The polymorphic behaviour and the crystal structure of one modification of poly(dimethylphosphazene)

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Poly(dimethyl phosphazene) displays, upon crystallization, a polymorphic behaviour showing two crystalline modifications, form I with a chain periodicity of 4.9 Å and a melting point of 146°C and form II with a chain periodicity of 5.85 Å and a melting point of 76°C. Form I, the only crystalline modification that is observed upon melting and recrystallization, has been completely characterized from a structural point of view through the study of X-ray diffraction patterns from oriented fibres and powder samples. A final structural refinement was carried out with the Rietveld method. The unit cell is monoclinic, space group $P2_1/c$ and the cell parameters are $a = 6.345(2)$, $b = 13.805(4)$, $c = 4.887(2)$ Å, $\beta = 110.45(3)$°.

(Keywords: crystallization; polymorphism; characterization; modification; X-ray diffraction; modelling; poly(dimethyl phosphazene))

INTRODUCTION

In the field of inorganic or organometallic polymers, one of the most innovative in recent years, polyphosphazenes represent the most versatile class from both the synthetic and the structural points of view.

The most commonly used synthetic route for polyphosphazenes is ring-opening polymerization of cyclic trimers, $[X_2PN]_3$ (X = Cl, F), and subsequent substitution of the halogen with a variety of organic groups. Polymers obtained by this procedure, developed by Allcock and coworkers[1], share a common structural feature, i.e. side chains are bonded to phosphorus through oxygen or nitrogen links, thus providing a depolymerization pathway that makes them unstable above ~200°C. Nevertheless, this class of macromolecules exhibits interesting properties and some of the present group have contributed to investigations concerning physicochemical characterization[2–5] and synthetic modifications[6–8] of these systems.

The development by Neilson[9] of the condensation polymerization of *N*-silylphosphoranimines has eliminated the requirement of –O– or –NH– links between the main chain and side groups in polyphosphazenes. Among these new polymers where aryl or alkyl substituents are directly attached to the –P=N– backbone, poly(dimethylphosphazene), $[NP(CH_3)_2]_n$ (PDMP), deserves particular attention owing to the very high thermal stability reported for the material (350–400°C)[10], which suggests a possible utilization of this polymer as a stationary phase in packed gas chromatographic columns[11]. Outstanding properties of PDMP membranes in separation processes have also been described[12].

The inherent interest of a complete structural characterization of PDMP appears obvious as, to our knowledge, it is the first one reported for polyphosphazenes with direct P–C bonds. The low scattering power of the side chain as compared with the backbone should, in principle, allow for a more accurate determination of the structural characteristics of the –P=N– backbone than in the case of poly(dichlorophosphazene), $[Cl_2PN]_n$ (PDCP)[13], or of polyphosphazenes with bulky substituents.

An additional reason that led us to the investigation of the solid-state structure of PDMP is the reported existence of two polymorphs[14,15] characterized by different chain periodicities.

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For the more common form I, a 4.9 Å periodicity has been determined[14]. Closely similar values (or multiples thereof) imply a possibly moderately distorted $(TC)_n$ (ref. 1) or $(TC\bar{T}\bar{C})_n$ (ref. 13) conformation, and despite the inherent flexibility of the -P=N- chain at least one polymorph with this axial periodicity has been reported for all polyphosphazene polymers.

The second crystalline modification of PDMP (form II)[15] represents one of the very rare cases[7] for which an axial periodicity (5.85 Å), implying a conformation that differs substantially from the alternating *cis–trans* sequence, has been proposed.

In the present paper the elucidation of the crystal structure of the widely occurring form I (4.9 Å repeat) of PDMP is presented. The thermal behaviour of PDMP, at least as far as it relates to polymorphism, is also discussed, while, with respect to form II, we are able to present only some speculative considerations, since it has proved impossible so far to obtain macroscopic samples containing high enough proportions of this polymorph.

Owing to the relatively low molecular weight[10] of PDMP, only moderately oriented fibres could be drawn, which allowed for lattice constants and space-group symmetry determination but not for a detailed crystal structure analysis. It was therefore deemed preferable to carry out the refinement with the Rietveld method[16] with data obtained from unoriented, melt-crystallized samples.

