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Structures of Isomers of 2,4,6,8-Tetramethoxy-1,3,5,7-tetramethyl-2,4,6,8-tetraoxocyclotetra-λ^5-phosphazane: Structure of the 2,*cis*-4,*trans*-6,*trans*-8 Isomer, Conformational Analysis and the Relation between Configuration and Conformation

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Abstract

The molecular rearrangement of the phosphazene $[NP(OCH_3)_2]_4$ by reaction with methyl iodide gives two geometric isomers of the cyclic phosphazane $[CH_3N.P(O)OCH_3]_4$. The less abundant product (the 2,*cis*-4,*trans*-6,*trans*-8 isomer, m.p. 485–487 K) forms monoclinic crystals with $a = 9{\cdot}87$ (1), $b = 10{\cdot}54$ (1), $c = 8{\cdot}47$ (1) Å, $\beta = 97{\cdot}0$ (1)°, space group $P2_1/n$, $Z = 2$, $V = 875$ Å^3, $D_m = 1{\cdot}615$, $D_c = 1{\cdot}625$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, μ(Mo $K\alpha$) = 0·49 mm^{-1}, $F(000) = 448$; systematic absences: $h0l$ when $(h + l)$ is odd and $0k0$ when k is odd. The atomic positions in the crystal were determined by least-squares refinement from X-ray diffractometer intensities. The final $R = 0{\cdot}045$ for 2328 reflexions. The molecule is centrosymmetric, the eight-

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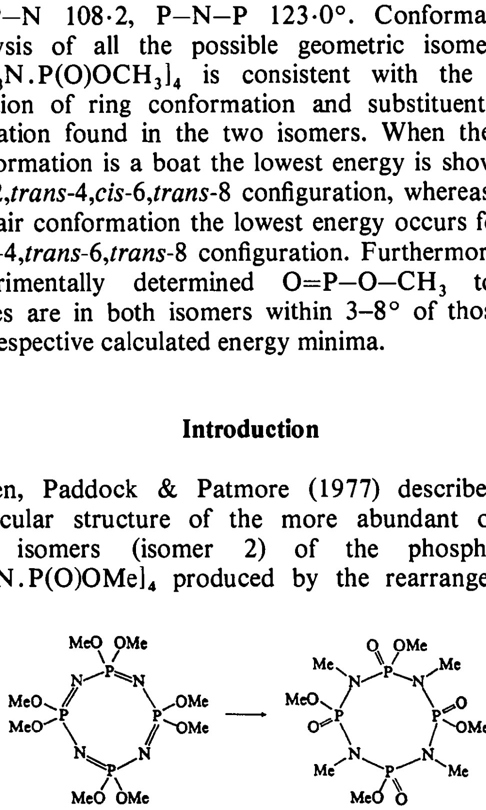
membered phosphazane ring having a chair conformation with approximate symmetry $2/m$, in contrast to the boat conformation in the more abundant isomer (2,*trans*-4,*cis*-6,*trans*-8). Mean bond lengths are: P—N 1·670, P=O 1·467, P—O 1·572, C—O 1·452, N—C 1·493 Å, and mean bond angles in the ring are: N—P—N 108·2, P—N—P 123·0°. Conformational analysis of all the possible geometric isomers of $[CH_3N.P(O)OCH_3]_4$ is consistent with the combination of ring conformation and substituent configuration found in the two isomers. When the ring conformation is a boat the lowest energy is shown by the 2,*trans*-4,*cis*-6,*trans*-8 configuration, whereas with a chair conformation the lowest energy occurs for the 2,*cis*-4,*trans*-6,*trans*-8 configuration. Furthermore, the experimentally determined $O{=}P{-}O{-}CH_3$ torsion angles are in both isomers within 3–8° of those for the respective calculated energy minima.

