research paper

Acta Cryst C STRUCTURAL CHEMISTRY

ISSN 2053-2296

Chiral one-dimensional hydrogen-bonded architectures constructed from single-enantiomer phosphoric triamides

Mahsa Eghbali Toularoud,[a] Mehrdad Pourayoubi,[a]* Michal Dušek,[b] Václav Eigner[b] and Krishnan Damodaran[c]

[a]Department of Chemistry, Faculty of Science, Ferdowsi University of Mashhad, Mashhad, Iran, [b]Institute of Physics of the Czech Academy of Sciences, Na Slovance 2, 182 21 Prague 8, Czech Republic, and [c]Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260, USA. *Correspondence e-mail: pourayoubi@um.ac.ir

Received 27 November 2017
Accepted 22 March 2018

Edited by B. D. Santarsiero, University of Illinois at Chicago, USA

Keywords: phosphoric triamide; dextrorotation; levorotation; crystal structure; NMR spectroscopy; Hirshfeld surface analysis; circular dichroism.

CCDC references: 1831741; 1831740

Supporting information: this article has supporting information at journals.iucr.org/c

The two single-enantiomer phosphoric triamides *N*-(2,6-difluorobenzoyl)-*N*′,*N*″-bis[(*S*)-(−)-α-methylbenzyl]phosphoric triamide, [2,6-F_2-C_6H_3C(O)NH]-[(*S*)-(−)-(C_6H_5)CH(CH_3)NH]$_2$P(O), denoted **L-1**, and *N*-(2,6-difluorobenzoyl)-*N*′,*N*″-bis[(*R*)-(+)-α-methylbenzyl]phosphoric triamide, [2,6-F_2-C_6H_3C(O)NH]-[(*R*)-(+)-(C_6H_5)CH(CH_3)NH]$_2$P(O), denoted **D-1**, both $C_{23}H_{24}F_2N_3O_2P$, have been investigated. In their structures, chiral one-dimensional hydrogen-bonded architectures are formed along [100], mediated by relatively strong N—H···O(P) and N—H···O(C) hydrogen bonds. Both assemblies include the noncentrosymmetric graph-set motifs $R_2^2(10)$, $R_2^1(6)$ and $C_2^2(8)$, and the compounds crystallize in the chiral space group *P*1. Due to the data collection of **L-1** at 120 K and of **D-1** at 95 K, the unit-cell dimensions and volume show a slight difference; the contraction in the volume of **D-1** with respect to that in **L-1** is about 0.3%. The asymmetric units of both structures consist of two independent phosphoric triamide molecules, with the main difference being seen in one of the torsion angles in the OPNHCH(CH_3)(C_6H_5) part. The Hirshfeld surface maps of these levo and dextro isomers are very similar; however, they are near mirror images of each other. For both structures, the full fingerprint plot of each symmetry-independent molecule shows an almost asymmetric shape as a result of its different environment in the crystal packing. It is notable that NMR spectroscopy could distinguish between compounds **L-1** and **D-1** that have different relative stereocentres; however, the differences in chemical shifts between them were found to be about 0.02 to 0.001 ppm under calibrated temperature conditions. In each molecule, the two chiral parts are also different in NMR media, in which chemical shifts and P–H and P–C couplings have been studied.

1. Introduction

Chiral compounds are of great importance, not only because of their numerous potential applications in different domains of chemistry-based sciences or their predominance in biological systems, but also due to their attractive structural features and topologies (Prins *et al.*, 1999). Many research teams have devoted their efforts to the design and discovery of various chiral compounds with different functional groups, and the alteration of structural requirements to achieve desired properties, most typically in nonlinear optics (Gu *et al.*, 2016), circularly polarized light-emitting devices (Zinna *et al.*, 2015), enantioselective catalysts (Headley & Marsden, 2007; Hua *et al.*, 1987) or medicine (De Luca *et al.*, 2017).

Phosphoric triamides have found widespread use in organic synthesis (Li *et al.*, 2012), coordination chemistry (Saneei *et al.*, 2016) and biochemistry (Manunza *et al.*, 1999). Chiral

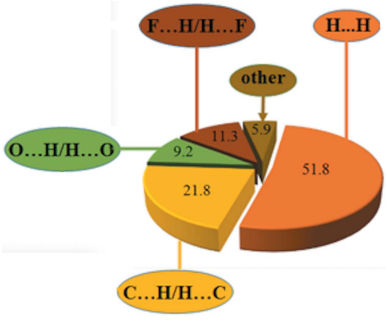
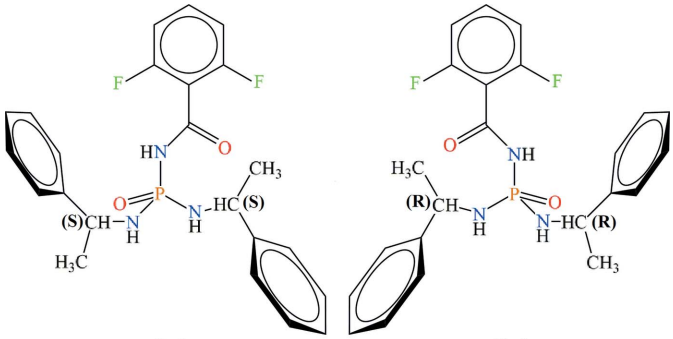


Table 1
Experimental details.

	L-1	D-1
Crystal data		
Chemical formula	$C_{23}H_{24}F_2N_3O_2P$	$C_{23}H_{24}F_2N_3O_2P$
M_r	443.4	443.4
Crystal system, space group	Triclinic, *P*1	Triclinic, *P*1
Temperature (K)	120	95
a, *b*, *c* (Å)	9.7608 (3), 10.6134 (3), 11.2721 (3)	9.7524 (2), 10.6117 (2), 11.2510 (2)
α, β, γ (°)	77.398 (2), 75.589 (2), 87.635 (2)	77.3381 (15), 75.6221 (16), 87.7313 (16)
V (Å^3)	1103.64 (6)	1100.33 (4)
Z	2	2
Radiation type	Cu *K*α	Cu *K*α
μ (mm^{-1})	1.47	1.46
Crystal size (mm)	0.53 × 0.19 × 0.08	0.29 × 0.09 × 0.07
Data collection		
Diffractometer	Agilent Xcalibur/Gemini ultra diffractometer with an AtlasS2 detector	Agilent SuperNova Dual Source diffractometer with an AtlasS2 detector
Absorption correction	Analytical (*CrysAlis PRO*; Rigaku OD, 2015)	Analytical (*CrysAlis PRO*; Rigaku OD, 2015)
T_{min}, T_{max}	0.562, 0.896	0.774, 0.917
No. of measured, independent and observed [$I > 3\sigma(I)$] reflections	21163, 7492, 6976	16006, 7660, 7383
R_{int}	0.051	0.034
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.598	0.607
Refinement		
$R[F^2 > 3\sigma(F^2)]$, $wR(F^2)$, *S*	0.047, 0.121, 1.71	0.039, 0.098, 1.50
No. of reflections	7492	7660
No. of parameters	578	578
No. of restraints	6	6
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.30, −0.31	0.17, −0.22
Absolute structure	3546 Friedel pairs used in the refinement	3604 Friedel pairs used in the refinement
Absolute structure parameter	0.014 (17)	−0.014 (14)

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *CrystalExplorer* (Wolff *et al.*, 2013), *JANA2006* (Version 24/09/2015; Petříček *et al.*, 2014), *SUPERFLIP* (Palatinus & Chapuis, 2007) and *MCE2005* (Rohlícek & Husák, 2007).

phosphoric triamides have been used as strong Lewis bases in asymmetric catalysis processes (Denmark & Stavenger, 2000; Buono *et al.*, 1999), as herbicides, plant-growth regulators (Diel & Maier, 1984) and insecticides (Reid & Marmor, 1978), and as moieties of nucleotides (Hah *et al.*, 1999).



L-1 **D-1**

In a series of recently published papers, crystal-engineering approaches have been used for the generating of 'empirical rules' for predicting the pattern of hydrogen bonding based on molecular structures (Pourayoubi *et al.*, 2014; Sabbaghi *et al.*, 2017). The structures of several new derivatives, determined by X-ray diffraction and archived in the Cambridge Structural Database (CSD; Groom *et al.*, 2016), were examined. These efforts included the study of both the molecular and crystal structure geometry (Pourayoubi *et al.*, 2012), and the patterns of intermolecular interactions (Pourayoubi *et al.*, 2014).

The crystal structures of chiral phosphoric triamides are absent in the CSD; therefore, we were interested in the synthesis and X-ray crystal structure analysis of chiral phosphoric triamide molecules in order to study the influence of chirality on the hydrogen-bond pattern. In a previous article, we reported the X-ray crystal structure of the first chiral $[RC(O)NH](R^1R^2N)_2P(O)$ phosphoric triamide, namely $[CCl_3C(O)NH][R\text{-}(+)(C_6H_5)CH(CH_3)NH]_2P(O)\cdot 0.25H_2O$ (Ariani *et al.*, 2017); however, an attempt to analyse its enantiomer by X-ray diffraction was unsuccessful.

It is noteworthy that single-enantiomer compounds with potential applications as ligands in coordination chemistry, such as phosphoric triamides, could be useful, since it would then be possible to design different metal-containing molecular assemblies. We report here the first pair of single-enantiomer phosphoric triamide structures, as levo- and dextrorotatory isomers, namely $[2,6\text{-}F_2\text{-}C_6H_3C(O)NH][(S)\text{-}(-)(C_6H_5)CH(CH_3)NH]_2P(O)$, denoted **L-1**, and $[2,6\text{-}F_2\text{-}C_6H_3C(O)NH][R\text{-}(+)(C_6H_5)CH(CH_3)NH]_2P(O)$, denoted **D-1** (see Scheme). The study is complemented by an investigation of the intermolecular interactions, incorporating a Hirshfeld surface-based analysis (Spackman & Jayatilaka, 2009). The

results of IR, MS, NMR and UV spectroscopic analyses, and circular dichroism (CD) are discussed.