EXPERIMENTAL

The synthesis of PDMP was carried out following published procedures[17]. Every intermediate in the synthetic pathway was characterized by i.r., ^1H, ^{13}C and ^{31}P n.m.r. spectroscopy, and purity was always over 96%. Polymerization was performed in a heavy glass ampoule (~30 ml capacity) sealed in vacuum (after monomer degassing by the freeze–pump–thaw method) and kept at 160°C for 70 h.

The reaction product was dissolved in methylene chloride, precipitated with hexane, vacuum dried and characterized by t.g.a., i.r. and ^{31}P n.m.r. spectroscopy. D.s.c. analysis was performed on a Perkin–Elmer DSC-4 instrument.

Powder diffraction data were collected, according to the conditions given in *Table 1*, on a computer-controlled Siemens D-500 instrument, while fibre diffraction patterns were recorded on a Weissenberg camera. In all diffraction experiments Cu Kα radiation was employed.

The experimental density of PDMP has been determined by flotation in $CaCl_2$ aqueous solutions.

Table 1 Powder diffraction pattern recording conditions

Instrument	Siemens D-500 goniometer equipped with step-scan attachment, proportional counter and Soller slits, controlled with an Olivetti M24 computer
Radiation (power)	Cu Kα, Ni-filtered (40 kV, 30 mA)
Divergence aperture (deg)	0.3
Receiving aperture (deg)	0.05
Step width (deg)	0.05 (2θ)
Count time (seconds per step)	30
Temperature	room

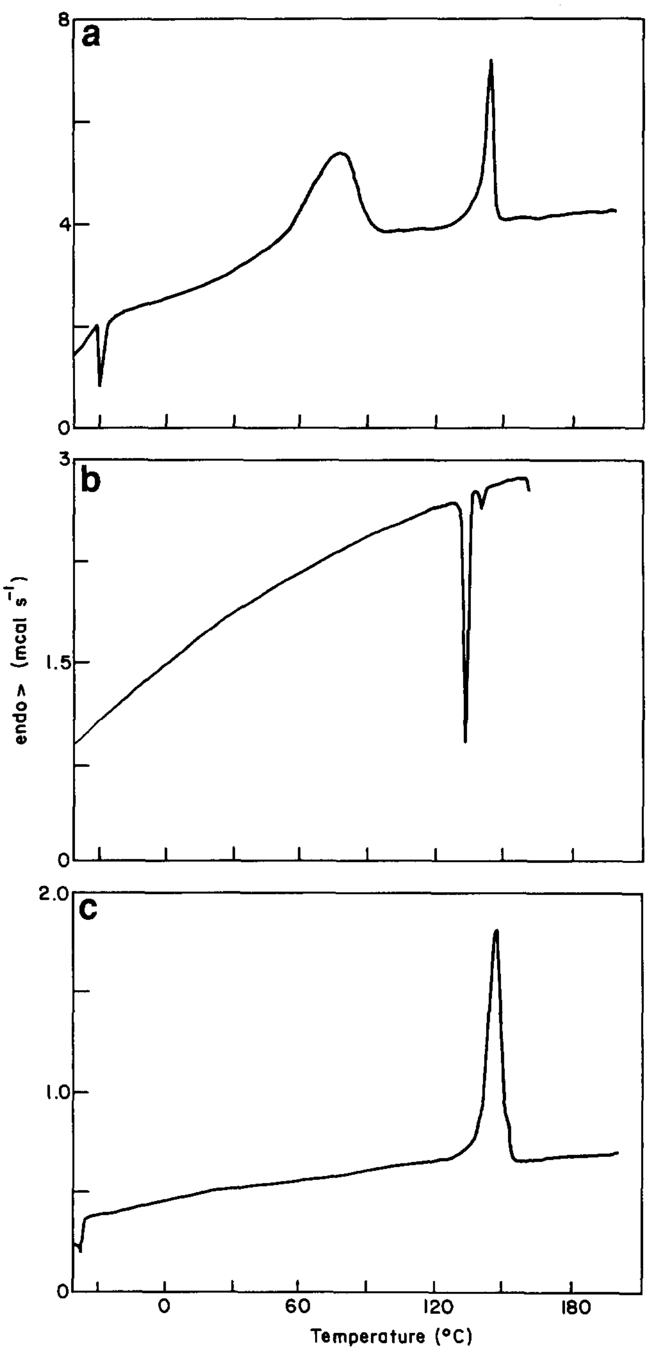

Figure 1 D.s.c. traces of (a) heating cycle of as-polymerized PDMP (heating rate 20°C min^{-1}), (b) subsequent cooling (rate −1°C min^{-1}) and (c) heating cycle of melt-crystallized PDMP (heating rate 20°C min^{-1})

