pmatrix} 0.10\,(2) & 0 & 0.09\,(1) \\ & 0.04\,(2) & 0 \\ & & 0.14\,(2) \end{pmatrix} \quad deg\,Å$$

zero, the L tensor has its principal axes parallel to a', **b**, and **c**. Bond lengths corrected for the effect of the molecular oscillations (Cruickshank, 1956, 1961a) are given in Table 5(b). The corrections are all approximately the same (0·004–0·005 Å with one exception).

Discussion

The molecule is the 2,*trans*-4,*cis*-6,*trans*-8 isomer (Fig. 1). The phosphazane ring has a boat conformation with the twofold axis passing through the centre of the ring.

Bond lengths and angles

Bond lengths and angles are compared in Table 9 with those in the phosphazene precursor [NP(OMe)₂]₄ and in the trimeric phosphazane homologue [MeN.P(O)OMe]₃. There is, as expected, a close correspondence between the molecular dimensions of the two phosphazanes but marked differences between them and the phosphazene. The rearrangement of [NP(OMe)₂]₄ to [MeN.P(O)OMe]₄ causes much of the π-bond density to be transferred from the P—N bonds to the P=O bond. The consequent changes in the molecular dimensions are an increase in the P—N length by ca 0·1 Å, a decrease in the ring angles N—P—N and P—N—P, and an increase in the O—P—O angle. However some π-bond density remains in the P—N bonds. Evidence for this is (a) the P—N bond, though longer than in [NP(OMe)₂]₄, is still ca 0·1 Å shorter than the estimated single bond length, and (b) the N atoms are in an essentially planar bonding en-

Table 9. *Molecular dimensions in* [MeN.P(O)OMe]$_4$ *and related molecules*

	[NP(OMe)$_2$]$_4$ (Ansell & Bullen, 1971)	[MeN.P(O)OMe]$_4$ (this work)	[MeN.P(O)OMe]$_3$ (Ansell & Bullen, 1968)
Mean bond lengths (Å)			
P—N	1·57	1·673	1·663
P=O	–	1·469	1·45
P—O	1·58	1·579	1·56
C—O	1·42	1·456	1·45
N—C	–	1·501	1·48
Mean bond angles (°)			
N—P—N	121·0	106·9	105·2
P—N—P	132·2	122·5	121·7
O—P—O	105·5	115·8	116·1
P—O—C	121·0	119·2	119·3
P—N—C	–	118·1	119·0

Table 10. *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 orthogonal axes a', b, and c.

Plane (i): P(1), P(2), P(1′), P(2′)
$$Y = 2·001$$
[P(1) and P(1′) 0·370, P(2) and P(2′) −0·370, N(1) −0·772, N(2) 0·759]

Plane (ii): N(1), P(1), P(2), C(3)
$$0·845X + 0·284Y − 0·453Z = 0·127$$
[N(1) −0·095, P(1) and P(2) 0·031, C(3) 0·033]

Plane (iii): N(2), P(1′), P(2), C(4)
$$0·462X − 0·277Y + 0·843Z = 4·064$$
[N(2) −0·069, P(1′) 0·022, P(2) 0·023, C(4) 0·024]

Fig. 2. Torsion angles (°) in the phosphorus–nitrogen rings of (*a*) [MeN.P(O)OMe]$_4$ and (*b*) [NP(OMe)$_2$]$_4$.

vironment [in the $\begin{smallmatrix} P \\ P \end{smallmatrix}$N—C groups the displacement of the N atoms from the plane of the three attached atoms is small: N(1) 0·13, N(2) 0·09 Å, Table 10]. The P—OMe bond also shows some π-bond character since, as in [NP(OMe)$_2$]$_4$, the P—O—C angle is close to 120° and the P—OMe bond is shorter than is estimated for a pure P—O single bond (1·71 Å, Cruickshank, 1961*b*).

The pattern of bond lengths and angles in [MeN.P(O)OMe]$_4$ is also similar to that found for the [NHPO$_2$]$_4^{4-}$ anion in its K and Cs salts (Berking & Mootz, 1971), except that the P—N—P angles are larger in the anions (K 131·9, Cs 128·9°).

Ring conformation

The exact symmetry of the molecule, and hence of the phosphazane ring, is a twofold axis coincident with the twofold axis in the crystal lattice (parallel to **b**), but the ring, which has a slightly distorted boat conformation, shows a close approximation to symmetry $\overline{4}$ as is seen from the pattern of torsion angles in Fig. 2(*a*). There is a similar pattern of torsion angles in the ring of
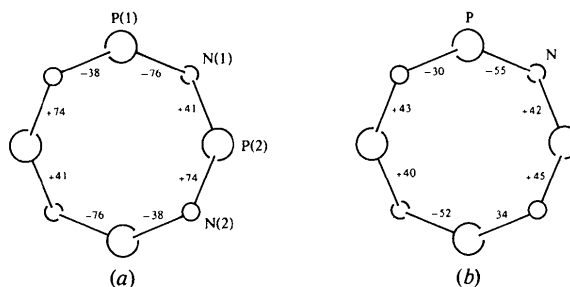
[NP(OMe)$_2$]$_4$ (Fig. 2*b*) but here the adjacent angles are more nearly equal in magnitude than in [MeN.P(O)OMe]$_4$, indicative of the closer approach to a saddle conformation (symmetry $\overline{4}2m$).