2. Experimental

2.1. Synthesis and crystallization

2.1.1. Preparation of [2,6-F_2-$C_6H_3C(O)NH]Cl_2P(O)$. The phosphorus–chlorine reagent [2,6-F_2-$C_6H_3C(O)NH]Cl_2P(O)$ was synthesized according to a literature method (Tarahhomi *et al.*, 2013) from the reaction between phosphorus pentachloride (9.5 mmol) and 2,6-F_2-$C_6H_3C(O)NH_2$ (9.5 mmol) in dry CCl_4 (20 ml) at 348 K (about 3 h), followed by treatment with formic acid (85%, 9.5 mmol) at ice-bath temperature.

2.1.2. Preparation of L-1. For the preparation of **L-1**, a solution of (*S*)-(−)-α-methylbenzylamine (4.2 mmol) and triethylamine (4.2 mmol) in $CHCl_3$ (10 ml) was added to a solution of [2,6-F_2-$C_6H_3C(O)NH]Cl_2P(O)$ (2.1 mmol) in the same solvent (20 ml). After stirring at 273 K for 4 h, the solvent was evaporated in a vacuum and the solid obtained was washed with distilled water. Single crystals of **L-1**, suitable for X-ray crystallography, were obtained from a solution of the product in a mixture of CH_3OH and $CHCl_3$ (1:1 *v*/*v*) by slow evaporation at room temperature (yield > 60%).

Analytical data: m.p. 504 K. IR (KBr, ν, cm^{-1}): 3247, 3081, 3029, 1745, 1671, 1626, 1588, 1471, 1423, 1287, 1238, 1199, 1116, 1079, 1044, 1011, 974, 892, 857, 820, 787, 744, 698. ^{1}H NMR (601 MHz, DMSO-d_6): δ 9.80 (*s*, 1H), 7.50 (*tt*, *J* = 8.5, 6.6 Hz, 1H), 7.39–7.31 (*m*, 4H), 7.31–7.24 (*m*, 4H), 7.22–7.11 (*m*, 4H), 4.97 (*t*, *J* = 10.5 Hz, 1H), 4.88 (*t*, *J* = 10.0 Hz, 1H), 4.45–4.37 (*m*, 1H), 4.37–4.29 (*m*, 1H), 1.40 (*d*, *J* = 6.9 Hz, 3H), 1.38 (*d*, *J* = 6.8 Hz, 3H); ^{13}C NMR (151 MHz, DMSO-d_6): δ 161.65, 158.77 (*dd*, *J* = 249.1, 7.8 Hz), 146.24 (*d*, *J* = 5.5 Hz), 145.89 (*d*, *J* = 5.6 Hz), 131.84 (*t*, *J* = 19.2 Hz), 127.98, 127.97, 126.34, 126.31, 126.06, 125.96, 115.35 (*td*, *J* = 22.5, 8.4 Hz), 111.84 (*d*, *J* = 23.7 Hz), 50.03, 49.68, 25.48 (*d*, *J* = 5.3 Hz), 24.92 (*d*, *J* = 4.9 Hz); ^{31}P{^{1}H} NMR (243 MHz, DMSO-d_6): δ 3.75; ^{19}F NMR (565 MHz, DMSO-d_6): δ −113.50 (*t*, *J* = 7.2 Hz). MS (70 eV, EI): 443 (6) $[M]^+$, 338 (20) $[M - C_8H_9]^+$, 323 (5) $[M - C_8H_9NH]^+$, 302 (3) $[M - C_7H_3F_2O]^+$, 167 (6) $[C_8H_{10}NOP]^+$, 156 (10) $[C_7H_4F_2NO]^+$, 141 (38) $[C_7H_3F_2O]^+$, 120 (100) $[C_8H_{10}N]^+$, 105 (55) $[C_8H_9]^+$, 77 (17) $[C_6H_5]^+$. UV ($CHCl_3$): λ_{max} = 258 nm. $[\alpha]_D^{25}$ = −43.0 (*c* 0.004, MeOH). CD band: $\Delta\varepsilon_{max}$ = −21 (272 nm).

2.1.3. Preparation of D-1. Compound **D-1** was synthesized by a similar method to that used for the preparation of **L-1**, but using (*R*)-(+)-α-methylbenzylamine instead of (*S*)-(−)-α-methylbenzylamine (yield > 60%).

Analytical data: m.p. 504 K. IR (KBr, ν, cm^{-1}): 3248, 3082, 3029, 2970, 2919, 1744, 1672, 1626, 1591, 1470, 1432, 1286, 1235, 1199, 1116, 1079, 1044, 1011, 975, 892, 860, 820, 786, 748, 697. MS (70 eV, EI): 443 (6) $[M]^+$, 338 (21) $[M - C_8H_9]^+$, 323 (5) $[M - C_8H_9NH]^+$, 167 (7) $[C_8H_{10}NOP]^+$, 141 (39) $[C_7H_3F_2O]^+$, 120 (100) $[C_8H_{10}N]^+$, 105 (56) $[C_8H_9]^+$, 77 (16) $[C_6H_5]^+$. UV ($CHCl_3$): λ_{max} = 259 nm. $[\alpha]_D^{25}$ = 44.5 (*c* 0.004, MeOH). CD band: $\Delta\varepsilon_{max}$ = +20 (270 nm). Details of the NMR experiments are given in the supporting information.

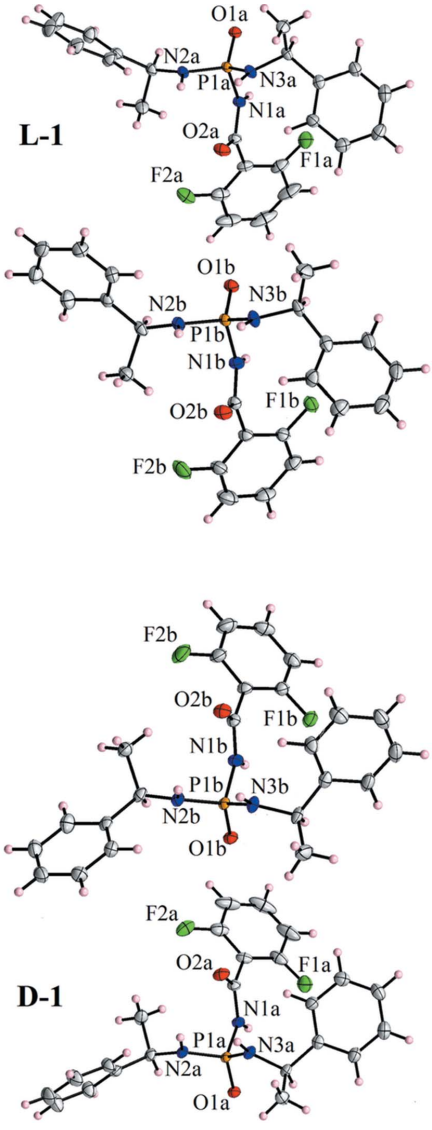


Figure 1
Displacement ellipsoid plots (50% probability) of the components of the asymmetric units of **L-1** and **D-1**, showing the atom-numbering schemes for non-H and non-C atoms. H atoms are drawn as spheres of arbitrary radii.

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. For **L-1** and **D-1**, all H atoms were discernible in difference Fourier maps and could be refined with reasonable geometries. According to common practice, H atoms bonded to C atoms were kept in ideal positions, with C—H = 0.96 Å, while the positions of H atoms on N atoms were refined freely. In both cases, U_{iso}(H) values were set at 1.2U_{eq}(C,N). All non-H atoms were refined using harmonic refinement.

3. Results and discussion

3.1. Description of the crystal structures

Both **L-1** and **D-1** crystallize in the chiral space group *P*1. The observed chirality can be understood in terms of chirality

transfer from the chiral phosphoric triamide molecule to the whole crystal packing. In the two structures, the unit-cell dimensions and volumes are slightly different, due to the fact that data collection was at different temperatures, *i.e.* 120 K for **L-1** and 95 K for **D-1**. We observed a contraction of about 0.3% in the volume of the unit cell measured at the lower temperature, as well as a contraction of the unit-cell dimensions *a*, *b* and *c*, with the most significant contraction (of about 0.19%) being in the *c* direction, $(c_{\mathbf{D\text{-}1}} - c_{\mathbf{L\text{-}1}})/c_{\mathbf{L\text{-}1}} \times 100$, where the weaker intermolecular contacts were observed. The Flack (1983) parameters of 0.014 (17) and −0.014 (14) for **L-1** and **D-1**, respectively, show that the absolute configurations, as assigned, are correct.

The asymmetric units of both structures consist of two symmetry-independent phosphoric triamide molecules (denoted with suffixes *a* and *b* hereafter). Fig. 1 shows the components of the asymmetric units of the two structures, with the atom-numbering schemes for the non-H and non-C atoms. The arrangement of the two molecules in the structure of **L-1** shows a near mirror-image relationship with respect to the molecules in the structure of **D-1**. The *a* and *b* molecules in each structure adopt similar conformations, which is apparent from the small differences in the torsion angles (see Tables 2 and 3). The most pronounced differences were observed in the pairs of torsion angles O1—P1—N3—C16, P1—N2—C8—C9 and P1—N2—C8—C10. On the other hand, the **L-1*a*** and **D-1*a*** molecules are very similar with regard to their bond lengths, angles and torsion angles; however, the torsion angles appear with opposite signs. For example, the P1*a*—N2*a*—C8*a*—C9*a* torsion angles in **L-1*a*** and **D-1*a*** are 88.4 (3) and −88.5 (2)°, respectively. In order to present the full-numbering scheme, molecule **D-1*a*** is shown as an example (Fig. 2). Furthermore, the spacefilling representation of two symmetry-independent molecules in the two structures is given, which shows that molecules specified with the same colours in two crystals are in a near mirror-image relationship with respect to each other (Fig. 3).

Selected geometric parameters and hydrogen-bond geometries for **L-1** and **D-1** are given in Tables 2–5. The P═O, P—N

Table 2
Selected geometric parameters (Å, °) for **L-1**.

