Structure of the Polytypic β-Form of $P_3N_3(OCH_2CF_2CF_2CH_2O)F_4$

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Abstract

Crystals of the β-form of the title compound, 1,1,3,3-tetrafluoro-5,5-(2,2,3,3-tetrafluorotetramethylenedioxy)-cyclotri(phosphazene), are triclinic, $P\bar{1}$, with lattice constants $a = 12.392\,(2)$, $b = 16.569\,(3)$, $c = 19.257\,(4)$ Å, $\alpha = 110.22\,(3)$, $\beta = 90.02\,(3)$, $\gamma = 97.10\,(3)°$ and $V = 3677.9\,(12)$ Å^3 with $Z = 12$, to yield $\rho_{calc} = 2.010$ Mg m^{-3} for $M_r = 371.0$ and $F(000) = 2184$. The structural data was refined to $R = 0.0548$ and $wR = 0.0567$ for 5536 observed reflections $[|F| \geq 3\sigma(F)]$ with a goodness-of-fit of 1.61 and a maximum residual of 0.47 e Å^{-3}. The six crystallographically independent molecules are all structurally equivalent, with approximately the same orientation for each molecule. The molecules are roughly arranged in layers lying parallel to the ac plane. Two types of these layers exist within the structure. Each layer exhibits approximate noncrystallographic symmetry elements. For layers at $y \sim \frac{1}{6}$ and $\frac{5}{6}$, the appropriate layer-group symmetry notation is $pc2a$, while the layer at $y \sim \frac{1}{2}$ has idealized $p2_1/c11$ symmetry. The difference in the symmetries of the two types of layers arises from different sequencing of molecules with right- and left-handed chirality. Both layer groups require β to be equal to 90°, explaining its observed value. The structure can be described as a polytype structure, in which stacking faults occur every third layer. An $ABAABA$ stacking pattern exists, where A corresponds to the layer at $y = \frac{1}{6}$ and $\frac{5}{6}$ while B corresponds to the layer at $y = \frac{1}{2}$. In addition, successive layers are related by the following set of idealized translation vectors $T_{A,B}$

$$T_{A,B} = T_{B,A} = (\tfrac{1}{2}, \tfrac{1}{3}, \tfrac{1}{3})$$
$$T_{A,A} = (0, \tfrac{1}{3}, \tfrac{1}{3}).$$

Superimposed upon these translation vectors is modulation of the chirality of the molecules.

1. Introduction

The title compound was synthesized by the University of Idaho group as part of a project studying the properties of compounds containing fluorinated derivatives of the P_3N_3 ring system (Elias, Kirchmeier, Shreeve & Hope, 1994). Crystals were inadvertently sent to two different crystallographic laboratories for structural anal-

ysis. Crystals analyzed by one group proved to have very conventional crystallographic properties (Elias, Kirchmeier & Shreeve, 1994); monoclinic, space group $P2_1/c$, with $a = 14.695\,(5)$, $b = 8.532\,(2)$, $c = 9.600\,(3)$ Å, $\beta = 102.38$, $V = 1175.6\,(6)$ Å^3, with $\rho = 2.096$ Mg m^{-3} for $Z = 4$. In this laboratory a different, triclinic, modification of the compound was found, with a surprising feature that the asymmetric unit contains six crystallographically independent molecules. In this paper we report on the structure determination and analysis of this unusual crystal modification.

2. Experimental

A summary of the experimental details is given in Table 1. A crystal was selected and mounted on a Nicolet R3 diffractometer upgraded to Siemens P4 specifications and equipped with a graphite monochromator and a Cu $K\alpha$ ($\lambda = 1.54184$ Å) X-ray tube. A preliminary reflection search identified the crystal as belonging to the triclinic crystal class and lattice constants were obtained by accurate centering of 30 high-angle reflections. The $XSCANS92$ data collection package (Siemens, 1992) was used for these and all subsequent manipulations. Since the large unit-cell volume (3677.9 Å) indicated the presence of multiple formula units in the asymmetric unit, and with the β angle essentially equal to 90°, a careful search was made for a higher symmetry unit cell and/or for evidence of twinning. Neither was found. Lp corrections were applied, but not absorption corrections.

The structure solution was obtained *via* the direct methods routine *TREF* in the *SHELXTL-Plus* (VMS) program (Sheldrick, 1991) on a VAX 3100 workstation. This led to the identification of six independent molecules in the asymmetric unit. Refinement, with anisotropic thermal parameters for non-H atoms, proceeded in a straightforward manner, with H atoms included at ideal locations with fixed isotropic thermal parameters ($U = 0.08$ Å^2). Final positional parameters are given in Table 2, while interatomic distances and angles are given in Table 3.* Fig. 1 illustrates the molecular geometry of one of the six molecules.

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* Lists of structure factors, anisotropic displacement parameters and H-atom coordinates, and *OFIT* diagrams and thermal ellipsoid plots have been deposited with the IUCr (Reference: CR0501). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Experimental details*

Crystal data

Chemical formula	$C_4H_4F_8N_3O_2P_3$
Chemical formula weight	371.0
Cell setting	Triclinic
Space group	$P\bar{1}$
a (Å)	12.392 (2)
b (Å)	16.569 (3)
c (Å)	19.257 (4)
α (°)	110.22 (3)
β (°)	90.02 (3)
γ (°)	97.10 (3)
V (Å^3)	3677.9 (12)
Z	12
D_x (Mg m^{-3})	2.010
Radiation type	Cu $K\alpha$
Wavelength (Å)	1.54184
θ range (°)	1.5–50
μ (mm^{-1})	5.584
Temperature (K)	293
Crystal size (mm)	$0.40 \times 0.30 \times 0.20$
Crystal color	Colorless

Data collection

Diffractometer	Siemens $R3m/V$
Monochromator	Highly oriented graphite crystal
Scan speed (° min^{-1})	Variable, 3.00–60
Scan range (ω,°)	1.00
Background measurement	Stationary crystal and stationary counter at the beginning and end of the scan, each for 25.0% of the total scan time
Data collection method	ω scans
Absorption correction	None
No. of measured reflections	8795
No. of independent reflections	7435
No. of observed reflections	5536
Criterion for observed reflections	$F > 3\sigma(F)$
R_{int}	0.018
θ_{max} (°)	50
Range of h, k, l	$-1 \rightarrow h \rightarrow 12$
	$-15 \rightarrow k \rightarrow 15$
	$-19 \rightarrow l \rightarrow 19$
No. of standard reflections	3
Frequency of standard reflections	Every 97 reflections

Refinement

Refinement on	Full-matrix least-squares
Quantity minimized	$\Sigma w(F_o - F_c)^2$
R	0.0548
wR	0.0567
S	1.61
No. of parameters used	1084
H-atom treatment	Riding model, fixed isotropic U
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.005F^2$
$(\Delta/\sigma)_{max}$	0.013
Data-to-parameter ratio	5.1:1
$\Delta\rho_{max}$ (e Å^{-3})	0.47
$\Delta\rho_{min}$ (e Å^{-3})	-0.40
Extinction coefficient	$\chi = 0.7 \times 10^{-3}$, where $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$
Source of atomic scattering factors	*SHELXTL-Plus* (Sheldrick, 1991)