THERMAL BEHAVIOUR AND POLYMORPHISM

The results of both our d.s.c. and X-ray diffraction investigations of PDMP are consistent with the existence of two crystalline modifications of this polymer. *Figure 1a* shows the first d.s.c. heating cycle of as-polymerized, solution-precipitated PDMP. Of the two endotherms, respectively at 76 and at 146°C, which are apparent from this trace, only the high-temperature transition, corresponding to the reported melting temperature[10,14] of PDMP, is reobserved in subsequent heating cycles (*Figure 1c*) following crystallization from the melt. Interestingly the ratios of the enthalpies associated with the two endotherms in the first heating cycle may vary

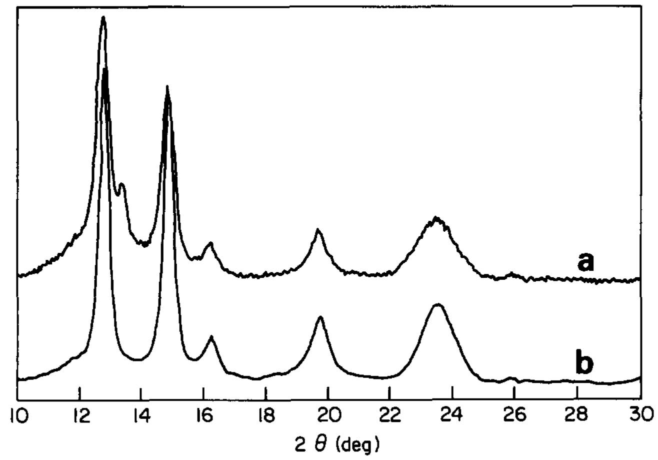

Figure 2 Powder diffraction patterns of (a) as-polymerized PDMP and (b) melt-crystallized PDMP

considerably for different polymer batches: the factors influencing this feature are however still unclear. The value we determined for the melting transition enthalpy is 15.5 cal g^{-1}, i.e. somewhat larger than previously reported[10], indicating a higher degree of crystallinity. D.s.c. cooling cycles (*Figure 1b*) show crystallization temperatures that are obviously cooling-rate-dependent; however, the observed supercoolings are modest (e.g. at -1°C $\min^{-1}$), consistent with the relatively low molecular weight of PDMP.

The described thermal behaviour is interpreted unequivocally with reference to the diffraction patterns of samples with different thermal history. The profiles of native PDMP (*Figure 2a*) display a sharp diffraction maximum at $2\theta = 13.4°$, whose relative intensity can be roughly correlated with the enthalpy associated with the low-temperature endotherm in the d.s.c. heating traces of the corresponding samples. Whereas other spectral features are, if at all, very modestly affected, the $2\theta = 13.4°$ diffraction peak is not observed in patterns recorded from native samples above 80°C or from melt-crystallized samples at room temperature (*Figure 2b*). Spectra recorded above 150°C are typically amorphous, indicating, in agreement with previous findings[14], that the 146°C endotherm is a crystalline-to-isotropic melt rather than a crystalline-to-mesophase transition, contrary to what is found in numerous polyphosphazenes with different side groups. The discussed evidence implies that melt-crystallized samples contain a single crystalline modification (form I), whereas in the raw polymer variable amounts of form I coexist with a second polymorph (form II) melting at 76°C and characterized by the $2\theta = 13.4°$ diffraction peak.