	Molecule **L-1*a***	Molecule **L-1*b***
P1—O1	1.481 (2)	1.477 (2)
P1—N1	1.703 (2)	1.699 (3)
P1—N2	1.621 (2)	1.619 (3)
P1—N3	1.624 (2)	1.620 (2)
N1—C1	1.351 (4)	1.358 (4)
N2—C8	1.461 (3)	1.447 (3)
N3—C16	1.459 (4)	1.458 (4)
O1—P1—N1	103.50 (12)	103.20 (12)
O1—P1—N2	115.22 (11)	116.02 (11)
O1—P1—N3	115.23 (13)	116.30 (13)
N1—P1—N2	109.74 (13)	109.56 (14)
N1—P1—N3	109.45 (11)	109.49 (12)
N2—P1—N3	103.69 (12)	102.25 (12)
P1—N1—C1	124.0 (2)	126.2 (2)
P1—N2—C8	123.39 (19)	125.02 (19)
P1—N3—C16	123.52 (19)	123.6 (2)
P1—N2—C8—C9	88.4 (3)	100.4 (3)
P1—N3—C16—C17	117.7 (2)	121.6 (3)
O1—P1—N1—C1	−176.68 (19)	−178.4 (2)
O1—P1—N2—C8	51.6 (3)	55.9 (3)
O1—P1—N3—C16	−25.2 (3)	−41.6 (3)
P1—N1—C1—O2	−2.2 (3)	1.0 (3)
P1—N2—C8—C10	−147.5 (2)	−134.6 (2)
P1—N3—C16—C18	−117.2 (2)	−115.4 (2)

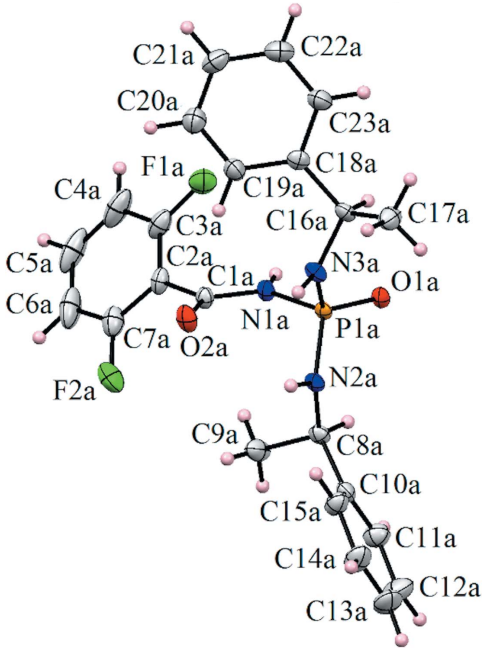


Figure 2
Displacement ellipsoid plot (50% probability) for one of the independent molecules (molecule *a*) of **D-1**, showing the atom-numbering scheme. H atoms are drawn as spheres of arbitrary radii.

Table 3
Selected geometric parameters (Å, °) for **D-1**.

	Molecule **D-1*a***	Molecule **D-1*b***
P1—O1	1.4808 (17)	1.4784 (17)
P1—N1	1.7081 (18)	1.6986 (19)
P1—N2	1.6219 (19)	1.618 (2)
P1—N3	1.6199 (17)	1.6181 (17)
N1—C1	1.355 (3)	1.367 (3)
N2—C8	1.469 (2)	1.459 (3)
N3—C16	1.463 (3)	1.460 (3)
O1—P1—N1	103.29 (9)	102.89 (9)
O1—P1—N2	115.49 (8)	116.28 (8)
O1—P1—N3	115.08 (10)	116.30 (10)
N1—P1—N2	109.87 (10)	109.74 (10)
N1—P1—N3	109.77 (8)	109.71 (9)
N2—P1—N3	103.37 (9)	101.94 (10)
P1—N1—C1	123.03 (15)	125.57 (16)
P1—N2—C8	122.96 (14)	124.36 (15)
P1—N3—C16	123.75 (16)	123.82 (16)
P1—N2—C8—C9	−88.5 (2)	−101.0 (2)
P1—N3—C16—C17	−117.68 (19)	−121.47 (19)
O1—P1—N1—C1	177.16 (16)	178.46 (17)
O1—P1—N2—C8	−51.78 (19)	−55.44 (19)
O1—P1—N3—C16	25.1 (2)	42.1 (2)
P1—N1—C1—O2	1.4 (3)	−1.2 (3)
P1—N2—C8—C10	147.93 (15)	134.66 (16)
P1—N3—C16—C18	116.90 (18)	115.40 (19)

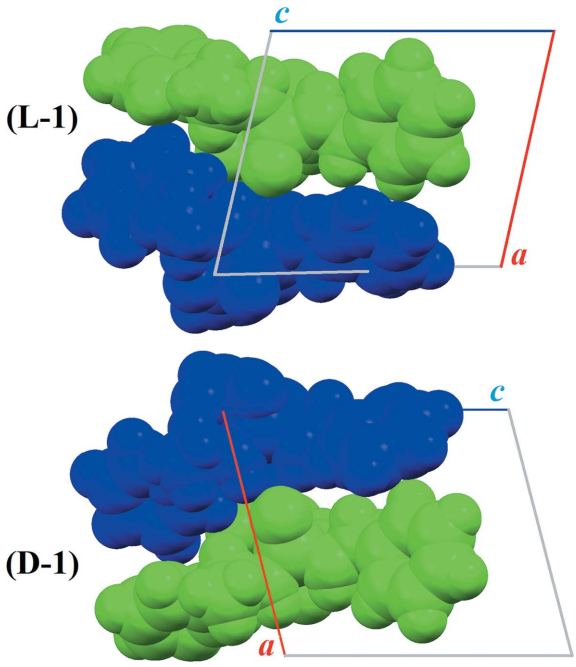


Figure 3
A spacefilling representation of the two symmetry-independent molecules in the structures of **L-1** and **D-1**.

Table 4
Hydrogen-bond geometry (Å, °) for **L-1**.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1*a*—H1n1*a*···O2*b*	0.86 (2)	2.019 (18)	2.874 (3)	172 (3)
N2*a*—H1n2*a*···O1*b*^{i}	0.860 (9)	2.111 (11)	2.919 (3)	156 (3)
N3*a*—H1n3*a*···O1*b*^{i}	0.86 (2)	2.12 (3)	2.942 (3)	160 (3)
N1*b*—H1n1*b*···O2*a*^{ii}	0.860 (17)	1.967 (15)	2.822 (3)	173 (3)
N2*b*—H1n2*b*···O1*a*	0.860 (14)	2.036 (13)	2.868 (3)	163 (3)
N3*b*—H1n3*b*···O1*a*	0.86 (2)	2.06 (3)	2.888 (3)	163 (3)
C5*a*—H1c5*a*···O1*a*^{iii}	0.96	2.35	3.278 (4)	162.01

Symmetry codes: (i) $x-1, y, z$; (ii) $x+1, y, z$; (iii) $x, y-1, z$.

Table 5
Hydrogen-bond geometry (Å, °) for **D-1**.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5*a*—H1c5*a*···O1*a*^{i}	0.96	2.34	3.271 (3)	162.23
N1*a*—H1n1*a*···O2*b*	0.862 (18)	2.006 (16)	2.863 (2)	173 (3)
N2*a*—H1n2*a*···O1*b*^{ii}	0.859 (12)	2.110 (12)	2.907 (2)	154 (3)
N3*a*—H1n3*a*···O1*b*^{ii}	0.861 (19)	2.13 (2)	2.938 (3)	155 (2)
N1*b*—H1n1*b*···O2*a*^{iii}	0.865 (16)	1.951 (14)	2.812 (2)	173 (2)
N2*b*—H1n2*b*···O1*a*	0.856 (10)	2.046 (13)	2.858 (2)	158 (3)
N3*b*—H1n3*b*···O1*a*	0.861 (17)	2.07 (2)	2.887 (3)	157 (2)

Symmetry codes: (i) $x, y+1, z$; (ii) $x+1, y, z$; (iii) $x-1, y, z$.

and C═O bond lengths are all within the ranges observed in analogous structures (Keikha *et al.*, 2016; Vahdani Alviri *et al.*, 2018). The P—N bond of the C(O)NHP(O) segment is longer than the other two P—N bonds. This is related to the interaction of the corresponding N atom with the C═O π system, which leads to a smaller C—N bond length in the C(O)NHP(O) segment with respect to the other two C—N bonds in each molecule. The P—N—C angles in isomers **L-1** and **D-1** [123.39 (19)–126.2 (2) and 122.96 (14)–125.57 (16)°, respectively] show less *p* character with respect to sp^2 hybridization; however, the sums of the surrounding angles at the N atoms (C—N—P + P—N—H + H—N—C) are near or equal to the bond-angle sum for ideal sp^2 hybridization (360°).

In both structures, the P atoms are within a distorted tetrahedral (N)(N)$_2$P(O) environment, with the angles at the P atom ranging from 103.50 (12) (O1*a*—P1*a*—N1*a*) to 115.23 (13)° (O1*a*—P1*a*—N3*a*) for **L-1*a***, from 102.25 (12) (N2*b*—P1*b*—N3*b*) to 116.30 (13)° (O1*b*—P1*b*—N3*b*) for **L-1*b***, from 103.29 (9) (O1*a*—P1*a*—N1*a*) to 115.49 (8)° (O1*a*—P1*a*—N2*a*) for **D-1*a*** and from 101.94 (10) (N2*b*—P1*b*—N3*b*) to 116.30 (10)° (O1*b*—P1*b*—N3*b*) for **D-1*b***. This means that in all four molecules, the largest angle is O1—P1—N2/N3, while the smallest angle in the *a* molecules is O1—P1—N1 and in the *b* molecules is N2—P1—N3.

In each molecule, the mean plane defined by atoms C1/O2/N1 is not coplanar with the mean plane defined by the atoms of the 2,6-F$_2$-C$_6$H$_3$ segment (see Table 6) and, typically, as in **L-1*b***, the angle between the mean planes is 53.4 (3)°.