Introduction

Bullen, Paddock & Patmore (1977) described the molecular structure of the more abundant of the two isomers (isomer 2) of the phosphazane [MeN.P(O)OMe]$_4$ produced by the rearrangement:



Isomer (2) has a 2,*trans*-4,*cis*-6,*trans*-8 configuration of the methoxy substituents and its phosphazane ring has a boat conformation with approximate symmetry $\bar{4}$, whereas the ring in its phosphazene precursor [NP(OMe)$_2$]$_4$ is closer to a saddle conformation with approximate symmetry $\bar{4}2m$ (Ansell & Bullen, 1971). The molecular structure of isomer (1), whose yield in the rearrangement reaction is only 10% of that of isomer (2), is described in the present paper. The structure differs from that of isomer (2) both in the configuration of the substituents and in the conformation of the ring, which is a chair, the molecular symmetry being $\bar{1}$.

Experimental

Crystals of isomer (1) are monoclinic, showing the following forms: pinacoid $\{\bar{1}01\}$, and prisms $\{110\}$ and $\{011\}$. The $\{\bar{1}01\}$ faces are usually much larger than the prism faces, giving the crystal a tabular habit. The cell dimensions and other data are given in the *Abstract*. X-ray intensities of the 17 layers $h0$–$16l$ were measured at 292–294 K on a Philips Pailred diffractometer with monochromated Mo $K\alpha$ radiation. Measurement of all reflexions with $\sin\theta/\lambda < 0{\cdot}74$ Å^{-1} and of some with $0{\cdot}74 \le \sin\theta/\lambda \le 0{\cdot}79$ Å^{-1} gave 3204 intensities of which 2328 were judged significant in having $I > 2\sigma_I$. The intensities of the eight $0k0$ reflexions could not be measured as the crystal was aligned with **b** parallel to the ω axis of the diffractometer. The intensities were corrected for Lorentz and polarization effects but not for absorption.

Least-squares refinement was carried out on the University of Essex PDP-10 computer with programs written by Professor G. M. Sheldrick. 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 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 of X-ray reflexions show the space group to be $P2_1/n$, so that the two molecules in the unit cell must occupy special positions at centres of symmetry. The molecule must be the 2,*cis*-4,*trans*-6,*trans*-8 isomer in order to be centrosymmetric. The molecular centres being taken at (0,0,0) and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, the positions of the P atoms were deduced from the Patterson function and the O, N and C atoms were then located from Fourier syntheses. Full-matrix least-squares refinement with anisotropic temperature factors for P, O and N atoms reduced R to 0·07. A difference synthesis calculated at this stage revealed the positions of the H atoms, which were then adjusted slightly to make C—H = 1·05 Å and to produce O—C—H and H—C—H angles close to 109°. Refinement was continued with H atoms included in the

Table 1. *Fractional atomic coordinates with e.s.d.'s and equivalent isotropic thermal parameters*

$U_{eq} = \frac{1}{3}$ trace **U**, **U** being referred to orthogonal axes.

	x	y	z	U_{eq} (Å^2)
P(1)	−0·05025 (5)	0·16249 (5)	0·16815 (6)	0·0229
P(2)	0·16855 (5)	−0·01652 (5)	0·10218 (6)	0·0213
N(1)	0·0956 (2)	0·1266 (2)	0·0982 (2)	0·0237
N(2)	−0·1711 (2)	0·0645 (2)	0·0843 (2)	0·0258
O(1)	−0·0399 (2)	0·1149 (2)	0·3446 (2)	0·0363
O(2)	0·3246 (2)	0·0083 (2)	0·1513 (2)	0·0352
O(3)	−0·0807 (2)	0·2978 (2)	0·1469 (2)	0·0374
O(4)	0·1009 (2)	−0·1046 (2)	0·2004 (2)	0·0320
C(1)	0·0370 (3)	0·1883 (3)	0·4694 (3)	0·0479
C(2)	0·3696 (3)	0·0601 (3)	0·3075 (3)	0·0402
C(3)	0·1565 (3)	0·2248 (2)	0·0022 (3)	0·0365
C(4)	−0·2879 (3)	0·0391 (3)	0·1757 (3)	0·0431