Previous data concerning a non-orthorhombic phase of PDMP[15] appear questionable as, with the proposed hexagonal unit cell ($a = b = 5.13$, $c = 5.85$ Å), values of Z of 1, 2 and 3 yield respectively density values of 0.93, 1.87 and 2.80 g cm^{-3}, all of which appear inconsistent with reasonable expectations. The single prominent diffraction peak we observe for form II of PDMP could reasonably be interpreted as the 100 reflection of a trigonal unit cell with $a = b = 7.63$ Å; furthermore, with a density close to the experimental value of 1.25 ± 0.01 g cm^{-3} and $Z = 3$, a c value of approximately 5.9 Å can be suggested. Indeed, assuming a trigonal lattice with one chain in the unit cell, the strongest equatorial reflection should be the 100, and the $Z = 3$ value required by density consideration is compatible with trigonal symmetry. Also the tentative value of the c axis appears to suggest that three monomeric units are required in the axial repeat. While these considerations concerning the second crystalline phase of PDMP are evidently largely speculative and further investigation is required on the subject, it is interesting to note that three-fold helical conformations have already been proposed[7] or implied[18] in the case of other polyphosphazenes.

LATTICE PARAMETER DETERMINATION AND STRUCTURAL REFINEMENT OF FORM I

Fibre diffraction patterns (*Figure 3*) obtained from melt-drawn PDMP confirmed an axial periodicity close to 4.90 Å and allowed for unambiguous determination of the lattice parameters of form I. Note that the fibre patterns, although modestly oriented because of the low molecular weight of PDMP, are indicative of high crystallinity, the broadness of some diffraction maxima in the powder spectra being due to overlapping reflections. While the equator of the fibre pattern and the powder diffraction maxima could be interpreted in terms of the orthorhombic unit cell proposed by Kojima and Magill[14] ($a = 13.9$, $b = 5.98$, $c = 4.90$ Å), some fibre layer-line reflections (see *Table 2*) were clearly inconsistent with this cell, indicating that an oblique lattice had to be taken into consideration. The closely comparable steric hindrance of methyl and chlorine substituents and the similarity of the lattice parameters to those of poly(dichlorophosphazene) (PDCP), recently determined by Chatani and Yatsuyanagi[13], suggested the possibility of quasi-iso-

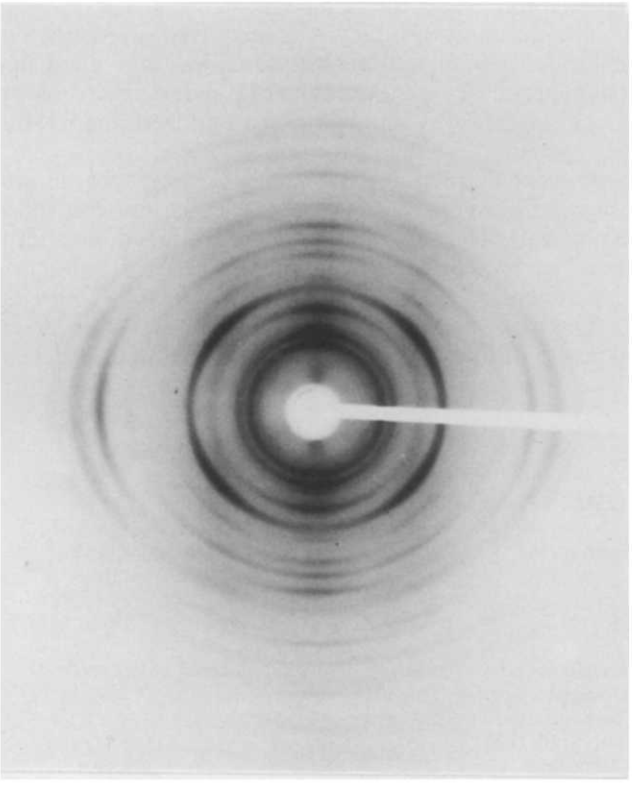

Figure 3 Fibre diffraction pattern of melt-drawn PDMP (Weissenberg camera)

Table 2 Comparison of observed spacings obtained from the oriented fibre X-ray diffraction pattern and the spacings calculated with the monoclinic cell (present work) and the orthorhombic cell (ref. 14). The asterisks label the most relevant inconsistencies of the orthorhombic cell