The O atom of the C═O group in the *b* molecules in both structures shows a close contact with an adjacent F atom in the other independent molecule [O···F = 2.976 (3) Å in **L-1** and 2.964 (2) Å in **D-1**]. In the C(O)NHP(O) segment, the interplanar angle between the mean planes defined by atoms C1/

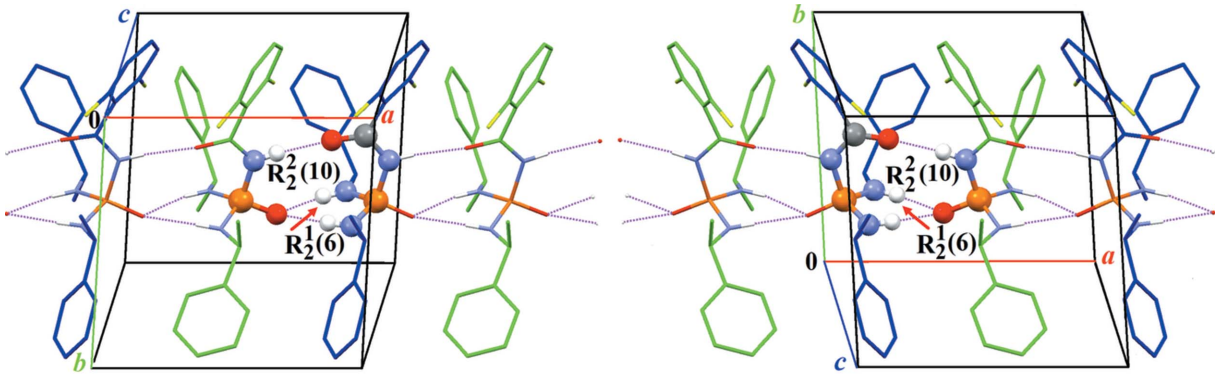


Figure 4
A view of the one-dimensional array of **L-1** and **D-1** built from N—H···O(P) and N—H···O(C) hydrogen bonds (dotted lines). H atoms not involved in hydrogen bonding have been omitted for clarity. Molecules with the same coloured C atoms are related by symmetry.

Table 6
Interplanar angles (°) for **L-1** and **D-1**.

Structure	Atoms defining plane 1	Atoms defining plane 2	Angle
L-1	C1*a*, O2*a*, N1*a*	C2*a*, C3*a*, C4*a*, C5*a*, C6*a*, C7*a*, F1*a*, F2*a*, H1c4*a*, H1c5*a*, H1c6*a*	51.3 (3)
L-1	C1*b*, O2*b*, N1*b*	C2*b*, C3*b*, C4*b*, C5*b*, C6*b*, C7*b*, F1*b*, F2*b*, H1c4*b*, H1c5*b*, H1c6*b*	53.4 (3)
D-1	C1*a*, O2*a*, N1*a*	C2*a*, C3*a*, C4*a*, C5*a*, C6*a*, C7*a*, F1*a*, F2*a*, H1c4*a*, H1c5*a*, H1c6*a*	51.1 (2)
D-1	C1*b*, O2*b*, N1*b*	C2*b*, C3*b*, C4*b*, C5*b*, C6*b*, C7*b*, F1*b*, F2*b*, H1c4*b*, H1c5*b*, H1c6*b*	53.3 (2)
L-1	C1*a*, O2*a*, N1*a*, H1n1*a*	P1*a*, O1*a*, N1*a*, H1n1*a*	2.7 (12)
L-1	C1*b*, O2*b*, N1*b*, H1n1*b*	P1*b*, O1*b*, N1*b*, H1n1*b*	1.5 (13)
D-1	C1*a*, O2*a*, N1*a*, H1n1*a*	P1*a*, O1*a*, N1*a*, H1n1*a*	2.2 (12)
D-1	C1*b*, O2*b*, N1*b*, H1n1*b*	P1*b*, O1*b*, N1*b*, H1n1*b*	1.5 (13)

O2/N1/H1n1 and P1/O1/N1/H1n1 shows an *anti* conformation of the C1—O2 and P1—O1 groups (see Table 6). As the *syn* and *anti* notations are usually applied to the conformation on a single bond, we derive the torsion angle O1—P1···C1—O2, with a hypothetical bond between P1···C1, as −177.2 (2)° in **D-1*b***. The N—H unit of the C(O)NHP(O) part adopts a *syn* conformation with respect to the P═O group, while the two other N—H units adopt an *anti* conformation with respect to the P═O group.

In both crystal structures, the two symmetry-independent molecules are linked through N—H···O hydrogen bonds in a tape arrangement along the *a* axis. This arrangement is shown in Fig. 4(*a*) for **L-1**, and a similar assembly, but nearly in a mirror-image position with respect to this arrangement, is seen for **D-1**, as shown in Fig. 4(*b*). These patterns include noncentrosymmetric hydrogen-bonded graph-set motifs $R_2^2(10)$ and $R_2^1(6)$ (for graph-set notation, see Etter *et al.*, 1990), with the O atom of phosphoryl group taking part in a three-centred ($N_PH\cdots$)($N_PH\cdots$)O grouping, while the O atom of the carbonyl group co-operates in an $N_{CP}H\cdots O$ hydrogen bond [N_{CP} is the N atom of the C(O)NHP(O) segment and N_P are the other two N atoms]. In this assembly, molecules *a* and *b* are arranged in the sequence *ababab* ... in both structures, leading to a chain $C_2^2(8)$ motif. It should be noted that the phosphoric triamide molecules include two dissymmetry centres, and in the crystal with two symmetry-independent molecules, we can consider four such dissymmetry centres, which are responsible for the chiral architecture formed. For both structures, the one-dimensional tape arrangement is extended through C—H···O hydrogen bonds into a two-dimensional architecture which includes a high-order hydrogen-bonded cyclic $R_6^5(28)$ motif. An example of this type of assembly is shown for compound **L-1** in Fig. 5.

3.2. Hirshfeld surface analysis and fingerprint plots

For a better understanding of the packing map, it was decided to use a graphical tool for identification of the intermolecular interactions within the crystal structure. In this respect, the Hirshfeld surface (HS) analysis, which uses three-dimensional maps, as well as two-dimensional fingerprint plots (Spackman & Jayatilaka, 2009), is very useful.

The HS mapped with d_{norm} (Spackman & McKinnon, 2002) and two-dimensional fingerprint plots were generated using *CrystalExplorer* (Wolff *et al.*, 2013). Each point on the HS is associated with the nearest distance from the point to nuclei inside (d_i) and outside (d_e) the surface. Moreover, the normalized contact distance (d_{norm}), based on the d_i, d_e and the van der Waals (vdW) radii of the corresponding atoms, assigns a particular intermolecular interaction *via* a colour-coded system. In the HS mapped with d_{norm}, red and blue colours are associated with distances shorter and longer than the vdW radii of neighbouring atoms, respectively, while white is used for contacts near the vdW separations (McKinnon *et al.*, 2007).

For **L-1** and **D-1**, the HSs are plotted separately for the two symmetry-independent phosphoric triamide molecules (Fig. 6). In these structures, the intermolecular contacts are similar, with the most important interactions being four N—H···O(P) (labels 1, 2, 4 and 5) and two N—H···O(C) (labels 3 and 6) hydrogen bonds, appearing as large red areas in the corresponding HS maps. In both structures, the C—H···OP hydrogen bond between two adjacent symmetry-related *a* molecules is visible as a moderate red area in the HS (Fig. 6*a* for **L-1** and Fig. 6*b* for **D-1**, label 7). Moreover, pale-red spots in Figs. 6(*c*) and 6(*d*) correspond to C—H···C (label 8), C—H···OP (label 9) and C—H···H—C (label 10) contacts between two adjacent symmetry-related *b* molecules in both structures.

The fingerprint plots (FPs) of the close contacts are very similar for the molecules with the same suffix in each structure,

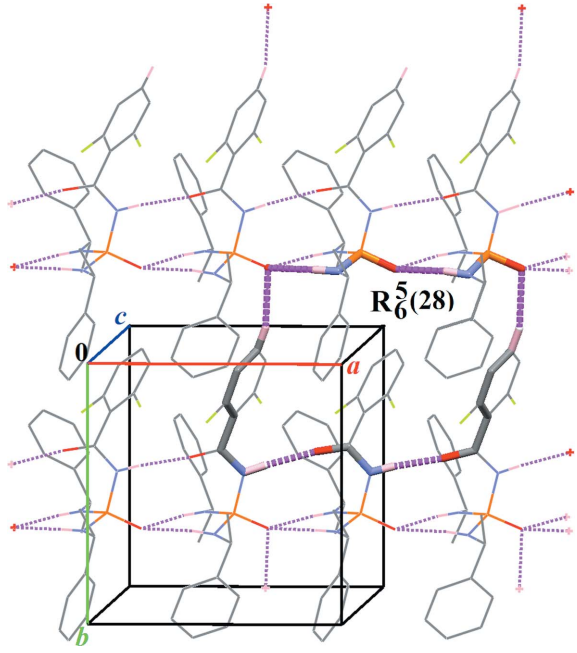


Figure 5
Part of the crystal packing of compound **L-1**, showing the two-dimensional arrangement along the *ab* plane, mediated by N—H···O and C—H···O hydrogen bonds. H atoms not involved in hydrogen bonding have been omitted for clarity.

and examples of the plots for molecule **L-1*a*** are given in Fig. 7; the contribution of each type of contact, relative to the corresponding structure, is given in Table S1 of the supporting information. In each structure, the FPs of the independent molecules are not identical because there are different molecular environments of the symmetry-independent molecules, as well as slightly different molecular conformations, as has been shown for structures with more than one component in the crystal (Fabbiani *et al.*, 2007). In both structures, the H···H, C···H/H···C, O···H/H···O and F···H/H···F contacts have considerable contributions, while the C···C, N···H/H···N, O···C/C···O, F···C/C···F and F···O/O···F contacts contribute negligibly. The H···H contacts represent the largest relative interaction in the four molecules of the two structures, typically amounting to 51.8% for **L-1*a*** and 53.9% for **L-1*b***, with one distinct spike for the shortest distance of $d_e = d_i \simeq 1.2$ Å. For molecule **L-1*a***, the proportions of the C···H/H···C, F···H/H···F and O···H/H···O contacts with respect to the total surface are 21.8, 11.3 and 9.2%, respectively, and similar contacts in molecule **L-1*b*** show 20.5, 11.5 and 9.2% proportions. In the FPs, the C···H/H···C contacts appear as two short spikes, while the O···H/H···O interactions reveal two sharp spikes. It should be noted that the shortest $d_i + d_e$ in spikes of O···H/H···O interactions is near 1.8 Å. Indeed,