It has been useful, in comparing phosphazene rings of symmetry $\overline{4}$, to note the heights of the P and N atoms (δ_P, δ_N) above and below a plane drawn through the centre of the molecule and perpendicular to the $\overline{4}$ axis (loosely termed the 'mean plane' of the ring). For [MeN.P(O)OMe]$_4$ where the mean plane is $y = 0·271$ (fractional coordinate), δ_P is 0·37 Å and δ_N is 0·77 or 0·76 Å [Table 10, plane (i)]. Taking a mean value of δ_N, the ratio δ_P/δ_N is 0·48. In the limit, δ_P/δ_N can range from 0 (ideal saddle) to 1 (ideal boat). [MeN.P(O)OMe]$_4$ occupies an intermediate position whereas among the phosphazenes [NP(OMe)$_2$]$_4$ is closer to a saddle ($\delta_P/\delta_N = 0·20$) and [NPCl$_2$]$_4$ is closer to a boat (0·75).

The phosphazane anion [NHPO$_2$]$_4^{4-}$ also has a boat form of ring in the acid H$_4$[NHPO$_2$]$_4$.2H$_2$O (Migchelsen, Olthof & Vos, 1965) but shows different conformations in its salts: K$_4$[NHPO$_2$]$_4$.4H$_2$O chair, Cs$_4$[NHPO$_2$]$_4$.6H$_2$O saddle. It would appear that the energy differences between these various conformations of phosphazane ring are small and that a change of ring conformation occurs when a comparatively
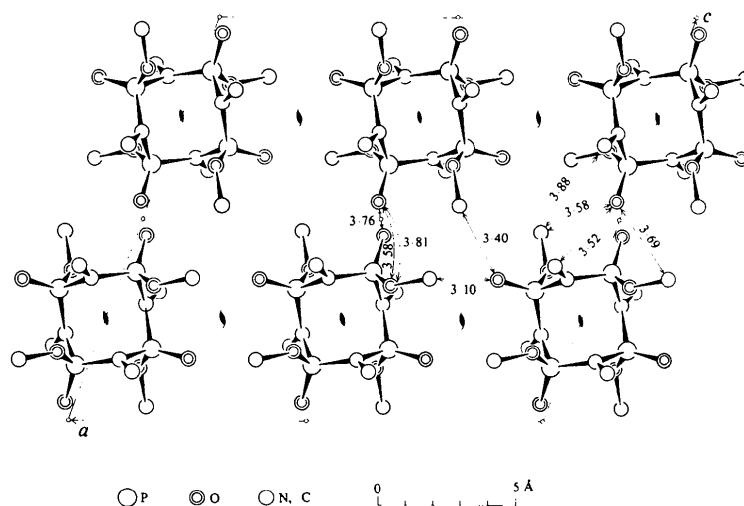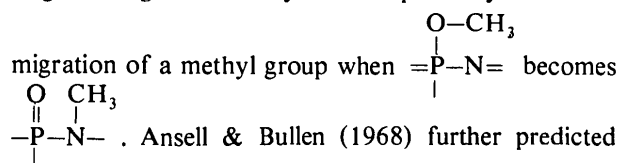
$\bigcirc$ P $\circledcirc$ O $\bigcirc$ N, C

Fig. 3. Projection of the structure down **b** with intermolecular distances (Å). The molecules centred at $x = \frac{1}{2}$ are raised by $\frac{1}{2}$**b** above molecules centred at $x = 0$.

minor change is made to the molecular environment (change of cation or in the substituent groups attached to the ring).

The P=O bonds all lie in equatorial directions, *i.e* close to the mean plane of the ring, while the P—OMe bonds are all axial, *i.e.* nearly parallel to the diad axis of the molecule (Fig. 1). In discussing the structure of the $[MeN.P(O)OMe]_3$ molecule Ansell & Bullen (1968) suggested that the mechanism of its formation by intra-molecular rearrangement of $[NP(OMe)_2]_3$ leads to production of that isomer which has the oxo groups placed so that the P=O bonds are coplanar with a neighbouring P—N—C system. Coplanarity facilitates

migration of a methyl group when

$$=\overset{\overset{\displaystyle O-CH_3}{|}}{P}-N= \text{ becomes}$$

$$\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle |}{}}{-P}}-\overset{\overset{\displaystyle CH_3}{|}}{N}-$$

. Ansell & Bullen (1968) further predicted that, because of this mechanism, an isomer of $[MeN.P(O)OMe]_3$ which has a chair-shaped ring (symmetry $\bar{3}$) would have all the methoxy groups in axial positions and all the oxo groups in equatorial positions. By the same argument a tetrameric phosphazane with ring symmetry $\bar{4}$ would also be formed with all its oxo groups equatorial. It may be of significance that isomer 2, the major product obtained by us, has this particular configuration of oxo groups although the reaction we used, involving methyl iodide, most likely has an inter-molecular mechanism.