Table 2. *Bond lengths* (Å) *with e.s.d.'s*

(*a*) Bond lengths from the least-squares refinement

P(1)–N(1)	1·666	P(1)–O(1)	1·568
P(1)–N(2)	1·669	P(2)–O(2)	1·567
P(2)–N(1)	1·670	σ	0·002
P(2)–N(2′)	1·661		
σ	0·002	P(1)–O(3)	1·464
		P(2)–O(4)	1·461
N(1)–C(3)	1·487	σ	0·002
N(2)–C(4)	1·490		
σ	0·003	C(1)–O(1)	1·447
		C(2)–O(2)	1·450
		σ	0·003

(*b*) Corrected for molecular oscillations

P(1)–N(1)	1·670	P(1)–O(1)	1·573
P(1)–N(2)	1·672	P(2)–O(2)	1·571
P(2)–N(1)	1·674	Mean	1·572 (2)
P(2)–N(2′)	1·665		
Mean	1·670 (2)*	P(1)–O(3)	1·468
		P(2)–O(4)	1·466
N(1)–C(3)	1·492	Mean	1·467 (2)
N(2)–C(4)	1·494		
Mean	1·493 (3)	C(1)–O(1)	1·450
		C(2)–O(2)	1·453
		Mean	1·452 (3)

* Possible error in the cell parameters has been taken into account in calculating the e.s.d.'s of the means.

Table 3. *Bond angles* (°)

E.s.d.'s are 0·1° for all angles at P and N atoms and 0·2° for angles at O atoms.

N(1)–P(1)–N(2)	108·1	N(1)–P(1)–O(1)	107·9
N(1)–P(2)–N(2′)	108·2	N(2)–P(1)–O(1)	99·7
P(1)–N(1)–P(2)	126·0	N(1)–P(2)–O(2)	105·2
P(1)–N(2)–P(2′)	120·0	N(2′)–P(2)–O(2)	100·1
O(1)–P(1)–O(3)	114·7	N(1)–P(1)–O(3)	110·5
O(2)–P(2)–O(4)	117·2	N(2)–P(1)–O(3)	115·2
P(1)–N(1)–C(3)	117·4	N(1)–P(2)–O(4)	111·1
P(2)–N(1)–C(3)	116·0	N(2′)–P(2)–O(4)	114·1
P(1)–N(2)–C(4)	116·6	P(1)–O(1)–C(1)	119·5
P(2′)–N(2)–C(4)	122·8	P(2)–O(2)–C(2)	119·2

calculations (with the coordinates listed elsewhere* and isotropic temperature factors $\overline{u^2} = 0\cdot06$ Å^2). Their positions were not refined. All other atoms were given anisotropic temperature factors. The weighting scheme was $w = (A/|F_o|)^2$ if $|F_o| \geq A$ and $w = (|F_o|/A)^2$ if $|F_o| < A$, the value of A being adjusted (final value 13·8 on an absolute scale) until the average $w\Delta^2$ (where $\Delta = |F_o| - |F_c|$) for groups of reflexions was almost uniform over the whole range of $|F_o|$. The final R is 0·045 for 2328 reflexions and $R' = (\sum w\Delta^2/\sum w|F_o|^2)^{1/2} = 0\cdot046$. In the last cycle all parameter shifts were $< 0\cdot14\sigma$.

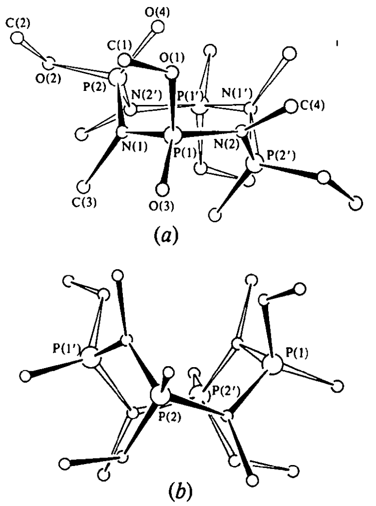


Fig. 1. Molecular shapes of the [MeN.P(O)OMe]$_4$ isomers: (*a*) *cis–cis–trans–trans*, and (*b*) *cis–trans–cis–trans*. Atoms with the corresponding primed and unprimed symbols are related by the molecular symmetry, either inversion (*a*) or twofold rotation (*b*).