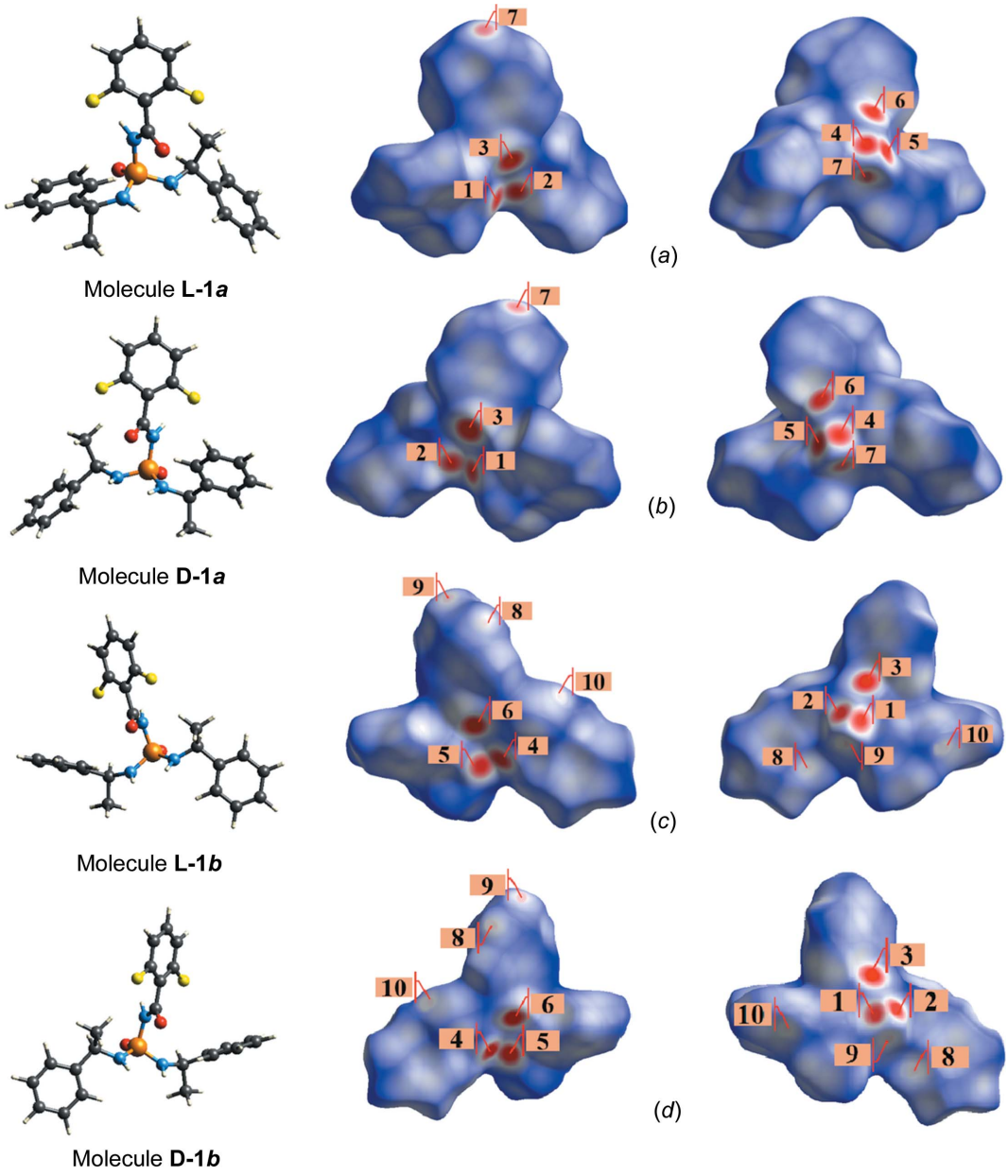


Figure 6
Front and back views of the Hirshfeld surfaces for molecules **L-1*a***, **D-1*a***, **L-1*b*** and **D-1*b***. For guidance, the 'ball-and-stick' representations of the phosphoric triamide molecules are shown on the left, with the orientations according to the middle figure. The interactions are numbered and defined here. For molecules **L-1*a***, **D-1*a***, **L-1*b*** and **D-1*b***: N3*a*—H1n3*a*···O1*b*—P1*b* (**1**), N2*a*—H1n2*a*···O1*b*—P1*b* (**2**), C1*a*—O2*a*···H1n1*b*—N1*b* (**3**), P1*a*—O1*a*···H1n2*b*—N2*b* (**4**), P1*a*—O1*a*···H1n3*b*—N3*b* (**5**) and N1*a*—H1n1*a*···O2*b*—C1*b* (**6**); for molecules **L-1*a*** and **D-1*a*** only: P1*a*—O1*a*···H1c5*a*—C5*a* (**7**); for molecules **L-1*b*** and **D-1*b*** only: C6*b*—H1c6*b*···C15*b* (**8**), C5*b*—H1c5*b*···O1*b*—P1*b* (**9**) and C9*b*—H1c9*b*···H1c19*b*—C19*b* (**10**).

sharp spikes in this region arise from the strong N—H···O interactions.

3.3. Spectroscopy

In the IR spectra, the N—H stretching frequencies occur at 3247 and 3081 cm^{-1} for **L-1**, and at 3248 and 3082 cm^{-1} for **D-1**. In both structures, the lower N—H stretching frequencies are assigned to the N—H unit of the C(O)NHP(O) segment, which is involved in a stronger hydrogen bond, as shown by the X-ray crystallographic analysis.

The NMR spectra of **L-1** and **D-1** are identical, except for very small shifts of values for similar signals. As temperature is important for absolute chemical shifts, the experiments for both samples were run under calibrated and equilibrated temperature conditions (303 K). Since the difference in chemical shifts between **L-1** and **D-1** are only about 0.02 to 0.001 ppm, we need to show that the reproducibility is at least ten times better than that. So, we ran each of the samples three times with excellent reproducibility. The details of the experiments are given in Table S2 of the supporting information. Under the equilibrated conditions, the main differences between the signals of **L-1** and **D-1** are related to the appearance of signals assigned to the $N_{CP}H$ protons, where a broad signal centred at 9.76 ppm for **L-1** and a doublet signal (J = 6.0 Hz) at 9.77 ppm for **D-1** are seen (see Fig. S1 in the supporting information); however, the widths at half-maxima for both these signals are almost the same, *i.e.* 18.0 Hz for **L-1** and 18.2 Hz for **D-1**.

It is quite interesting to see that even ^{31}P and ^{19}F show a difference in the chemical shifts between the two samples, and it is notable that NMR could distinguish compounds that have different relative stereocentres. For **L-1** and **D-1**, the ^{31}P

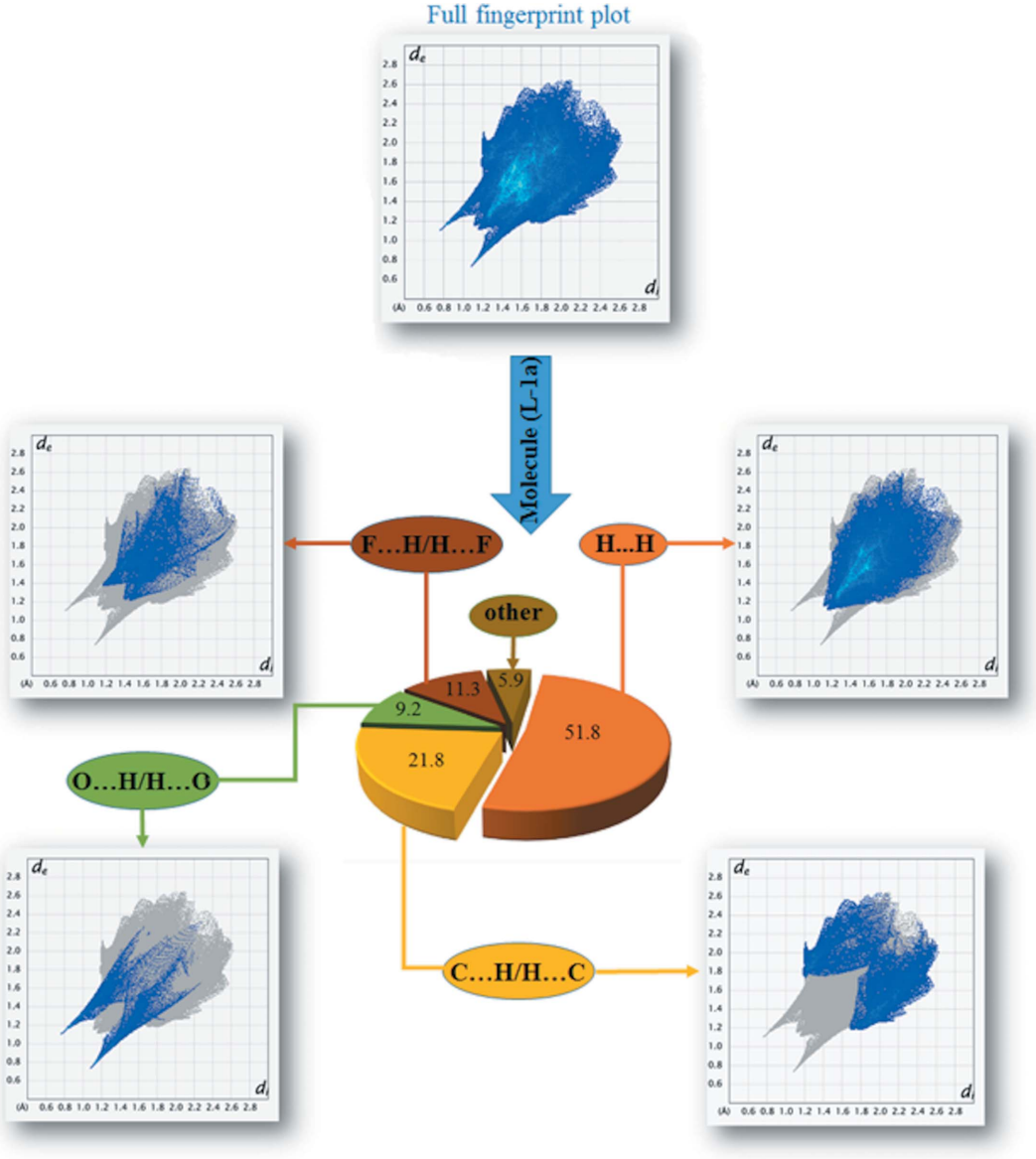


Figure 7
Schematic illustration of the fingerprint plots of molecule **L-1*a***. Different colours have been used for different atom pair contacts.

signals appear at 3.78 and 3.80 ppm, respectively. The values given are the averages of different runs. The ^{19}F chemical shifts are at −113.49 and −113.48 ppm, respectively. As the spectra are very similar, the details of the ^{1}H and ^{13}C NMR analyses are only discussed for one of the samples.