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j.$$

	x	y	z	U_{eq}
Molecule (1)				
P(1)	0.3483 (2)	0.1802 (1)	0.3244 (1)	0.043 (1)
P(2)	0.5636 (2)	0.1813 (2)	0.3544 (1)	0.049 (1)
P(3)	0.4224 (2)	0.2058 (1)	0.4650 (1)	0.042 (1)
N(1)	0.3298 (5)	0.2002 (4)	0.4091 (3)	0.046 (3)
N(2)	0.4697 (5)	0.1767 (4)	0.3000 (3)	0.051 (3)

Table 2 (*cont.*)

	x	y	z	U_{eq}
N(3)	0.5406 (5)	0.1966 (4)	0.4375 (3)	0.048 (3)
O(1)	0.2938 (4)	0.2515 (3)	0.3052 (3)	0.049 (2)
O(2)	0.2825 (4)	0.0918 (3)	0.2735 (3)	0.049 (2)
F(1)	0.6556 (3)	0.2488 (3)	0.3513 (2)	0.070 (2)
F(2)	0.6233 (4)	0.1018 (3)	0.3237 (3)	0.079 (2)
F(3)	0.3916 (3)	0.1409 (3)	0.5039 (2)	0.063 (2)
F(4)	0.4264 (3)	0.2877 (3)	0.5312 (2)	0.059 (2)
F(5)	0.0232 (4)	0.0755 (3)	0.1885 (3)	0.089 (3)
F(6)	0.1821 (4)	0.0582 (3)	0.1417 (3)	0.088 (3)
F(7)	0.1199 (4)	0.2055 (4)	0.1455 (3)	0.093 (3)
F(8)	0.0833 (4)	0.2399 (3)	0.2624 (3)	0.070 (2)
C(1)	0.1673 (6)	0.0805 (5)	0.2678 (4)	0.052 (4)
C(2)	0.1312 (7)	0.1023 (6)	0.2033 (5)	0.054 (4)
C(3)	0.1504 (7)	0.1982 (6)	0.2116 (5)	0.054 (4)
C(4)	0.2649 (6)	0.2432 (6)	0.2300 (4)	0.057 (4)
Molecule (2)				
P(4)	0.3952 (2)	0.5072 (1)	0.8583 (1)	0.043 (1)
P(5)	0.6036 (2)	0.4880 (2)	0.8171 (1)	0.048 (1)
P(6)	0.4637 (2)	0.5255 (2)	0.7290 (1)	0.059 (1)
N(4)	0.5782 (5)	0.5062 (5)	0.7443 (3)	0.062 (4)
N(5)	0.5150 (5)	0.4946 (4)	0.8751 (3)	0.047 (3)
N(6)	0.3731 (5)	0.5255 (5)	0.7848 (3)	0.056 (3)
O(3)	0.3108 (4)	0.4274 (3)	0.8551 (3)	0.051 (2)
O(4)	0.3652 (4)	0.5835 (3)	0.9293 (3)	0.042 (2)
F(10)	0.6461 (4)	0.4008 (3)	0.7957 (3)	0.076 (2)
F(11)	0.7074 (3)	0.5444 (3)	0.8545 (3)	0.077 (3)
F(12)	0.4249 (4)	0.4673 (5)	0.6529 (3)	0.113 (4)
F(13)	0.1525 (4)	0.4180 (3)	1.0064 (3)	0.066 (2)
F(14)	0.4745 (5)	0.6121 (4)	0.7157 (3)	0.109 (4)
F(15)	0.1064 (3)	0.4293 (3)	0.9021 (2)	0.059 (2)
F(16)	0.2692 (4)	0.5707 (3)	1.0514 (2)	0.060 (2)
F(17)	0.1088 (4)	0.5770 (3)	1.0101 (3)	0.068 (2)
C(5)	0.2864 (6)	0.4087 (5)	0.9217 (4)	0.051 (4)
C(6)	0.1871 (6)	0.4515 (5)	0.9542 (4)	0.041 (4)
C(7)	0.2046 (6)	0.5504 (5)	0.9888 (4)	0.040 (4)
C(8)	0.2534 (6)	0.5979 (5)	0.9417 (4)	0.044 (4)
Molecule (3)				
P(7)	0.1075 (2)	0.5104 (1)	0.3587 (1)	0.044 (1)
P(8)	-0.1072 (2)	0.4953 (2)	0.3184 (1)	0.053 (1)
P(9)	0.0459 (2)	0.5251 (2)	0.2279 (1)	0.067 (1)
N(7)	-0.0752 (5)	0.5107 (5)	0.2446 (4)	0.065 (4)
N(8)	-0.0164 (5)	0.5001 (4)	0.3756 (3)	0.049 (3)
N(9)	0.1346 (5)	0.5254 (5)	0.2851 (3)	0.059 (3)
O(5)	0.1634 (4)	0.4294 (3)	0.3570 (3)	0.054 (2)
O(6)	0.1635 (4)	0.5870 (3)	0.4283 (3)	0.043 (2)
F(20)	-0.1878 (4)	0.5571 (4)	0.3561 (3)	0.090 (3)
F(21)	-0.1838 (4)	0.4111 (3)	0.3000 (3)	0.084 (3)
F(22)	0.0672 (4)	0.6094 (5)	0.2114 (3)	0.122 (4)
F(23)	0.0623 (4)	0.4637 (5)	0.1529 (3)	0.126 (4)
F(24)	0.2514 (4)	0.5759 (3)	0.5515 (2)	0.063 (2)
F(25)	0.4148 (3)	0.5807 (3)	0.5130 (3)	0.069 (2)
F(26)	0.3174 (4)	0.4239 (3)	0.5103 (3)	0.068 (2)
F(27)	0.3682 (3)	0.4320 (3)	0.4051 (3)	0.063 (2)
C(9)	0.1827 (6)	0.4131 (5)	0.4247 (4)	0.046 (4)
C(10)	0.2786 (6)	0.6008 (5)	0.4416 (4)	0.043 (4)
C(11)	0.3102 (6)	0.5545 (5)	0.4899 (4)	0.040 (4)
C(12)	0.2936 (7)	0.4550 (5)	0.4561 (4)	0.043 (4)
Molecule (4)				
P(10)	-0.0420 (2)	0.8288 (1)	0.1784 (1)	0.047 (1)
P(11)	0.1707 (2)	0.8199 (1)	0.1432 (1)	0.048 (1)
P(12)	0.0195 (2)	0.8088 (2)	0.0377 (1)	0.054 (1)
N(10)	0.0805 (5)	0.8316 (4)	0.2012 (3)	0.051 (3)
N(11)	-0.0697 (5)	0.8141 (4)	0.0954 (3)	0.057 (3)
N(12)	0.1399 (5)	0.8104 (4)	0.0615 (3)	0.053 (3)
O(7)	-0.1196 (4)	0.7565 (3)	0.1958 (3)	0.052 (2)
O(8)	-0.0763 (4)	0.9165 (3)	0.2329 (3)	0.059 (3)
F(30)	0.2322 (4)	0.7457 (3)	0.1431 (3)	0.071 (2)
F(31)	0.2640 (3)	0.8939 (3)	0.1735 (3)	0.067 (2)
F(32)	0.0155 (4)	0.8797 (3)	0.0054 (3)	0.084 (3)
F(33)	-0.0121 (4)	0.7306 (3)	-0.0317 (2)	0.079 (2)
F(34)	-0.2824 (5)	0.7948 (4)	0.3522 (3)	0.111 (4)
F(35)	-0.3267 (4)	0.7677 (3)	0.2361 (3)	0.075 (3)