Table 4. *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	0·13–0·14	0·14–0·16	0·15–0·16
O	0·14–0·15	0·18–0·21	0·21–0·23
N	0·14	0·15	0·17–0·19
C	0·14–0·16	0·19–0·21	0·23–0·27

The final atomic coordinates and equivalent isotropic thermal parameters are listed in Table 1.* The molecular shape and numbering of the atoms are shown in Fig. 1(*a*). Bond lengths are given in Table 2 and bond angles in Table 3.

The amplitudes of vibration corresponding to the deposited anisotropic thermal parameters are given in Table 4. A rigid-body libration analysis of the molecule (Schomaker & Trueblood, 1968) gave the results shown in Table 5. As the molecule is centrosymmetric **S** is necessarily equal to zero and the origin of the libration tensor must be placed at the molecular centre. Bond lengths corrected for the effect of the molecular oscillations (Cruickshank, 1956, 1961) are given in Table 2(*b*). The corrections range from 0·003 to 0·005 Å.

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* See following footnote.

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35755 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 5. *Molecular-vibration tensors referred to orthogonal axes a′, b, and c with the point* (0,0,0) *as origin*

$$\mathbf{T}\,(\text{Å}^2) = \begin{pmatrix} 0\cdot025\,(1) & -0\cdot003\,(1) & 0\cdot003\,(1) \\ & 0\cdot018\,(1) & 0\cdot007\,(1) \\ & & 0\cdot017\,(1) \end{pmatrix}$$

$$\mathbf{L}\,(\text{deg}^2) = \begin{pmatrix} 9\cdot5\,(3) & 1\cdot3\,(3) & 2\cdot3\,(3) \\ & 7\cdot9\,(3) & 4\cdot3\,(3) \\ & & 6\cdot6\,(6) \end{pmatrix}$$

Discussion

Bond lengths and angles

The mean bond lengths and angles are similar in the two isomers (Table 6), none of the differences between bond lengths being significant. As in isomer (2), the mean P—N length indicates that there is some π bonding in the phosphazane ring, though much less than in the phosphazene $[NP(OMe)_2]_4$. A fuller discussion of the differences in bond lengths and bond character between $[MeN.P(O)OMe]_4$ and $[NP(OMe)_2]_4$ has been given for isomer (2) (Bullen, Paddock & Patmore, 1977) and the same conclusions apply to isomer (1). The significant difference between the mean N—P—N angles in the two isomers is surprising in view of the close similarity of other angles.

Ring conformation and conformational analysis of the isomers

The phosphazane ring in the *cis–cis–trans–trans* isomer (1) has the chair conformation (Fig. 1*a*). It is centrosymmetric and has approximate symmetry $2/m$, six of the eight atoms in the ring being almost coplanar [Table 7, plane (i)] while the other two, P(2) and P(2′), lie 0·96 Å from the mean plane of these six. The departure from symmetry $2/m$ is shown by the differences between torsion angles across the ring (Fig. 2*a*). A chair conformation is also found for the phosphazane anion $[NHPO_2]_4^{4-}$ in $K_4[NHPO_2]_4.4H_2O$, with the torsion angles shown in Fig. 2(*b*) (Berking & Mootz, 1971). The pattern of torsion angles in isomer (1) is broadly similar to that in the anion but the ring in isomer (1) is more highly puckered near P(2) and P(2′). It is also more highly puckered than chair forms of the phosphazene ring. In several chlorophosphazenes with this conformation the largest ring torsion angle is *ca* 76° (Burr, Carlisle & Bullen, 1974), although in one other case, $N_4P_4(NHCH_3)_4(C_6H_5)_4$, there is a torsion angle of 95°. The torsion angles in phosphazanes are expected to be larger than those in phosphazenes because the ring bond angles (particularly N—P—N) are smaller.