In the ^{1}H NMR spectrum of **L-1**, besides the $N_{CP}H$ proton already discussed above, the two other N—H protons appear as two triplets at 4.97 (J = 10.5 Hz) and 4.88 ppm (J = 10.0 Hz), because of the coupling on one hand with the C—H unit and on the other hand with phosphorus. The ten protons of the phenyl rings appear as three separate multiplet signals at 7.31–7.39, 7.24–7.31 and 7.11–7.22 ppm, which belong to the H atoms bonded to C11/C15/C19/C23, C12/C14/C20/C22 and C13/C21, respectively, with the integration areas confirming four protons for the first two signals and two protons for the third signal (the numbering used is according to the X-ray crystal structure). Moreover, the protons bonded to C4 and C6 (for the 2,6-F_2-C_6H_3 ring) are mixed with the peaks at 7.11–7.22 ppm. The '*tt*' signal at 7.50 ppm corresponds to the *para*-H atom of the 2,6-F_2-C_6H_3 segment (the proton bonded to atom C5). A comparison of this signal at 400 and 600 MHz is given in Fig. S2 (see supporting information), to show the couplings resolved at a lower field. The doublet signals at 1.38 (J = 6.8 Hz) and 1.40 ppm (J = 6.9 Hz) belong to the protons of two CH_3 groups. Two multiplets, in the range 4.29–4.45 ppm, appear for the two C—H protons of the chiral segments.

In the ^{13}C NMR spectrum of **L-1**, the '*dd*' signal of C3/C7, *i.e.* the C atom bonded to fluorine, arises from ^{1}J and ^{3}J couplings between the C and two F atoms. The *ipso*-C atoms of two $(C_6H_5)CH(CH_3)(NH)$ groups are revealed at 146.24 ($^{3}J_{C-P}$ = 5.5 Hz) and 145.89 ppm ($^{3}J_{C-P}$ = 5.6 Hz). The *para*-C atom of the 2,6-F_2-C_6H_3 part appears as a triplet at 131.84 ppm, with $^{3}J_{C-F}$ = 19.2 Hz. The *ipso*-C atom of the 2,6-F_2-C_6H_3 part shows a '*td*' pattern due to $^{2}J_{C-F}$ = 22.5 Hz from the two F atoms and $^{3}J_{C-P}$ = 8.4 Hz. The C4/C6 signal appears as a '*dd*' pattern arising from ^{2}J and ^{4}J couplings with F atoms; however, the ^{4}J coupling is too weak and is not well resolved. In the aliphatic region, the signals of the C—H units appear as singlets, while the signals of the methyl groups appear as doublets (at 25.48 and 24.92 ppm, with $^{3}J_{C-P}$ = 5.3 and 4.9 Hz, respectively).

The mass spectra of both compounds reveal the presence of the molecular ion peak at m/z = 443 in a 70 eV experiment. The ion peaks at m/z 338, 141, 120 (base peak), and 105 belong to the $[M - C_8H_9]^+$, $[C_7H_3F_2O]^+$, $[C_8H_{10}N]^+$ and $[C_8H_9]^+$ cations, respectively.

The ultraviolet (UV) absorption spectra were recorded in chloroform. The absorption bands at 258/259 nm for **L-1**/**D-1** and at 214 nm for both **L-1** and **D-1** are attributed to $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ transitions, respectively. Furthermore, there are other bands overlapping with the band attributed to $\pi\rightarrow\pi^*$ with slightly lower intensities.

3.4. Optical rotation

The specific optical rotations were calculated by the $[\alpha] = \alpha/L.c$ formula, where α is optical rotation, L is optical path length (dm), c is concentration (g ml^{-1}), and levorotation and dextrorotation are designated by (−) and (+), respectively. The specific rotations are measured as $[\alpha]_D^{25}$ = −43.0 (c 0.004, MeOH) for **L-1** and $[\alpha]_D^{25}$ = 44.5 (c 0.004, MeOH) for **D-1**.

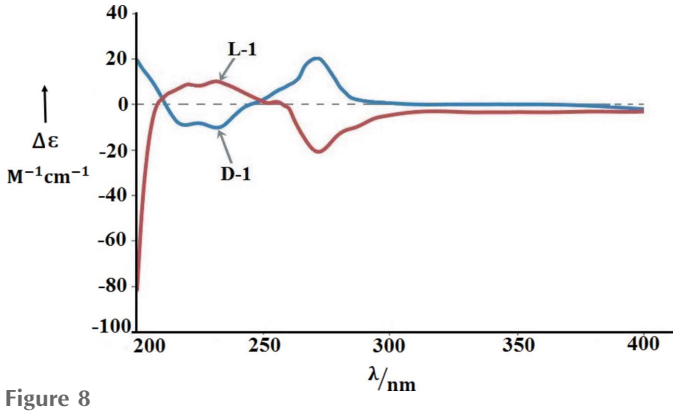


Figure 8
CD spectra of **L-1** and **D-1** in $CHCl_3$ solution.

To examine the chiroptical properties of both enantiopure compounds in solution, the circular dichroism (CD) spectra were investigated for a 2.3 mM solution in chloroform (Fig. 8). The CD spectra exhibit opposing signals, with the maximum intensity of the negative peak at 272 nm for **L-1** and a similar positive peak at 270 nm for **D-1**. The strong Cotton effect up to 272/270 nm is according to the spectral region characteristic of the $n\rightarrow\pi^*$ transition bands of the phosphoric triamide molecule. For **L-1**, the CD sign is negative at wavelengths below 208 nm, while it is positive between 208 and 251 nm. For **D-1**, opposite signs are observed below 211 nm and from 211 to 246 nm. The CD patterns of **L-1** and **D-1** are nearly mirror images in the range 200–400 nm.

Acknowledgements

Support of this investigation by Ferdowsi University of Mashhad is gratefully acknowledged.

Funding information

Funding for this research was provided by: Ferdowsi University of Mashhad (award No. 3/42356); Czech Science Foundation (grant No. 14-03276-S).

References

Ariani, M., Pourayoubi, M., Dušek, M., Vahdani Alviri, B., Eigner, V. & Damodaran, K. (2017). *X-Ray Struct. Anal. Online*, **33**, 17–19.
Buono, G., Chiodi, O. & Wills, M. (1999). *Synlett*, pp. 377–388.
De Luca, L., Chiminazzo, A., Sperni, L., Strukul, G. & Scarso, A. (2017). *ChemistrySelect*, **2**, 3262–3267.
Denmark, S. E. & Stavenger, R. A. (2000). *Acc. Chem. Res.* **33**, 432–440.
Diel, P. J. & Maier, L. (1984). *Phosphorus Sulfur Silicon Relat. Elem.* **20**, 313–321.
Etter, M. C., MacDonald, J. C. & Bernstein, J. (1990). *Acta Cryst.* B**46**, 256–262.
Fabbiani, F. P. A., Leech, C. K., Shankland, K., Johnston, A., Fernandes, P., Florence, A. J. & Shankland, N. (2007). *Acta Cryst.* C**63**, o659–o663.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.
Gu, B., Zhao, C., Baev, A., Yong, K.-T., Wen, S. & Prasad, P. N. (2016). *Adv. Opt. Photonics*, **8**, 328–369.
Hah, J. H., Gil, J. M. & Oh, D. Y. (1999). *Tetrahedron Lett.* **40**, 8235–8238.
Headley, C. E. & Marsden, S. P. (2007). *J. Org. Chem.* **72**, 7185–7189.
Hua, D. H., Chan-Yu-King, R., McKie, J. A. & Myer, L. (1987). *J. Am. Chem. Soc.* **109**, 5026–5029.
Keikha, M., Pourayoubi, M., Tarahhomi, A. & van der Lee, A. (2016). *Acta Cryst.* C**72**, 251–259.
Li, X.-J., Jiang, F.-L., Wu, M.-Y., Zhang, S.-Q., Zhou, Y.-F. & Hong, M.-C. (2012). *Inorg. Chem.* **51**, 4116–4122.
Manunza, B., Deiana, S., Pintore, M. & Gessa, C. (1999). *Soil Biol. Biochem.* **31**, 789–796.
McKinnon, J. J., Jayatilaka, D. & Spackman, M. A. (2007). *Chem. Commun.* pp. 3814–3816.
Palatinus, L. & Chapuis, G. (2007). *J. Appl. Cryst.* **40**, 786–790.
Petříček, V., Dušek, M. & Palatinus, L. (2014). *Z. Kristallogr.* **229**, 345–352.
Pourayoubi, M., Nečas, M. & Negari, M. (2012). *Acta Cryst.* C**68**, o51–o56.
Pourayoubi, M., Toghraee, M., Zhu, J., Dušek, M., Bereciartua, P. J. & Eigner, V. (2014). *CrystEngComm*, **16**, 10870–10887.
Prins, L. J., Huskens, J., de Jong, F., Timmerman, P. & Reinhoudt, D. N. (1999). *Nature*, **398**, 498–502.
Reid, J. R. & Marmor, R. S. (1978). *J. Org. Chem.* **43**, 999–1001.
Rigaku OD (2015). *CrysAlis PRO*. Rigaku Oxford Diffraction Ltd, Yarnton, Oxfordshire, England.
Rohlícek, J. & Husák, M. (2007). *J. Appl. Cryst.* **40**, 600–601.
Sabbaghi, F., Pourayoubi, M., Farhadipour, A., Ghorbanian, N. & Andreev, P. V. (2017). *Acta Cryst.* C**73**, 508–516.
Saneei, A., Pourayoubi, M., Crochet, A. & Fromm, K. M. (2016). *Acta Cryst.* C**72**, 230–233.
Spackman, M. A. & Jayatilaka, D. (2009). *CrystEngComm*, **11**, 19–32.
Spackman, M. A. & McKinnon, J. J. (2002). *CrystEngComm*, **4**, 378–392.
Tarahhomi, A., Pourayoubi, M., Golen, J. A., Zargaran, P., Elahi, B., Rheingold, A. L., Leyva Ramírez, M. A. & Mancilla Percino, T. (2013). *Acta Cryst.* B**69**, 260–270.
Vahdani Alviri, B., Pourayoubi, M., Saneei, A., Keikha, M., van der Lee, A., Crochet, A., Ajees, A. A., Nečas, M., Fromm, K. M., Damodaran, K. & Jenny, T. A. (2018). *Tetrahedron*, **74**, 28–41.
Wolff, S. K., Grimwood, D. J., McKinnon, J. J., Turner, M. J., Jayatilaka, D. & Spackman, M. A. (2013). *CrystalExplorer*. University of Western Australia.
Zinna, F., Giovanella, U. & Di Bari, L. (2015). *Adv. Mater.* **27**, 1791–1795.