Table 2 (*cont.*)

	x	y	z	U_{eq}
F(36)	−0.3329 (5)	0.9297 (4)	0.3159 (3)	0.101 (3)
F(37)	−0.1695 (5)	0.9431 (4)	0.3635 (3)	0.106 (3)
C(13)	−0.2480 (8)	0.8063 (7)	0.2888 (5)	0.067 (5)
C(14)	−0.2342 (8)	0.9025 (7)	0.3022 (5)	0.062 (5)
C(15)	−0.1885 (7)	0.9281 (5)	0.2386 (5)	0.064 (4)
C(16)	−0.1469 (7)	0.7613 (6)	0.2690 (4)	0.058 (4)

Molecule (5)

	x	y	z	U_{eq}
P(13)	0.4579 (2)	0.8176 (1)	0.9637 (1)	0.046 (1)
P(14)	0.6668 (2)	0.7966 (2)	0.9913 (1)	0.050 (1)
P(15)	0.5135 (2)	0.7886 (2)	1.0894 (1)	0.055 (1)
N(13)	0.4254 (5)	0.7990 (4)	1.0358 (3)	0.045 (3)
N(14)	0.6336 (5)	0.7869 (4)	1.0666 (3)	0.058 (3)
N(15)	0.5797 (5)	0.8105 (4)	0.9400 (3)	0.054 (3)
O(9)	0.3747 (4)	0.7544 (3)	0.9010 (3)	0.056 (3)
O(10)	0.4359 (4)	0.9112 (3)	0.9677 (3)	0.051 (2)
F(40)	0.7635 (3)	0.8668 (3)	1.0041 (3)	0.072 (2)
F(41)	0.7229 (4)	0.7200 (3)	0.9474 (3)	0.088 (3)
F(42)	0.4777 (4)	0.7092 (3)	1.1103 (3)	0.089 (3)
F(43)	0.5122 (4)	0.8579 (4)	1.1653 (2)	0.085 (3)
F(44)	0.1737 (4)	0.7842 (3)	0.8777 (3)	0.079 (3)
F(45)	0.2169 (4)	0.8220 (4)	0.7831 (3)	0.099 (3)
F(46)	0.1804 (4)	0.9508 (4)	0.9114 (3)	0.098 (3)
F(47)	0.3408 (5)	0.9614 (4)	0.8662 (3)	0.096 (3)
C(17)	0.3492 (7)	0.7721 (6)	0.8366 (4)	0.059 (4)
C(18)	0.2549 (8)	0.8235 (7)	0.8499 (5)	0.064 (5)
C(19)	0.2765 (7)	0.9169 (6)	0.9017 (6)	0.064 (5)
C(20)	0.3271 (7)	0.9335 (5)	0.9756 (5)	0.062 (4)

Molecule (6)

	x	y	z	U_{eq}
P(16)	0.1437 (2)	0.8223 (1)	0.4638 (1)	0.044 (1)
P(17)	−0.0704 (2)	0.8110 (2)	0.4964 (1)	0.054 (1)
P(18)	0.0799 (2)	0.7883 (1)	0.5874 (1)	0.046 (1)
N(16)	−0.0399 (5)	0.7936 (4)	0.5680 (3)	0.054 (3)
N(17)	0.1706 (5)	0.8006 (4)	0.5347 (3)	0.041 (3)
N(18)	0.0213 (5)	0.8192 (4)	0.4421 (3)	0.053 (3)
O(11)	0.2001 (4)	0.9145 (3)	0.4691 (3)	0.052 (2)
O(12)	0.2031 (4)	0.7575 (3)	0.3988 (3)	0.050 (2)
F(50)	0.0841 (4)	0.7049 (3)	0.6028 (3)	0.077 (3)
F(51)	0.1095 (4)	0.8506 (3)	0.6656 (2)	0.075 (2)
F(52)	−0.1621 (4)	0.7422 (4)	0.4543 (3)	0.088 (3)
F(53)	−0.1315 (4)	0.8895 (3)	0.5167 (3)	0.088 (3)
F(54)	0.4155 (4)	0.7844 (3)	0.3768 (3)	0.077 (3)
F(55)	0.3865 (4)	0.8252 (3)	0.2832 (3)	0.085 (3)
F(56)	0.4683 (4)	0.9518 (4)	0.4109 (3)	0.092 (3)
F(57)	0.3101 (4)	0.9646 (3)	0.3676 (3)	0.085 (3)
C(21)	0.2372 (6)	0.7776 (5)	0.3353 (4)	0.049 (4)
C(22)	0.3495 (7)	0.8260 (6)	0.3500 (4)	0.052 (4)
C(23)	0.3618 (7)	0.9199 (6)	0.4019 (5)	0.058 (5)
C(24)	0.3170 (7)	0.9344 (5)	0.4774 (4)	0.054 (4)

Table 3. *Bond lengths (Å) and angles (°)*

Molecule(1)

P(1)—N(2)	1.578 (6)	P(1)—N(1)	1.571 (6)
P(1)—O(2)	1.576 (5)	P(1)—O(1)	1.576 (6)
P(2)—N(3)	1.564 (7)	P(2)—N(2)	1.542 (7)
P(2)—F(2)	1.528 (6)	P(2)—F(1)	1.511 (5)
P(3)—N(3)	1.565 (6)	P(3)—N(1)	1.545 (6)
P(3)—F(4)	1.503 (4)	P(3)—F(3)	1.522 (6)
O(2)—C(1)	1.416 (9)	O(1)—C(4)	1.448 (10)
F(6)—C(2)	1.362 (9)	F(5)—C(2)	1.354 (9)
F(8)—C(3)	1.341 (10)	F(7)—C(3)	1.378 (11)
C(2)—C(3)	1.529 (14)	C(1)—C(2)	1.491 (14)
		C(3)—C(4)	1.499 (11)

Molecule (2)

P(4)—N(6)	1.577 (8)	P(4)—N(5)	1.574 (6)
P(4)—O(4)	1.589 (4)	P(4)—O(3)	1.565 (5)
P(5)—N(5)	1.553 (6)	P(5)—N(4)	1.573 (8)
P(5)—F(11)	1.511 (5)	P(5)—F(10)	1.519 (6)
P(6)—N(6)	1.554 (7)	P(6)—N(4)	1.543 (7)
P(6)—F(14)	1.531 (8)	P(6)—F(12)	1.488 (5)
O(4)—C(8)	1.441 (9)	O(3)—C(5)	1.443 (11)
F(15)—C(6)	1.341 (9)	F(13)—C(6)	1.351 (10)

Table 3 (*cont.*)

F(17)—C(7)	1.333 (9)	F(16)—C(7)	1.365 (9)
C(6)—C(7)	1.528 (10)	C(5)—C(6)	1.522 (11)
		C(7)—C(8)	1.478 (13)

Molecule (3)