Table 6. *Molecular dimensions in the isomers of* $[MeN.P(O)OMe]_4$ *and in* $[MeN.P(O)OMe]_3$

	$[MeN.P(O)OMe]_4$ Isomer (1) (this work)	Isomer (2) (Bullen, Paddock & Patmore, 1977)	$[MeN.P(O)OMe]_3$ (Ansell & Bullen, 1968)
Mean bond lengths (Å)			
P—N	1·670	1·673	1·663
P=O	1·467	1·469	1·45
P—O	1·572	1·579	1·56
C—O	1·452	1·456	1·45
N—C	1·493	1·501	1·48
Mean bond angles (°)			
N—P—N	108·2	106·9	105·2
P—N—P	123·0	122·5	121·7
O—P—O	116·0	115·8	116·1
P—O—C	119·4	119·2	119·3
P—N—C	118·2	118·1	119·0

Table 7. *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*.

E.s.d.'s (derived from the e.s.d.'s given in Table 1) are 0·001 Å for distances <0·02 Å and 0·002 Å for the remainder.

Plane (i): N(1), P(1), N(2), N(1′), P(1′), N(2′)

$$0\cdot207X - 0\cdot592Y + 0\cdot779Z = 0$$

[P(1) 0·041, N(1) −0·037, N(2) −0·033]

Plane (ii): N(1), P(1), P(2), C(3)

$$0\cdot550X + 0\cdot283Y + 0\cdot786Z = 1\cdot399$$

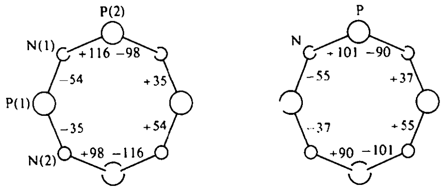
[N(1) 0·057, P(1), P(2) and C(3) all −0·019]

Plane (iii): N(2), P(1), P(2′), C(4)

$$0\cdot500X - 0\cdot809Y + 0\cdot310Z = -1\cdot154$$

[N(2) 0·053, P(1) −0·016, P(2′) −0·017, C(4) −0·019]

In contrast to isomer (1) the *cis–trans–cis–trans* isomer (2) has a boat form of ring (Fig. 1*b*) with approximate symmetry $\bar{4}$ (Bullen, Paddock & Patmore, 1977), as does the anion in the acid $H_4[NHPO_2]_4.2H_2O$ (Migchelsen, Olthof & Vos, 1965). Yet again, in $Cs_4[NHPO_2]_4.6H_2O$ a saddle



(*a*) (*b*)

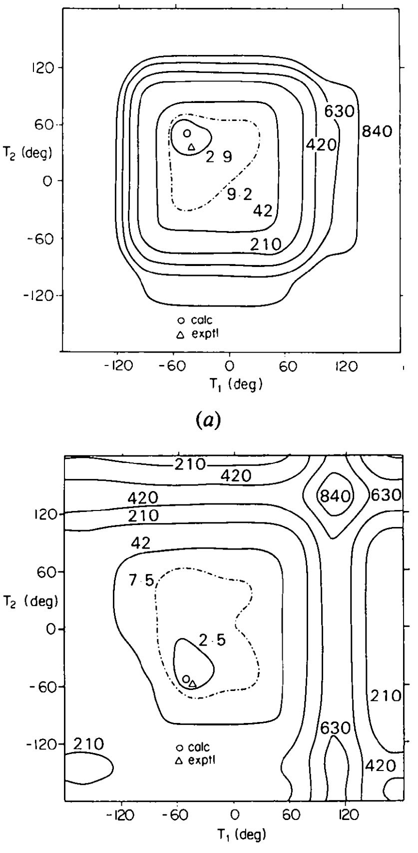
Fig. 2. Torsion angles (°) in the rings of (*a*) $[MeN.P(O)OMe]_4$ (isomer 1) (e.s.d.'s all less than 0·3°), and (*b*) $K_4[NHPO_2]_4.4H_2O$.