Intermolecular distances

The arrangement of the molecules in the unit cell and the intermolecular distances less than 4 Å are shown in

Fig. 3. The following contacts between molecules related by the **b** translation are omitted from the diagram: $O(1)\cdots C(3)(x, 1 + y, z)$ 3·58, $O(2)\cdots C(4)$ $(x, -1 + y, z)$ 3·57, $C(1)\cdots C(3)(x, 1 + y, z)$ 3·57, and $C(2)\cdots C(4)(x, -1 + y, z)$ 3·64 Å. The shortest contacts of each type are $O\cdots O$ 3·58, $CH_3\cdots CH_3$ 3·57, $O\cdots CH_3$ 3·10 Å. The $O\cdots CH_3$ distance of 3·10 Å is markedly shorter than others of the same type. A similar short $O\cdots CH_3$ distance (3·07 Å) was found in $[MeN.P(O)OMe]_3$ (Ansell & Bullen, 1968). It is possibly indicative of $CH\cdots O$ hydrogen-bonding (Sutor, 1963).

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The Crystal and Molecular Structure of the 2:1 Molecular Complex of Theophylline with Phenobarbital

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The 2:1 molecular complex of theophylline with phenobarbital crystallizes in the orthorhombic space group *Pnma*, with the unit-cell dimensions $a = 6.991$ (5), $b = 25.554$ (17), $c = 15.129$ (7) Å. The approximate structure in the space group $Pn2_1a$ was initially solved by the application of *MULTAN*. The correct structure was then refined in *Pnma* to give a final R index of 0.095. The phenobarbital molecule has mirror symmetry and participates in weak N—H···N hydrogen bonds to two symmetrically related theophylline molecules. The N(7) atom of theophylline forms a hydrogen bond with the O(2) atom of the adjacent theophylline molecule, and the C(8) atom of theophylline may form a weak C—H···O hydrogen bond with the O(4) atom of the adjacent phenobarbital.

Introduction

Xanthines and barbiturates form crystalline complexes with a variety of other molecular series as well as with each other. In fact, theophylline and phenobarbital form a molecular complex (Higgins & Dunker, 1944; Bender & Nelson, 1973) with a 2:1 molar ratio, similar to the complex of phenobarbital with 8-bromo-9-ethyladenine (Kim & Rich, 1968). However, the modes of hydrogen bonding in these two complexes seem to be distinct: the ring N(1) atom of theophylline is unable to participate in a hydrogen bond, while the N(1) atom of adenine may take part in the hydrogen-

bond formation (see Fig. 1). Phenobarbital (a derivative of uracil) is physiologically used as a sedative hypnotic agent, while theophylline (a derivative of xanthine) is effective as a diuretic and cardiac stimulant; these two drugs are frequently used at the same time. To explore the possibility that the specific interaction between phenobarbital and theophylline may play a significant role in the multiple pharmacological effect of these drugs, the crystal structure analysis of the 2:1 molecular complex of theophylline with phenobarbital was carried out, and the mode of the specific hydrogen bonding was elucidated.

Experimental

Colourless needles were obtained by distillation of a 50% aqueous ethanol solution of theophylline and phenobarbital in a 2:1 molar ratio under reduced pressure. The unit-cell dimensions were initially obtained from precession photographs and refined by a diffractometer: $a = 6.991$ (5), $b = 25.554$ (17), $c = 15.129$ (7) Å. The density (measured by the flotation method) is 1.459 g cm^{-3}, which is in good agreement with that calculated for four units of two theophylline and one phenobarbital in a unit cell. The observed ex-
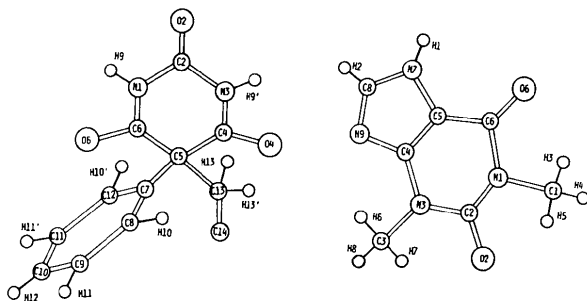

Fig. 1. Theophylline and phenobarbital (atomic numbering).