P(7)—N(9)	1.552 (8)	P(7)—N(8)	1.571 (6)
P(7)—O(6)	1.579 (4)	P(7)—O(5)	1.575 (6)
P(8)—N(8)	1.550 (7)	P(8)—N(7)	1.570 (8)
P(8)—F(21)	1.518 (5)	P(8)—F(20)	1.520 (6)
P(9)—N(9)	1.554 (7)	P(9)—N(7)	1.542 (7)
P(9)—F(23)	1.483 (6)	P(9)—F(22)	1.528 (9)
O(6)—C(10)	1.426 (8)	O(5)—C(9)	1.446 (11)
F(25)—C(11)	1.340 (8)	F(24)—C(11)	1.356 (9)
F(27)—C(12)	1.339 (9)	F(26)—C(12)	1.360 (11)
C(10)—C(11)	1.474 (13)	C(9)—C(12)	1.486 (10)
		C(11)—C(12)	1.536 (10)

Molecule (4)

P(10)—N(11)	1.561 (7)	P(10)—N(10)	1.571 (6)
P(10)—O(8)	1.579 (5)	P(10)—O(7)	1.570 (6)
P(11)—N(12)	1.570 (7)	P(11)—N(10)	1.561 (6)
P(11)—F(31)	1.528 (4)	P(11)—F(30)	1.523 (6)
P(12)—N(12)	1.555 (6)	P(12)—N(11)	1.557 (7)
P(12)—F(33)	1.516 (4)	P(12)—F(32)	1.512 (7)
O(8)—C(15)	1.426 (10)	O(7)—C(16)	1.427 (10)
F(35)—C(13)	1.338 (10)	F(34)—C(13)	1.359 (12)
F(37)—C(14)	1.344 (10)	F(36)—C(14)	1.351 (12)
C(13)—C(16)	1.519 (14)	C(13)—C(14)	1.511 (16)
		C(14)—C(15)	1.515 (15)

Molecule (5)

P(13)—N(15)	1.583 (6)	P(13)—N(13)	1.566 (7)
P(13)—O(10)	1.584 (6)	P(13)—O(9)	1.573 (5)
P(14)—N(15)	1.553 (7)	P(14)—N(14)	1.563 (8)
P(14)—F(41)	1.513 (5)	P(14)—F(40)	1.519 (5)
P(15)—N(14)	1.553 (7)	P(15)—N(13)	1.567 (5)
P(15)—F(43)	1.516 (5)	P(15)—F(42)	1.519 (7)
O(10)—C(20)	1.435 (10)	O(9)—C(17)	1.414 (11)
F(45)—C(18)	1.360 (11)	F(44)—C(18)	1.344 (12)
F(47)—C(19)	1.361 (13)	F(46)—C(19)	1.364 (11)
C(18)—C(19)	1.513 (13)	C(17)—C(18)	1.500 (14)
		C(19)—C(20)	1.476 (14)

Molecule (6)

P(16)—N(18)	1.563 (6)	P(16)—N(17)	1.572 (7)
P(16)—O(12)	1.591 (5)	P(16)—O(11)	1.568 (6)
P(17)—N(18)	1.569 (7)	P(17)—N(16)	1.559 (8)
P(17)—F(53)	1.519 (6)	P(17)—F(52)	1.513 (5)
P(18)—N(17)	1.556 (6)	P(18)—N(16)	1.551 (7)
P(18)—F(51)	1.516 (4)	P(18)—F(50)	1.518 (6)
O(12)—C(21)	1.424 (10)	O(11)—C(24)	1.441 (9)
F(55)—C(22)	1.361 (10)	F(54)—C(22)	1.340 (12)
F(57)—C(23)	1.361 (13)	F(56)—C(23)	1.347 (10)
C(22)—C(23)	1.519 (12)	C(21)—C(22)	1.493 (11)
		C(23)—C(24)	1.507 (12)

Molecule (1)

N(1)—P(1)—O(1)	104.4 (3)	N(1)—P(1)—N(2)	116.5 (3)
N(1)—P(1)—O(2)	113.0 (3)	N(2)—P(1)—O(1)	112.5 (4)
O(1)—P(1)—O(2)	104.2 (3)	N(2)—P(1)—O(2)	105.7 (3)
N(2)—P(2)—F(1)	109.4 (4)	N(2)—P(2)—N(3)	119.7 (3)
N(2)—P(2)—F(2)	110.3 (3)	N(3)—P(2)—F(1)	108.4 (3)
F(1)—P(2)—F(2)	97.7 (3)	N(3)—P(2)—F(2)	109.0 (4)
N(1)—P(3)—F(3)	109.9 (3)	N(1)—P(3)—N(3)	119.1 (3)
N(1)—P(3)—F(4)	110.6 (3)	N(3)—P(3)—F(3)	108.7 (4)
F(3)—P(3)—F(4)	98.2 (3)	N(3)—P(3)—F(4)	108.3 (3)
P(1)—N(2)—P(2)	121.8 (4)	P(1)—N(1)—P(3)	122.4 (4)
P(1)—O(1)—C(4)	122.6 (5)	P(2)—N(3)—P(3)	120.0 (4)
O(2)—C(1)—C(2)	109.2 (7)	P(1)—O(2)—C(1)	121.0 (4)
F(5)—C(2)—C(1)	109.5 (8)	F(5)—C(2)—F(6)	106.5 (6)
F(5)—C(2)—C(3)	107.2 (8)	F(6)—C(2)—C(1)	109.8 (8)
C(1)—C(2)—C(3)	116.3 (6)	F(6)—C(2)—C(3)	107.1 (8)
F(7)—C(3)—C(2)	108.3 (6)	F(7)—C(3)—F(8)	107.0 (8)
F(7)—C(3)—C(4)	106.0 (8)	F(8)—C(3)—C(2)	107.7 (7)
C(2)—C(3)—C(4)	117.1 (8)	F(8)—C(3)—C(4)	110.4 (6)
		O(1)—C(4)—C(3)	108.1 (7)

Table 3 (cont.)

Molecule (2)

N(5)—P(4)—O(3)	112.3 (4)	N(5)—P(4)—N(6)	117.0 (3)
N(5)—P(4)—O(4)	105.2 (3)	N(6)—P(4)—O(3)	105.9 (3)
O(3)—P(4)—O(4)	104.2 (3)	N(6)—P(4)—O(4)	111.5 (3)
N(4)—P(5)—F(10)	108.5 (3)	N(4)—P(5)—N(5)	119.6 (4)
N(4)—P(5)—F(11)	108.8 (4)	N(5)—P(5)—F(10)	110.5 (4)
F(10)—P(5)—F(11)	97.7 (3)	N(5)—P(5)—F(11)	109.5 (3)
N(4)—P(6)—F(12)	108.2 (3)	N(4)—P(6)—N(6)	120.1 (4)
N(4)—P(6)—F(14)	108.9 (4)	N(6)—P(6)—F(12)	110.5 (3)
F(12)—P(6)—F(14)	98.4 (4)	N(6)—P(6)—F(14)	108.6 (4)
P(4)—N(5)—P(5)	121.3 (4)	P(5)—N(4)—P(6)	119.8 (4)
P(4)—O(3)—C(5)	120.3 (4)	P(4)—N(6)—P(6)	121.7 (4)
O(3)—C(5)—C(6)	108.3 (7)	P(4)—O(4)—C(8)	120.3 (4)
F(13)—C(6)—C(5)	106.7 (7)	F(13)—C(6)—F(15)	106.9 (6)
F(13)—C(6)—C(7)	109.0 (6)	F(15)—C(6)—C(5)	110.0 (6)
C(5)—C(6)—C(7)	116.2 (6)	F(15)—C(6)—C(7)	107.7 (7)
F(16)—C(7)—C(6)	106.6 (7)	F(16)—C(7)—F(17)	107.1 (6)
F(16)—C(7)—C(8)	109.4 (6)	F(17)—C(7)—C(6)	108.1 (6)
C(6)—C(7)—C(8)	116.4 (6)	F(17)—C(7)—C(8)	108.8 (7)
		O(4)—C(8)—C(7)	110.4 (7)