conformation of the ring is found (Berking & Mootz, 1971). As different ring conformations occur when changes are made merely (i) in the geometrical configuration of substituents in [MeN.P(O)OMe]$_4$ or (ii) in the nature of the cation in M_4[NHPO$_2$]$_4$, it may be inferred that the energy differences between the various ring conformations are small. Does it then follow that the conformation in [MeN.P(O)OMe]$_4$ is determined by the configuration of the substituents?

Among the phosphazenes there seems to be a correlation between ring symmetry and the symmetry of the substituent configuration. Thus *cis–cis–trans–trans* isomers have the centrosymmetric chair conformation of ring [*e.g.* $N_4P_4Cl_4(C_6H_5)_4$, Burr, Carlisle & Bullen (1974)] while *cis–trans–cis–trans* isomers have noncentrosymmetric saddle or boat conformations [*e.g.* $N_4P_4F_4(NMe_2)_4$, Begley, Millington, King & Sowerby (1974)]. Isomers (1) and (2) of [MeN.P(O)OMe]$_4$ also follow this correlation. Since ring π bonding, which in phosphazenes might be another factor affecting the conformation, is weak in phosphazanes, the occurrence of chair and boat conformations respectively in these two isomers supports the view that the conformation is strongly influenced, if not actually determined, by the substituent configuration. Lattice forces in the crystal may also have some effect but it seems unlikely that the correlation referred to above could apply so widely as it would were they a major factor.

To answer this and related questions, we have carried out conformational analyses on all possible configurations of [MeN.P(O)OMe]$_4$, in both boat and chair conformations. The coordinates of the P and N atoms were taken to be those found experimentally [isomer (1), this work; isomer (2), Bullen, Paddock & Patmore (1977)]. The coordinates of the exocyclic atoms were found by calculation, the assumed molecular parameters being P—O 1·576, P=O 1·468, O—C 1·454 Å, P—O—C 119·2°. The OPO plane was assumed to be perpendicular to the local NPN plane; the P—O and P=O bonds make equal angles (57·9°) with the external bisector of N—P—N. Torsion angles about the P—O bonds were measured relative to the reference position in which the O—C bond is eclipsed by the neighbouring P=O bond. Steric interactions between the (O)Me groups and all the other atoms and methyl groups were calculated as a function of the torsion angles. The 6/12 potential function and potential constants were the same as those used for the methoxyphosphazenes (Dougill & Paddock, 1974); the same potential constants were used for both types of O atom. Polar contributions to the energy were calculated less systematically, as explained below.

Preliminary calculations of the steric interactions in both boat and chair conformations, with their experimental configurations, showed that the lowest energies are obtained with equal C—O—P=O torsion angles at P(1) and P(1′), and at P(2) and P(2′), in conformity with the molecular symmetry, and the more accurate calculations were carried out with one torsion angle for each pair. The results for the two conformations are shown in Fig. 3. All six types of interaction: (O)Me with (O)Me, (N)Me, =O, —O, P, and N, are significant. Both attractive and repulsive components are important, omission of either giving unrealistic structures. Polar interactions were expected to modify the steric results, but the observed structures, in which the O—C bond is nearly *trans* to a ring bond, are incompatible with a non-zero charge on the (O)Me group. For the boat, the torsion angles calculated for steric interactions only (T_1 = −49, T_2 = +50°) compare well with the observed values (−41, +46°). For the chair, the calculated values are −49, −53° (observed −46, −60°). The potential functions are evidently realistic within about 0·8 kJ mol^{-1}. The energy minimum is shallow, which reduces the accuracy with which the torsion angles can be calculated.