Fibre pattern, d_{obs} (Å)	Monoclinic cell		Orthorhombic cell	
	d_{calc} (Å)	Indices	d_{calc} (Å)	Indices
Layer 0				
6.86	6.90	020	6.95	200
5.93	5.94	100	5.98	010
5.40	5.46	110	5.49	110
4.51	4.50	120	4.53	210
3.45	3.45	040	3.47	400
2.98	2.97 2.98	200 140	2.99 3.00	020 410
2.75	2.73	220	2.75	220
2.50	2.49 2.50	230 150	2.51 2.52	320 510
2.29	2.25	240	2.27	420
Layer 1				
4.21	4.24	111	4.00	201*
3.78	3.74 3.82	121 021	3.79	011
3.23	3.20 3.25	131 031	3.33	211*
2.75	2.73 2.76	141 041	2.83	401*
Layer 2				
2.48	2.44	102	2.45	002
2.31	2.30	122	2.31	202
2.14	2.12	222	2.15	212

morphism between the two crystal structures. The refined unit cell for PDMP is $a = 6.345(2)$, $b = 13.805(4)$, $c = 4.887(2)$ Å, $\beta = 110.45(3)°$, very similar to that detected for crystalline PDCP[13] ($a = 5.98$, $b = 12.99$, $c = 4.92$ Å, $\beta = 111.7°$). It can be noted that, while the c axis values for the two structures are nearly identical, the a and b lattice parameters in PDMP are both 6% larger than in PDCP. With four monomer units in the unit cell, the calculated density value for PDMP is 1.24 g cm^{-3}, in good agreement with the experimentally determined value of 1.25 ± 0.01 g cm^{-3}. The systematic absences in the fibre spectrum of PDMP were consistent with the same space group reported for PDCP, i.e. $P2_1/c$.

The crystal structure refinement was carried out with the Rietveld method, through the best fitting of the whole X-ray diffraction powder profile[16].

As a consequence of the similarity between the crystal data of PDCP and those of the form I of PDMP, we assumed the molecular arrangement of PDCP in the crystal to be a good starting point for the refinement of the structural parameters of PDMP, substantial differences only being expected in the steric hindrance of the methyl groups as compared to that of the chlorine atoms. This choice turned out again to be correct, and small adjustments of the atomic parameters were sufficient to obtain a satisfactory agreement between the observed and the calculated profiles.

Since the asymmetric unit coincides with the chemical repeat unit, the positions of only four non-hydrogen atoms had to be adjusted. Each macromolecule contains the space group glide plane as the molecular symmetry operator, which allows the polymer chain to propagate along the c axis.

Nine structural parameters were refined in the last cycles: three translations and three rotations, applied to the four non-hydrogen atoms belonging to the constitutional repeat unit treated as a rigid body, one P–C distance (the same for both methyl groups), one P–N distance and the C–P–N bond angle. These parameters were not allowed, however, to vary in a completely free way. The values of the first six are in fact strictly correlated with the second P–N distance and the N–P–N and the P–N–P bond angles; while the last three have a self-explanatory meaning.

Reasonable values for these six geometrical features were adopted as non-rigid restraints in the refinement procedure in order to avoid reaching results that, although producing a good fit with the observed profile, could hardly be accepted from a physical point of view.

Thermal parameters were allowed to vary only at the end of the refinement procedure. Hydrogen atoms were finally inserted at calculated positions.

In *Table 3* we report the refined atomic parameters of non-hydrogen atoms and in *Table 4* we list the most significant geometrical features of the polymer chain in the crystalline state.

Non-structural parameters were refined as well. The background line, which roughly separates the crystalline from the amorphous contribution, has been described through a bell-shaped curve centred at $2\theta = 12.6°$ superimposed onto a segmented line where the nodes were arbitrarily spaced on the 2θ scale and refined on the intensity scale[19]. Diffraction peaks were represented by Cauchy curves with a full width at half-maximum (FWHM) depending on the given *hkl* triplet through the average crystallite dimensions along the three crystallographic axes[20], considered as refinable parameters, as well as on the position on the 2θ scale. An overall zero correction on the experimental 2θ scale was adopted and a small preferred orientation detected along the 001 direction.