supporting information

Acta Cryst. (2018). C**74** [https://doi.org/10.1107/S2053229618004734]

Chiral one-dimensional hydrogen-bonded architectures constructed from single-enantiomer phosphoric triamides

Mahsa Eghbali Toularoud, Mehrdad Pourayoubi, Michal Dušek, Václav Eigner and Krishnan Damodaran

Computing details

For both structures, data collection: *CrysAlis PRO* (Rigaku OD, 2015); cell refinement: *CrysAlis PRO* (Rigaku OD, 2015); data reduction: *CrysAlis PRO* (Rigaku OD, 2015); program(s) used to solve structure: JANA2006 (Version 24/09/2015; Petříček *et al.*, 2014); program(s) used to refine structure: JANA2006 (Version 24/09/2015; Petříček *et al.*, 2014); molecular graphics: *CrystalExplorer* (Wolff *et al.*, 2013); software used to prepare material for publication: JANA2006 (Version 24/09/2015; Petříček *et al.*, 2014), *SUPERFLIP* (Palatinus & Chapuis, 2007) and *MCE2005* (Rohlícek & Husák, 2007).

N-(2,6-Difluorobenzoyl)-*N*′,*N*′′-bis[(*S*)-(-)-α-methylbenzyl]phosphoric triamide (I)

Crystal data

$C_{23}H_{24}F_2N_3O_2P$
M_r = 443.4
Triclinic, *P*1
Hall symbol: P 1
a = 9.7608 (3) Å
b = 10.6134 (3) Å
c = 11.2721 (3) Å
α = 77.398 (2)°
β = 75.589 (2)°
γ = 87.635 (2)°
V = 1103.64 (6) Å^3
Z = 2
F(000) = 464
D_x = 1.334 Mg m^{-3}
Cu *Kα* radiation, λ = 1.54184 Å
Cell parameters from 14044 reflections
θ = 4.1–67.2°
μ = 1.47 mm^{-1}
T = 120 K
Prism, colourless
0.53 × 0.19 × 0.08 mm

Data collection

Agilent Xcalibur/Gemini ultra diffractometer with an AtlasS2 detector
Radiation source: X-ray tube
Mirror monochromator
Detector resolution: 5.1783 pixels mm^{-1}
ω scans
Absorption correction: analytical (CrysAlis PRO; Rigaku OD, 2015)
T_{min} = 0.562, T_{max} = 0.896
21163 measured reflections
7492 independent reflections
6976 reflections with $I > 3\sigma(I)$
R_{int} = 0.051
θ_{max} = 67.2°, θ_{min} = 4.2°
h = −11→11
k = −12→12
l = −13→13

Refinement

Refinement on F^2
$R[F > 3\sigma(F)] = 0.047$
$wR(F) = 0.121$
$S = 1.71$
7492 reflections
578 parameters
6 restraints
177 constraints

H atoms treated by a mixture of independent and constrained refinement
Weighting scheme based on measured s.u.'s $w = 1/(\sigma^2(I) + 0.0016I^2)$
$(\Delta/\sigma)_{max} = 0.038$
$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.31$ e Å^{-3}
Absolute structure: 3546 of Friedel pairs used in the refinement
Absolute structure parameter: 0.014 (17)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
P1a	0.42969 (8)	0.70347 (7)	0.88573 (6)	0.01478 (19)
P1b	0.93005 (8)	0.70016 (7)	0.87843 (6)	0.0155 (2)
F1a	0.5086 (2)	0.30564 (19)	1.06091 (18)	0.0402 (7)
F2a	0.3523 (2)	0.3273 (2)	0.69523 (18)	0.0480 (8)
F1b	1.0313 (2)	0.32193 (17)	1.06766 (15)	0.0316 (6)
F2b	0.8561 (3)	0.2938 (2)	0.7220 (2)	0.0472 (8)
O1a	0.56352 (19)	0.76047 (18)	0.89095 (16)	0.0186 (6)
O2a	0.2576 (2)	0.4860 (2)	0.8713 (2)	0.0267 (7)
O1b	1.0676 (2)	0.75981 (18)	0.86840 (17)	0.0199 (6)
O2b	0.7535 (2)	0.4649 (2)	0.8922 (2)	0.0270 (7)
N1a	0.4696 (2)	0.5453 (2)	0.8883 (2)	0.0193 (7)
N2a	0.3729 (2)	0.7653 (2)	0.7623 (2)	0.0182 (7)
N3a	0.2950 (2)	0.7135 (2)	1.0014 (2)	0.0191 (7)
N1b	0.9696 (3)	0.5418 (2)	0.8846 (2)	0.0215 (8)
N2b	0.8565 (2)	0.7539 (2)	0.7637 (2)	0.0195 (7)
N3b	0.8044 (2)	0.7135 (2)	0.9995 (2)	0.0215 (8)
C1a	0.3791 (3)	0.4570 (3)	0.8789 (2)	0.0192 (8)
C2a	0.4316 (3)	0.3239 (3)	0.8761 (3)	0.0237 (9)
C3a	0.4958 (3)	0.2516 (3)	0.9652 (3)	0.0323 (10)
C4a	0.5419 (4)	0.1282 (3)	0.9637 (4)	0.0504 (15)
C5a	0.5248 (4)	0.0723 (4)	0.8694 (4)	0.0557 (16)
C6a	0.4603 (4)	0.1387 (4)	0.7779 (4)	0.0511 (15)
C7a	0.4152 (4)	0.2616 (3)	0.7837 (3)	0.0342 (11)
C8a	0.4603 (3)	0.7797 (3)	0.6343 (2)	0.0205 (9)
C9a	0.4546 (4)	0.6600 (3)	0.5804 (3)	0.0327 (11)
C10a	0.4202 (3)	0.8990 (3)	0.5472 (2)	0.0213 (9)
C11a	0.5229 (3)	0.9569 (3)	0.4419 (3)	0.0322 (10)
C12a	0.4906 (4)	1.0599 (4)	0.3554 (3)	0.0416 (12)
C13a	0.3523 (4)	1.1058 (3)	0.3731 (3)	0.0396 (12)
C14a	0.2513 (4)	1.0499 (3)	0.4773 (3)	0.0360 (11)
C15a	0.2839 (3)	0.9467 (3)	0.5650 (3)	0.0282 (10)
C16a	0.3078 (3)	0.7245 (3)	1.1250 (2)	0.0203 (9)
C17a	0.2456 (3)	0.8532 (3)	1.1517 (3)	0.0293 (10)
C18a	0.2412 (3)	0.6102 (3)	1.2291 (2)	0.0203 (9)

C19a	0.1802 (3)	0.5051 (3)	1.2045 (3)	0.0271 (10)
C20a	0.1256 (4)	0.4021 (3)	1.3009 (3)	0.0343 (11)
C21a	0.1295 (4)	0.4001 (3)	1.4229 (3)	0.0341 (11)
C22a	0.1914 (4)	0.5041 (3)	1.4479 (3)	0.0347 (11)
C23a	0.2457 (3)	0.6075 (3)	1.3525 (3)	0.0300 (10)
C1b	0.8781 (3)	0.4461 (3)	0.8914 (2)	0.0197 (9)
C2b	0.9415 (3)	0.3151 (3)	0.8940 (3)	0.0217 (9)
C3b	1.0192 (3)	0.2573 (3)	0.9789 (2)	0.0225 (9)
C4b	1.0823 (3)	0.1402 (3)	0.9798 (3)	0.0304 (10)
C5b	1.0669 (4)	0.0719 (3)	0.8914 (3)	0.0356 (11)
C6b	0.9891 (4)	0.1230 (3)	0.8053 (3)	0.0419 (13)
C7b	0.9289 (3)	0.2418 (3)	0.8085 (3)	0.0299 (10)
C8b	0.9219 (3)	0.7565 (3)	0.6330 (2)	0.0216 (9)
C9b	0.8700 (3)	0.6444 (3)	0.5896 (3)	0.0299 (10)
C10b	0.8997 (3)	0.8862 (3)	0.5501 (2)	0.0210 (9)
C11b	0.9569 (3)	0.9079 (3)	0.4211 (3)	0.0327 (10)
C12b	0.9377 (3)	1.0240 (3)	0.3432 (3)	0.0342 (11)
C13b	0.8602 (4)	1.1209 (3)	0.3922 (3)	0.0339 (11)
C14b	0.8035 (4)	1.1001 (3)	0.5201 (3)	0.0326 (11)
C15b	0.8221 (3)	0.9846 (3)	0.5983 (2)	0.0272 (9)
C16b	0.8251 (3)	0.6982 (3)	1.1256 (2)	0.0254 (10)
C17b	0.7811 (5)	0.8217 (3)	1.1726 (3)	0.0446 (13)
C18b	0.7456 (3)	0.5832 (3)	1.2179 (2)	0.0233 (9)
C19b	0.7849 (4)	0.5382 (3)	1.3303 (3)	0.0341 (11)
C20b	0.7097 (4)	0.4404 (3)	1.4222 (3)	0.0421 (13)
C21b	0.5930 (4)	0.3847 (3)	1.4044 (3)	0.0406 (12)
C22b	0.5550 (4)	0.4259 (3)	1.2908 (3)	0.0370 (11)
C23b	0.6310 (3)	0.5237 (3)	1.1992 (3)	0.0281 (10)
H1n1a	0.5517 (16)	0.519 (3)	0.897 (3)	0.0232*
H1n2a	0.2832 (7)	0.754 (3)	0.775 (3)	0.0219*
H1n3a	0.2156 (17)	0.725 (3)	0.981 (3)	0.0229*
H1n1b	1.0552 (13)	0.521 (3)	0.887 (3)	0.0258*
H1n2b	0.7657 (3)	0.752 (3)	0.788 (3)	0.0234*
H1n3b	0.7227 (16)	0.727 (3)	0.984 (3)	0.0258*
H1c4a	0.585472	0.081706	1.027517	0.0605*
H1c5a	0.557726	−0.013751	0.866686	0.0668*
H1c6a	0.447712	0.099488	0.712181	0.0613*
H1c8a	0.555862	0.790094	0.639283	0.0246*
H1c9a	0.509728	0.67571	0.49513	0.0392*
H2c9a	0.492292	0.58757	0.629251	0.0392*
H3c9a	0.358272	0.641667	0.583119	0.0392*
H1c11a	0.617653	0.924764	0.429132	0.0387*
H1c12a	0.562681	1.099817	0.283514	0.05*
H1c13a	0.328311	1.176165	0.312557	0.0475*
H1c14a	0.156687	1.082278	0.489927	0.0432*
H1c15a	0.212086	0.908615	0.637905	0.0338*
H1c16a	0.406511	0.72268	1.1241	0.0243*
H1c17a	0.255892	0.862125	1.231992	0.0352*