Molecule (3)

N(8)—P(7)—O(5)	112.2 (4)	N(8)—P(7)—N(9)	116.2 (4)
N(8)—P(7)—O(6)	105.3 (3)	N(9)—P(7)—O(5)	106.0 (3)
O(5)—P(7)—O(6)	104.6 (3)	N(9)—P(7)—O(6)	112.0 (3)
N(7)—P(8)—F(20)	108.3 (4)	N(7)—P(8)—N(8)	119.5 (4)
N(7)—P(8)—F(21)	109.2 (3)	N(8)—P(8)—F(20)	109.4 (3)
F(20)—P(8)—F(21)	97.8 (3)	N(8)—P(8)—F(21)	110.5 (4)
N(7)—P(9)—F(22)	108.5 (4)	N(7)—P(9)—N(9)	119.3 (4)
N(7)—P(9)—F(23)	108.3 (3)	N(9)—P(9)—F(22)	109.0 (4)
F(22)—P(9)—F(23)	98.2 (4)	N(9)—P(9)—F(23)	111.5 (4)
P(7)—N(8)—P(8)	121.9 (4)	P(8)—N(7)—P(9)	119.7 (5)
P(7)—O(5)—C(9)	120.3 (4)	P(7)—N(9)—P(9)	123.1 (4)
O(5)—C(9)—C(12)	108.9 (7)	P(7)—O(6)—C(10)	121.0 (4)
F(24)—C(11)—F(25)	106.4 (6)	O(6)—C(10)—C(11)	110.6 (6)
F(25)—C(11)—C(10)	109.7 (7)	F(24)—C(11)—C(10)	109.4 (6)
F(25)—C(11)—C(12)	108.3 (7)	F(24)—C(11)—C(12)	106.4 (7)
F(26)—C(12)—F(27)	106.6 (7)	C(10)—C(11)—C(12)	116.1 (6)
F(27)—C(12)—C(9)	111.0 (6)	F(26)—C(12)—C(9)	107.2 (7)
F(27)—C(12)—C(11)	107.3 (6)	F(26)—C(12)—C(11)	107.7 (6)
		C(9)—C(12)—C(11)	116.6 (7)

Molecule (4)

N(10)—P(10)—O(7)	112.9 (4)	N(10)—P(10)—N(11)	117.2 (3)
N(10)—P(10)—O(8)	104.6 (3)	N(11)—P(10)—O(7)	104.8 (3)
O(7)—P(10)—O(8)	104.1 (3)	N(11)—P(10)—O(8)	112.6 (4)
N(10)—P(11)—F(30)	109.9 (4)	N(10)—P(11)—N(12)	119.6 (3)
N(10)—P(11)—F(31)	109.0 (3)	N(12)—P(11)—F(30)	109.7 (3)
F(30)—P(11)—F(31)	97.9 (3)	N(12)—P(11)—F(31)	108.7 (3)
N(11)—P(12)—F(32)	110.0 (4)	N(11)—P(12)—N(12)	119.1 (4)
N(11)—P(12)—F(33)	109.8 (3)	N(12)—P(12)—F(32)	108.0 (4)
F(32)—P(12)—F(33)	99.0 (3)	N(12)—P(12)—F(33)	109.1 (3)
P(10)—N(11)—P(12)	122.5 (4)	P(10)—N(10)—P(11)	121.3 (4)
P(10)—O(7)—C(16)	123.5 (4)	P(11)—N(12)—P(12)	120.1 (4)
F(34)—C(13)—F(35)	107.7 (8)	P(10)—O(8)—C(15)	119.8 (4)
F(35)—C(13)—C(14)	108.0 (9)	F(34)—C(13)—C(14)	107.9 (7)
F(35)—C(13)—C(16)	109.9 (7)	F(34)—C(13)—C(16)	106.3 (9)
F(36)—C(14)—F(37)	107.7 (7)	C(14)—C(13)—C(16)	116.6 (8)
F(37)—C(14)—C(13)	108.1 (9)	F(36)—C(14)—C(13)	107.8 (8)
F(37)—C(14)—C(15)	109.6 (7)	F(36)—C(14)—C(15)	108.2 (9)
O(8)—C(15)—C(14)	109.4 (8)	C(13)—C(14)—C(15)	115.2 (7)
		O(7)—C(16)—C(13)	108.6 (8)

Molecule (5)

N(13)—P(13)—O(9)	105.4 (3)	N(13)—P(13)—N(15)	117.6 (4)
N(13)—P(13)—O(10)	112.0 (3)	N(15)—P(13)—O(9)	111.6 (3)
O(9)—P(13)—O(10)	103.9 (3)	N(15)—P(13)—O(10)	105.6 (4)
N(14)—P(14)—F(40)	109.9 (3)	N(14)—P(14)—N(15)	119.8 (4)
N(14)—P(14)—F(41)	109.0 (4)	N(15)—P(14)—F(40)	109.1 (4)
F(40)—P(14)—F(41)	97.9 (3)	N(15)—P(14)—F(41)	109.0 (3)
N(13)—P(15)—F(42)	110.1 (3)	N(13)—P(15)—N(14)	119.4 (4)
N(13)—P(15)—F(43)	110.0 (3)	N(14)—P(15)—F(42)	108.7 (4)
F(42)—P(15)—F(43)	98.7 (3)	N(14)—P(15)—F(43)	107.9 (3)
P(14)—N(14)—P(15)	120.4 (5)	P(13)—N(15)—P(14)	121.2 (4)
P(13)—O(9)—C(17)	122.2 (5)	P(13)—N(15)—P(14)	121.1 (5)
O(9)—C(17)—C(18)	109.8 (7)	P(13)—O(10)—C(20)	119.9 (5)

Molecule (6) *(continued in right column)*

Table 3 (cont.)

F(44)—C(18)—C(17)	109.4 (9)	F(44)—C(18)—F(45)	106.6 (7)
F(44)—C(18)—C(19)	106.8 (7)	F(45)—C(18)—C(17)	107.9 (7)
C(17)—C(18)—C(19)	116.8 (7)	F(45)—C(18)—C(19)	108.8 (9)
F(46)—C(19)—C(18)	108.5 (7)	F(46)—C(19)—F(47)	106.3 (9)
F(46)—C(19)—C(20)	108.1 (7)	F(47)—C(19)—C(18)	107.1 (8)
C(18)—C(19)—C(20)	117.5 (10)	F(47)—C(19)—C(20)	108.9 (7)
		O(10)—C(20)—C(19)	109.5 (7)

Molecule (6)