In *Table 5* we report the refined values of all non-structural parameters. The final disagreement factor

Table 3 Refined cell parameters and atomic parameters for non-hydrogen atoms

$a = 6.345(2)$ Å		Monoclinic
$b = 13.805(4)$ Å	$\beta = 110.45(3)°$	Space group $P2_1/c$
$c = 4.887(3)$ Å		$Z = 4$, $D_c = 1.24$ g cm^{-3}

	x	y	z	B (Å^2)
N	0.0268(19)	0.2160(6)	−0.0658(38)	12
P	0.0542(24)	0.1923(10)	0.2624(39)	10
C(1)	0.3227(34)	0.1363(18)	0.4462(41)	4
C(2)	−0.1442(42)	0.1006(11)	0.2731(49)	4

Table 4 Internal coordinates for poly(dimethylphosphazene)

Bond lengths (Å)			
N–P	1.586(27)	P–N′	1.561(17)
P–C(1)	1.799(26)	P–C(2)	1.799(26)
Bond angles (deg)			
N–P–N′	112.5(1.0)	P–N′–P′	135.9(1.0)
N–P–C(1)	110.1(1.3)	N–P–C(2)	110.1(1.3)
C(1)–P–C(2)	103.5(1.2)		
Torsion angles (deg)			
N–P–N′–P′	174.1(1.3)		
P–N′–P′–N″	23.9(1.0)		

Table 5 Non-refined structural parameters

Zero correction (2θ) (deg)	−0.008(3)
Profile function parameters[a]	
U	11.9(3.5)
V	−1.6(0.5)
W	different for each *hkl* triplet[b]
m	1
Preferred orientation parameter[c]	
G	0.017(3)
Background parameters. Intensities (count × 10^3) at the points of the segmented line.	
2θ (deg)	Intensity
5	0.035(1)
9	0.036(1)
18	0.062(1)
21	0.045(2)
23	0.054(4)
26	0.040(2)
30	0.041(1)
37	0.025(1)
48	0.025(1)
60	0.027(1)
Parameters of the 'bell-shaped' curve.	
BA (integrated intensity)	80(3)
BW (bell width at half height) (deg)	1.88(8)
BC (bell centre, 2θ) (deg)	12.59(3)
m (parameter of Pearson VII function)	1
Average crystallite dimensions (Å) L_a, L_b, L_c	172(13), 87(2), 52(5)

[a] Peak shapes are calculated analytically through a Pearson VII function: $f(z) = (C/H_k)[1 + 4(2^{1/m} - 1)z^2]^{-m}$ with $z = (2\theta_i - 2\theta_k)/H_k$ and $H_k^2 = U \tan^2 \theta_k + V \tan \theta_k + W$; $m = 1$ means a peak profile following a Cauchy distribution

[b] Half height widths are calculated from the average crystallite dimensions through a computational procedure proposed by Perego *et al.*[20]

[c] Preferred orientation parameter $PO = \exp(-G\alpha_k^2)$, α_k being the angle between the scattering vector of the kth reflection and the scattering vector of a fixed (preferred) orientation, in this case the 0 0 1 reflection

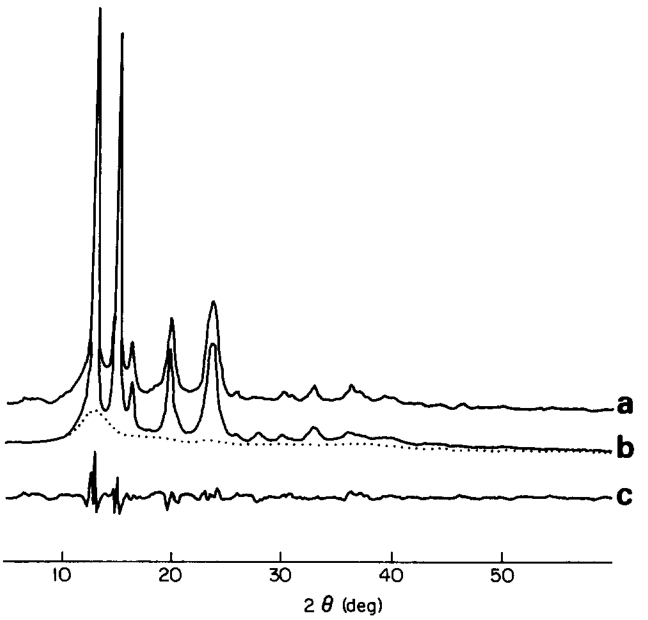

Figure 4 The observed powder X-ray diffraction profile (a) of PDMP (form I) is compared to the calculated profile (b). Curve (c) is the difference profile, while the dotted curve represents the amorphous contribution