(*a*)

(*b*)

Fig. 3. Energy contours for (*a*) boat and (*b*) chair, in kJ mol^{-1} above the calculated minimum, as a function of the C—O—P=O torsion angles, T_1 at P(1) and T_2 at P(2). Both actual structures correspond to energies 0·8 kJ mol^{-1} above the calculated minimum. The broken lines mark the separation of net-attractive interactions (inside) and net-repulsive interactions.

The functions can be applied to the problem of the relationship between configuration and conformation. Configurational changes were introduced by allowing each O=P—O—Me group to be turned through 180° about the OPO bisector. Initially several different (constant) values were assumed for the four torsion angles. Low energies were obtained when the torsion angles were approximately equal for methoxy groups on alternate P atoms, so that, for simplicity, further work was carried out with two independent torsion angles only. It is likely that the approximation is good enough to answer the important qualitative questions.

For an eight-membered oxophosphazane ring without symmetry there are 16 distinguishable configurations: (*A*) *cis–trans–cis–trans* (2); (*B*) *cis–cis–trans–trans* (4); (*C*) *cis–cis–cis–trans* (8); and (*D*) *cis–cis–cis–cis* (2). (*A*) and (*B*) have potential symmetries $\bar{4}$ and $\bar{1}$. The various sub-configurations differ in energy but, since the different chair (or the different boat) forms can be interconverted by pseudorotations involving only torsional motion about the P—N bonds, we need consider only the sub-configuration of lowest energy. For the boat skeletal conformation the (least) configurational energies increase in the order $(A) < (C) < (D) < (B)$, and for the chair conformation $(B) < (C) < (D) < (A)$.

For configurations (*A*) and (*B*) this result provides some numerical support for the suggestion above, that maximum stability is attained by (*A*) in the boat, and by (*B*) in the chair conformation. In both cases configurational and conformational symmetries match. For both chairs and boats, however, the total range of energies is only about 2 kJ mol^{-1}, and these results, by themselves, cannot account for the fact that configurations (*C*) and (*D*) have not been found experimentally.

The possibility that polar effects are important in this connexion is suggested by the structure of isomer (2), in which all the phosphoryl groups are in equatorial positions. While the polarity of the phosphoryl group does not affect the torsion angle of an uncharged methyl group, its effect on the energies of the different ring conformations may be decisive. It is difficult to investigate the polar effects systematically since six different groups are involved, and the bond dipole moments are not well enough established. We have simplified the problem by including only the biggest effect, which is the mutual repulsion of the phosphoryl O atoms, assumed to bear a charge of 0·4 e. Calculation of the energy for the various conformations shows that the most stable configuration is *cis–trans–cis–trans*, with the boat skeletal conformation, corresponding to the most abundant isomer (2). The next higher in energy (by 4·2 kJ mol^{-1}) is *cis–cis–trans–trans*, with the chair skeletal conformation, corresponding to isomer (1). The difference is increased by a smaller difference in the steric energies in the same sense. In the series of chair conformations the energy of the *cis–cis–cis–trans* configuration is not much higher (10 kJ mol^{-1} above the stable boat) and it is not inconceivable that it might be found as a minor component in the preparative reaction. The energies of the other configurations lie appreciably higher.

Although simplified, these results account for the main features of the isomerization reaction. The observed configurations and their associated conformations are those which offer the least electrostatic repulsion between the phosphoryl atoms, the difference between the most stable boat and the most stable chair being accentuated by a difference in the non-polar steric energies, in the same sense. Isomer (2) is the more abundant of the two, partly because the saddle structure of $[NP(OMe)_2]_4$ allows an easy transfer of a methyl group from O to N (Ansell & Bullen, 1968) and partly because the product is of low energy. The second factor is operative whether the reaction is intra- or intermolecular. Isomer (1) is less abundant, partly because coplanarity of two of the Me—O—P=N groupings requires a pseudorotational change, and partly because the phosphoryl repulsive energies are greater, tending to prevent isomerization.