N(17)—P(16)—O(11)	111.9 (3)	N(17)—P(16)—N(18)	117.9 (4)
N(17)—P(16)—O(12)	105.1 (3)	N(18)—P(16)—O(11)	105.8 (4)
O(11)—P(16)—O(12)	103.9 (3)	N(18)—P(16)—O(12)	111.5 (3)
N(16)—P(17)—F(52)	108.3 (4)	N(16)—P(17)—N(18)	119.0 (4)
N(16)—P(17)—F(53)	109.5 (3)	N(18)—P(17)—F(52)	109.5 (3)
F(52)—P(17)—F(53)	98.6 (3)	N(18)—P(17)—F(53)	109.9 (4)
N(16)—P(18)—F(50)	108.6 (3)	N(16)—P(18)—N(17)	119.5 (4)
N(16)—P(18)—F(51)	108.5 (3)	N(17)—P(18)—F(50)	110.8 (3)
F(50)—P(18)—F(51)	97.2 (3)	N(17)—P(18)—F(51)	109.9 (3)
P(16)—N(17)—P(18)	121.1 (4)	P(17)—N(16)—P(18)	120.8 (4)
P(16)—O(11)—C(24)	120.1 (5)	P(16)—N(18)—P(17)	120.9 (5)
O(12)—C(21)—C(22)	109.8 (6)	P(16)—O(12)—C(21)	122.0 (5)
F(54)—C(22)—C(21)	110.2 (8)	F(54)—C(22)—F(55)	107.3 (7)
F(54)—C(22)—C(23)	107.6 (7)	F(55)—C(22)—C(21)	106.6 (6)
C(21)—C(22)—C(23)	117.0 (7)	F(55)—C(22)—C(23)	107.7 (8)
F(56)—C(23)—C(22)	108.7 (7)	F(56)—C(23)—F(57)	108.1 (8)
F(56)—C(23)—C(24)	108.3 (6)	F(57)—C(23)—C(22)	106.9 (7)
C(22)—C(23)—C(24)	115.4 (8)	F(57)—C(23)—C(24)	109.2 (7)
		O(11)—C(24)—C(23)	108.6 (6)

3. Structure description

The structure contains six crystallographically inequivalent, but structurally equivalent, molecules. This can be seen in Fig. 2, where superpositions of the molecular geometries of the most similar pair and the most dissimilar pair are shown. These were prepared by the routine *OFIT* in *SHELXTL-Plus* (Sheldrick, 1991). The two most similar molecules were (1) [containing P(1)] and (4) [containing P(10)], in which the average r.m.s. deviation of the non-H atoms is 0.0615 Å. The worst fit was between molecules (5) and (6) [containing P(13) and P(16), respectively], where the average r.m.s. deviation is 0.2711 Å. The P_3N_3 ring in each molecule is essentially planar, with maximum deviations from each plane ranging from 0.035 to 0.053 Å from the six molecules. The seven-membered PO_2C_4 rings assume
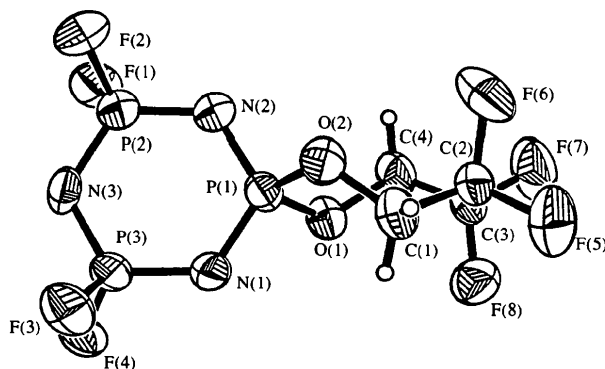

Fig. 1. Thermal ellipsoid plot of one of the six crystallographic molecules in the β-phase; probability ellipsoids are at the $X\%$ level.

a twisted, all *gauche*, conformation, as can be seen in Fig. 1 for one of the molecules. Bond distances and angles in the six molecules are essentially identical and no significant differences exist among them. For example, the average P—N bond distances are 1.562 Å for all molecules, within the range 1.557–1.564 Å for individual molecules. Individual P—O bond lengths range from 1.542 to 1.591 Å. The twist in the seven-membered ring gives a sense of chirality to the individual molecules, although the overall structure is racemic due to the presence of the centrosymmetric nature of the structure. It is this chirality that plays a central role in defining the rather unusual nature of this crystal structure. For the purpose of subsequent discussion we define p and n isomers (Diagram I), depending on the sign of the O—P—O—C dihedral angle (p = positive, n = negative).

Examination of the structure reveals that the molecules lie in planes parallel to the ac plane, as seen in Fig. 3. In addition, the planes of each of the P_3N_3 groups lie approximately parallel to that plane also. Some tilting

of the P_3N_3 groups does exist, creating a washboard effect when the P_3N_3 rings are examined. The sense of pleating that leads to the washboard effect is different in the two layers. For the layers at $y = \frac{1}{6}$ (and $\frac{5}{6}$) the pleating is parallel to c (Fig. 3a), while for the layers at $y = \frac{1}{2}$ the pleating is parallel to a (Fig. 3b). The layer at $y = \frac{1}{6}$ (and the equivalent layer at $y = \frac{5}{6}$) contains four independent molecules. No crystallographic symmetry elements (except for unit-cell translations) exist in this layer. In contrast, the layer at $y = \frac{1}{2}$ contains only two independent molecules due to the existence of inversion symmetry elements.

The arrangement of the molecules in these two layers is almost identical, as can be seen in Figs. 4(a) and (b), except for a relative translation that occurs between the two layers. A subtle difference does exist when the chirality of the molecules is considered. To demonstrate this difference, it is convenient to examine the herringbone packing of molecules contained between the dashed lines in Figs. 4(a) and (b). In the layers at $y = \frac{1}{2}$, all molecules in a given herringbone arrangement have the same chirality. In contrast, for the layers at $y = \frac{1}{6}$ the chirality of the molecules alternates as one proceeds along the herringbone.

It is instructive to consider the local (noncrystallographic) symmetry of the two types of layers. The chirality of the molecules plays an important role in determining this symmetry. For the $y = \frac{1}{6}$ layers, the herringbone structure defines
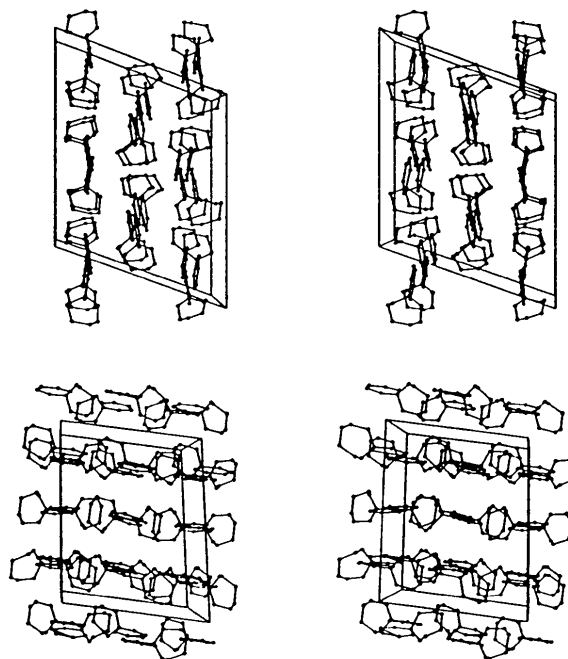

Fig. 2. Stick diagrams illustrating the superposition of: (a) the two most similar molecules, molecules (1) (solid lines) and (4) (dashed lines), and (b) the two least similar molecules, molecules (5) (solid lines) and (6) (dashed lines).

Diagram I.