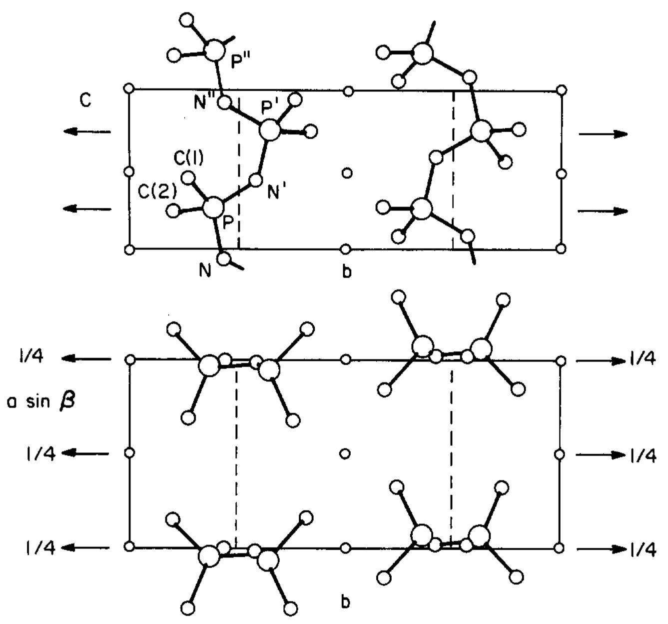

Figure 5 Projections along $a \sin \beta$ and c of the PDMP (form I) crystal structure (the internal coordinates for PDMP—see labelled portion of diagram—are given in *Table 4*)

($R_2 = \sum |I_{obs} - I_{calc}|/\sum I_{net}$ where $I_{net} = I_{obs} - I_{backg}$) is 0.13.

In *Figure 4* we display a comparison between the observed (curve a) and the calculated (curve b) powder profiles, whereas curve c is the difference profile.

DESCRIPTION OF THE STRUCTURE

The crystal structure is shown in *Figure 5*, projected along the $a \sin \beta$ and c directions in order to compare it with the structure of PDCP, which is shown along these axes as well[13].

The polymer chain conformation is, like PDCP, of the glide type, while for some other poly(organophosphazenes) 2/1 helical conformations have been proposed.

Internal coordinates of PDMP display minor differences from those of PDCP. The most interesting is, in our opinion, the substantial equality of the two P–N bond lengths along the main-chain backbone. The difference between 1.586(27) and 1.561(17) Å is in fact small when compared with the high e.s.d. values affecting these estimates, while the differences with respect to the corresponding bond lengths detected in PDCP (1.67(8) and 1.44(5) Å respectively) may be meaningful. It should be noted, however, that the crystallographic analysis of both cyclic[21–24] and linear[25] phosphazene oligomers appears to support models with only marginally different P–N bond lengths rather than a tendency towards alternating bonds of substantially differing lengths (P–N mean values: 1.596 Å for $N_4P_4(CH_3)_8$; 1.586 Å for $N_5P_5(CH_3)_{10}$; 1.526 Å for $N_5P_5Cl_{10}$; and 1.571 Å for $N_5P_5Br_{10}$).

Bond angles are in the expected range when compared with the average values obtained from the structure of decamethylcyclopentaphosphazene determined from single-crystal X-ray diffraction data[22]. The P–N–P angle (135.9(1.0)°) is to be compared with an average value of 132.9°, while the N–P–N angle (112.5(1.0)°) is slightly smaller than the average value of 118.7°, and the C–P–C angle (103.5(1.2)°) compares quite well with the average value of 104.3°.

Torsion angles indicate a sequence of *trans* (174.1(1.3)°, *T*) and distorted *cis* (23.9(1.0)°, *C'*) rotational states. While *T* is almost the same as in PDCP (175°), the value of *C'* is significantly smaller than the corresponding torsion in PDCP (31°).

Consistent with the larger van der Waals radius of methyl groups as compared to Cl, while the shortest intermolecular methyl–methyl interaction in the form I PDMP crystal structure is 3.79 Å, all others being larger than 3.89 Å, the shortest intermolecular Cl–Cl contact in PDCP is 3.63 Å, all others being larger than 3.71 Å.

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