Our calculations show that if the PN framework has the chair conformation, the lowest energy is attained when the arrangement of the substituents has the same symmetry. Although this is what is found experimentally there is some discrepancy between calculation and observation, as follows. In the limit of high symmetry (2/*m*) there are two possible conformations. That found in the crystal has the substituents *cis–cis–trans–trans** (Fig. 1*a*) and its pseudo twofold axis is through P(1), P(1'). Torsional motion about the P—N bonds (with $\bar{1}$ symmetry retained) transforms the conformation to the other limiting form, in which the skeletal geometry is identical with that of the starting conformation but the twofold axis now passes through P(2), P(2'). The effect of the transformation when followed by a reorientation which makes the direction of the twofold axis correspond to that of Fig. 1(*a*) is to interchange O(2) and O(4); this is not a configurational change, although it appears to be so at first sight. It is this second form (*cis–trans–trans–cis*) and not the observed one which is calculated to have the lower energy. The occurrence of the 'wrong' chair form may be a result of packing forces or of over-simplification of the polar calculations; since the two conformations are in the same conformational family their interconversion would be easy.

Intermolecular distances

The arrangement of the molecules in the unit cell and the intermolecular distances <3·9 Å are shown in Fig.

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* At P(2), P(1'), P(2'), P(1), in that order.

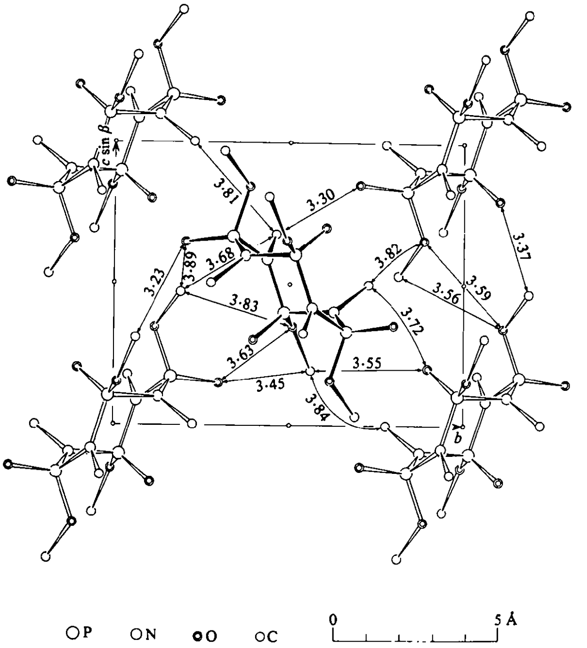

Fig. 4. Projection of the crystal structure down **a** with intermolecular distances (Å). E.s.d.'s of the distances are all <0·01 Å.

4. The following contacts between molecules related by the *a* lattice translation are omitted from the diagram: O(2)···C(4)(1 + *x*,*y*,*z*) 3·82 and C(2)···C(4)(1 + *x*, *y*,*z*) 3·69 Å. The shortest contacts of each type are: O···O 3·59, CH_3···CH_3 3·68, O···CH_3 3·23 Å. The corresponding shortest contacts found in the crystal of isomer (2) are 3·58, 3·57, and 3·10 Å respectively.

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The Structure of (2*R*,5*S*,8*R*,11*S*)-1,4,7,10-Tetrabenzyl-2,5,8,11-tetraethyl-1,4,7,10-tetraazacyclododecane

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Abstract

$C_{44}H_{60}N_4$, tetragonal, $P4_2/n$, $a = 27{\cdot}949\ (14)$, $c = 12{\cdot}505\ (8)$ Å, $U = 9768\ (12)$ Å^3, $Z = 10$, $D_c = 1{\cdot}096$, $D_o = 1{\cdot}04$ Mg m^{-3}. $R = 7{\cdot}3\%$ for 3837 independent reflections. The 12-membered ring has a tub form with the methylene groups at the corners. The chirality of the asymmetric carbon has a significant effect on the form of the ring.

Introduction

A series of investigations on the polymerization of chiral aziridines have been performed in our Institute.

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