Fig. 3. Stereographic packing diagrams, illustrating the layering of the molecules. As viewed: (a) the c direction, with b vertical; (b) the a direction, with c vertical.

an *a*-glide-type symmetry element parallel to **c**. Adjacent herringbone structures are related to a *c*-glide symmetry element parallel to **a**. Each of these layers thus has approximate *pc2a* slab-group symmetry. In contrast, the herringbone structures in the $y = \frac{1}{2}$ layers have a 2_1-type screw axis parallel to **a**. Adjacent herringbone structures retain the *c*-glide relationship. Thus, these layers have $p2_1/c11$ slab-group symmetry. The existence of the glide planes perpendicular to **a** in both layers requires that the β angle be 90°, as observed experimentally. (The γ angle does not have to be 90°, since there is no noncrystallographic symmetry element relating adjacent layers in the **b** direction.)

3.1. *Stacking of layers*

The layers stack in the **b** direction with an ...*ABAABA*... repeat pattern, where *A* represents the *pc2a* layer and *B* the $p2_1/c11$ layer. We select within each layer a common reference point which brings adjacent layers into juxtaposition. For convenience, we choose these to be coincident with the pseudotwofold axis in the *A* layer and with the center of inversion in the *B* layer. These points are labeled with an asterisk in Figs. 4(*a*)–(*d*). The relative displacements of adjacent layers can then be represented by translation vectors $T_{ij} = (\Delta a, \Delta b, \Delta c)$, where *i* and *j* specify the layer types. In this notation, the observed structure is characterized by the relations

(a)

(b)

(c)

(d)
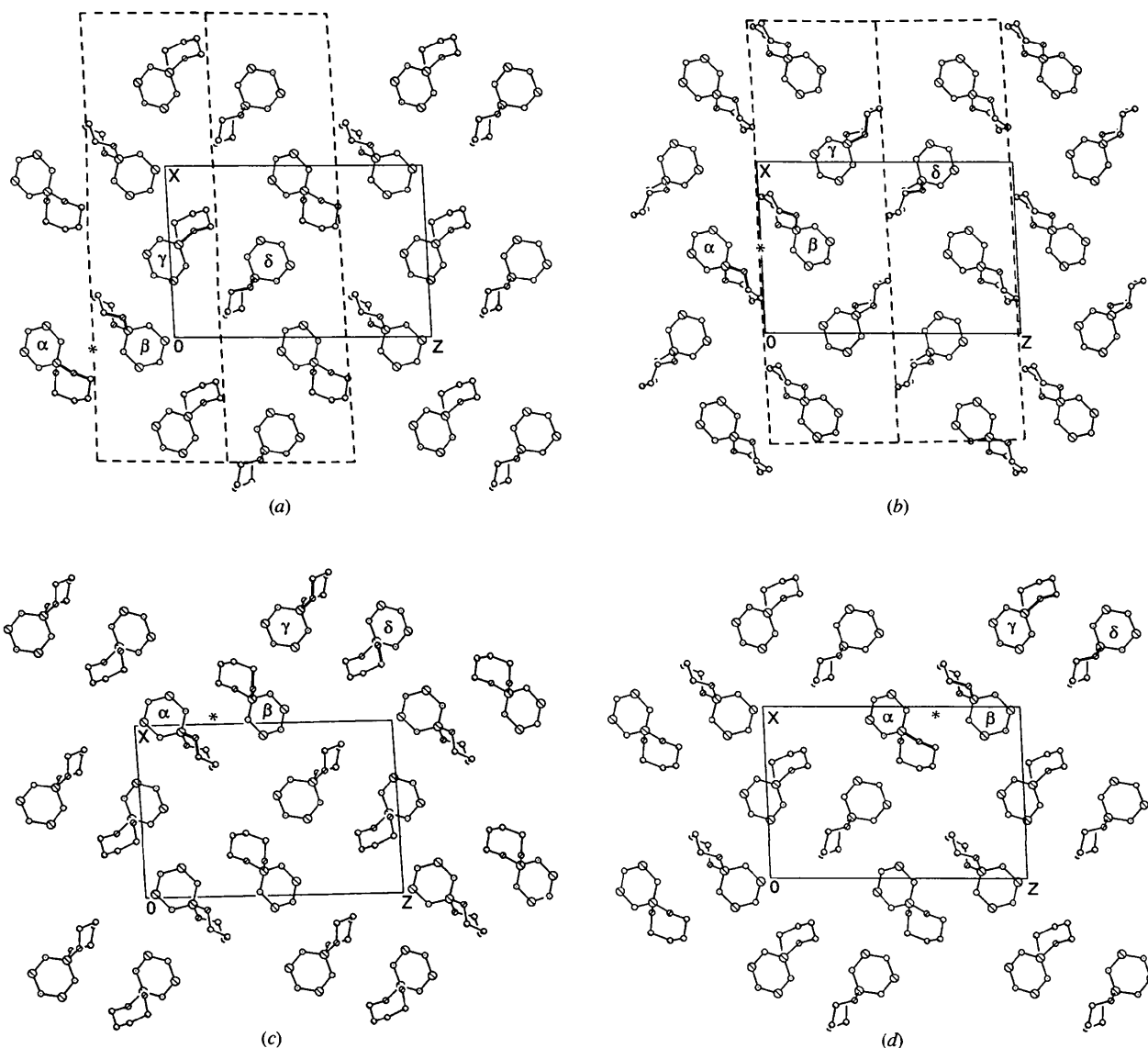
Fig. 4. Illustration of the molecular arrangements in the layers at: (*a*) $y = \frac{1}{6}$, (*b*) $y = \frac{1}{2}$, (*c*) $y = \frac{5}{6}$ and (*d*) $y = \frac{7}{6}$. The vertical dashed lines delineate the herringbone structural features running parallel to **b**.

$$T_{AB} = T_{BA} = (\tfrac{1}{2},\tfrac{1}{3},\tfrac{1}{3}) \qquad (1)$$

and

$$T_{AA} = (0,\tfrac{1}{3},\tfrac{1}{3}). \qquad (2)$$

This leads to two distinct types of stacking of molecules between adjacent layers. In the *AB*-type stacking (Fig. 5*a*), two different arrangements are observed. In one arrangement (type *a*), the seven-membered rings lie almost on top of one another and the inorganic rings avoid each other. Ignoring chirality of the seven-membered rings, the two molecules are related by a pseudotwofold screw axis (perpendicular to the *ac* plane). In the second stacking arrangement (type *b*) the molecules are related by a pseudoglide plane (perpendicular to the *c* axis) and the inorganic rings lie almost on top of each other.

(a)

(b)
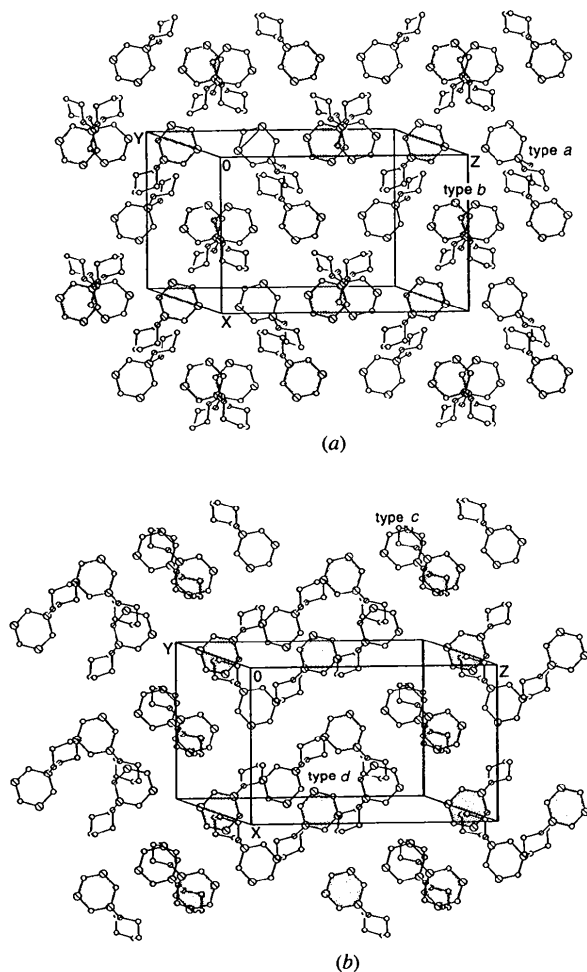
Fig. 5. Illustrations of the stacking of the adjacent layers: (*a*) layers at $y = \tfrac{1}{6}$ and $y = \tfrac{1}{2}$ (*AB*-type stacking); (*b*) layers at $y = \tfrac{5}{6}$ and $y = \tfrac{7}{6}$ (*AA*-type stacking). The P_3N_3 rings for the molecules of the lower layer are crosshatched for clarity.

The arrangement associated with the *AA* stacking is much more complicated. For one stacking pair (type *c*), the seven-membered ring lies directly over the inorganic ring. Again, the two molecules are related by a pseudotwofold screw axis. The other six molecules (three from each layer) define a six-membered ring (type *d*) with the seven-membered ring abutting the organic ring on an adjacent molecule.

3.2. *Modulated structure description*

The results of these stacking sequences is that the chirality of the molecules is modulated between layers. Referring to Fig. 4, the modulation of the chirality in the four molecular sites, labeled α, β, γ and δ, is given by the sequences

$$\alpha : n,p,p$$
$$\beta : n,n,p$$
$$\gamma : p,n,n$$
$$\delta : p,p,n. \qquad (3)$$

The modulation waves that can lead to the sequences of modulation are shown in Fig. 6. The wavevector is given by $\mathbf{k} = (\tfrac{1}{3},0,0)$ in the unmodulated structure, but the relative phases are different for the four molecules. The modulation wave for each site is represented in Fig. 6.

4. Comparison with the α-phase

The crystal structure of the α-phase has been reported separately (Elias, Kirchmeier & Shreeve, 1994). The two structures have many common features. The molecules in the two phases have almost identical geometry, as shown by the overlapping stick models in Fig. 7. The
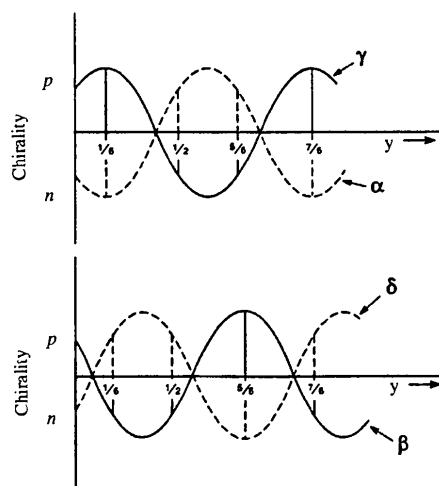

Fig. 6. Schematic diagram illustrating modulation of the chirality of the four molecular sites (α, β, γ, δ) identified in Fig. 4.
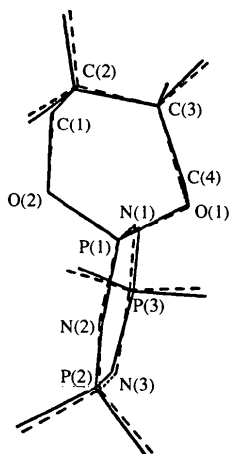
Fig. 7. Stick diagram illustrating the superposition of molecule (1) of the β-phase (dashed lines) with the molecule in the α-phase (solid lines).
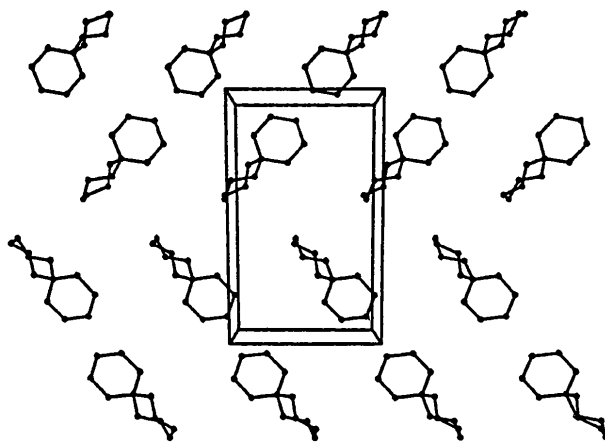

Fig. 8. Arrangement of layers in the α-phase as viewed from the b direction. The origin is at the upper left corner with a vertical and c horizontal.

Fig. 9. Stacking of adjacent layers in the α-phase.

for the β-phase. There is a much smaller average interlayer spacing for the α-phase (4.68 Å) *versus* the β-phase (5.143 Å).

5. Conclusions

The compound C₄H₄F₈N₃O₂P₃ has been shown to exist in two crystalline phases: a normal monoclinic (α-phase) structure and a polytypic triclinic (β-phase) structure. No simple structural relation exists between these two phases. In the β-phase modulation of the basic a′ translational vector occurs, as well as modulation of the chirality of the molecules.

In the β-phase the molecules lie in layers in the *ab* plane and it is convenient to describe the structure in terms of these layers. Two distinct types of layers are observed. Both show idealized monoclinic slab-layer symmetry. Modulation of the chirality of the molecules in different layers is so severe that the *a* glide plane perpendicular to *c* in one layer type is transformed into a 2₁ screw axis parallel to *a* in the other layer type. However, the observed ... *ABAABA* ... stacking pattern reduces the symmetry to P1.

A search for other possible phases has not been made at this time.

molecules in the α-phase also lie in layers, this time lying parallel to the *ab* plane. Again, the P₃N₃ rings lie roughly in this plane. As seen in Fig. 8, however, the arrangement within each layer is much simpler, as is the stacking between layers (Fig. 9). Comparison with the corresponding diagrams for the β-phase reveals that there is no simple structural relation between these two crystal structures. Within each layer of the α-phase, the inorganic rings lay head-to-head (defining the seven-membered ring as the tail) and stacking occurs such that the inorganic rings almost overlap. This is in contrast to the much more complicated stacking patterns observed
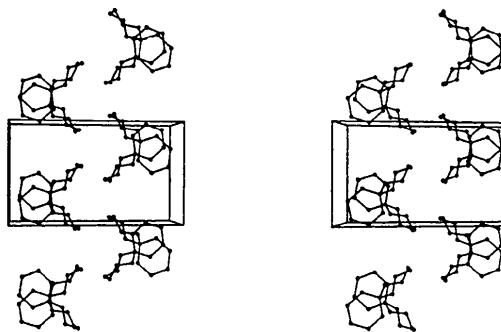
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