H2c17a	0.294717	0.922963	1.087811	0.0352*
H3c17a	0.147048	0.855228	1.152057	0.0352*
H1c19a	0.176156	0.504521	1.120374	0.0326*
H1c20a	0.083993	0.33035	1.282784	0.0412*
H1c21a	0.090281	0.328179	1.489352	0.0409*
H1c22a	0.196098	0.503706	1.532064	0.0416*
H1c23a	0.287364	0.67901	1.371072	0.036*
H1c4b	1.136127	0.105687	1.039828	0.0365*
H1c5b	1.11031	−0.010774	0.890171	0.0427*
H1c6b	0.977386	0.076233	0.744438	0.0503*
H1c8b	1.021704	0.746021	0.624882	0.0259*
H1c9b	0.922789	0.643642	0.505619	0.0358*
H2c9b	0.883182	0.564432	0.644478	0.0358*
H3c9b	0.771347	0.654769	0.591375	0.0358*
H1c11b	1.010646	0.841365	0.385657	0.0392*
H1c12b	0.978358	1.037267	0.254574	0.0411*
H1c13b	0.846	1.201279	0.338293	0.0407*
H1c14b	0.750284	1.167145	0.555186	0.0392*
H1c15b	0.781179	0.971916	0.686835	0.0326*
H1c16b	0.923797	0.682112	1.120119	0.0304*
H1c17b	0.791586	0.811117	1.256696	0.0535*
H2c17b	0.839945	0.892379	1.119104	0.0535*
H3c17b	0.684089	0.839455	1.171712	0.0535*
H1c19b	0.865845	0.575859	1.344067	0.041*
H1c20b	0.738611	0.410967	1.498953	0.0505*
H1c21b	0.538781	0.318605	1.469283	0.0488*
H1c22b	0.475878	0.386164	1.276321	0.0444*
H1c23b	0.604158	0.550906	1.121233	0.0337*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P1a	0.0129 (3)	0.0149 (3)	0.0189 (3)	0.0016 (2)	−0.0083 (2)	−0.0036 (2)
P1b	0.0137 (3)	0.0164 (3)	0.0191 (3)	0.0015 (2)	−0.0091 (2)	−0.0035 (2)
F1a	0.0465 (11)	0.0335 (11)	0.0442 (10)	0.0007 (9)	−0.0264 (9)	0.0017 (8)
F2a	0.0647 (14)	0.0466 (13)	0.0428 (11)	−0.0048 (11)	−0.0213 (10)	−0.0211 (9)
F1b	0.0435 (11)	0.0275 (9)	0.0320 (8)	0.0067 (8)	−0.0226 (8)	−0.0098 (7)
F2b	0.0636 (14)	0.0430 (12)	0.0550 (12)	0.0098 (11)	−0.0432 (11)	−0.0212 (9)
O1a	0.0158 (9)	0.0164 (9)	0.0261 (9)	0.0022 (7)	−0.0101 (7)	−0.0045 (7)
O2a	0.0179 (10)	0.0259 (11)	0.0418 (11)	0.0039 (8)	−0.0150 (8)	−0.0109 (9)
O1b	0.0160 (9)	0.0195 (10)	0.0274 (9)	0.0010 (8)	−0.0112 (7)	−0.0051 (7)
O2b	0.0183 (10)	0.0243 (11)	0.0417 (11)	0.0014 (9)	−0.0143 (8)	−0.0064 (8)
N1a	0.0166 (11)	0.0168 (12)	0.0275 (11)	0.0010 (9)	−0.0120 (9)	−0.0037 (9)
N2a	0.0146 (11)	0.0214 (12)	0.0214 (10)	0.0017 (9)	−0.0102 (9)	−0.0040 (9)
N3a	0.0116 (10)	0.0260 (13)	0.0230 (11)	0.0045 (9)	−0.0097 (8)	−0.0069 (9)
N1b	0.0160 (11)	0.0188 (12)	0.0326 (11)	0.0001 (10)	−0.0135 (10)	−0.0034 (9)
N2b	0.0165 (11)	0.0225 (12)	0.0229 (11)	0.0035 (10)	−0.0117 (9)	−0.0048 (9)
N3b	0.0158 (11)	0.0308 (13)	0.0210 (11)	0.0050 (10)	−0.0109 (9)	−0.0060 (9)

C1a	0.0167 (13)	0.0175 (14)	0.0245 (12)	0.0 (11)	−0.0072 (10)	−0.0046 (10)
C2a	0.0191 (13)	0.0165 (14)	0.0345 (14)	−0.0002 (11)	−0.0039 (11)	−0.0066 (11)
C3a	0.0245 (15)	0.0210 (15)	0.0460 (17)	0.0011 (13)	−0.0072 (13)	0.0025 (12)
C4a	0.039 (2)	0.0206 (18)	0.081 (3)	0.0037 (16)	−0.0086 (19)	0.0048 (17)
C5a	0.041 (2)	0.0179 (18)	0.090 (3)	0.0035 (16)	0.013 (2)	−0.0085 (19)
C6a	0.051 (2)	0.031 (2)	0.068 (3)	−0.0104 (18)	0.0102 (19)	−0.0286 (18)
C7a	0.0332 (17)	0.0282 (17)	0.0401 (17)	−0.0043 (14)	0.0001 (14)	−0.0144 (13)
C8a	0.0207 (14)	0.0213 (14)	0.0221 (12)	0.0034 (11)	−0.0103 (11)	−0.0051 (10)
C9a	0.054 (2)	0.0222 (16)	0.0268 (13)	0.0086 (14)	−0.0164 (13)	−0.0086 (11)
C10a	0.0232 (14)	0.0221 (14)	0.0225 (12)	0.0010 (12)	−0.0106 (11)	−0.0072 (10)
C11a	0.0301 (16)	0.0335 (17)	0.0317 (14)	0.0011 (13)	−0.0088 (12)	−0.0029 (12)
C12a	0.041 (2)	0.040 (2)	0.0334 (16)	−0.0029 (16)	−0.0046 (14)	0.0085 (14)
C13a	0.047 (2)	0.0285 (19)	0.0431 (17)	0.0028 (16)	−0.0236 (15)	0.0077 (13)
C14a	0.0298 (17)	0.0281 (18)	0.0485 (18)	0.0025 (14)	−0.0182 (14)	0.0043 (13)
C15a	0.0249 (15)	0.0250 (16)	0.0330 (14)	−0.0011 (12)	−0.0118 (12)	0.0027 (11)
C16a	0.0211 (13)	0.0244 (15)	0.0186 (12)	0.0003 (11)	−0.0104 (10)	−0.0052 (10)
C17a	0.0379 (17)	0.0236 (15)	0.0245 (13)	0.0002 (13)	−0.0032 (12)	−0.0063 (11)
C18a	0.0171 (13)	0.0216 (15)	0.0233 (12)	0.0063 (11)	−0.0086 (10)	−0.0038 (10)
C19a	0.0315 (16)	0.0251 (15)	0.0290 (14)	−0.0003 (13)	−0.0143 (12)	−0.0064 (11)
C20a	0.0391 (18)	0.0276 (17)	0.0377 (16)	−0.0031 (14)	−0.0128 (14)	−0.0056 (12)
C21a	0.0367 (17)	0.0285 (17)	0.0314 (15)	0.0005 (14)	−0.0084 (13)	0.0056 (12)
C22a	0.0404 (18)	0.0393 (19)	0.0239 (14)	0.0029 (15)	−0.0115 (12)	−0.0020 (12)
C23a	0.0357 (16)	0.0324 (17)	0.0251 (13)	0.0010 (13)	−0.0140 (12)	−0.0059 (11)
C1b	0.0175 (14)	0.0190 (14)	0.0242 (12)	0.0005 (11)	−0.0089 (10)	−0.0040 (10)
C2b	0.0200 (13)	0.0197 (15)	0.0280 (13)	−0.0005 (12)	−0.0094 (11)	−0.0061 (11)
C3b	0.0229 (14)	0.0209 (14)	0.0248 (12)	−0.0009 (11)	−0.0075 (11)	−0.0055 (10)
C4b	0.0306 (16)	0.0226 (16)	0.0364 (15)	0.0032 (13)	−0.0108 (13)	−0.0005 (12)
C5b	0.0396 (19)	0.0195 (16)	0.0459 (17)	0.0050 (14)	−0.0052 (15)	−0.0102 (13)
C6b	0.054 (2)	0.0312 (19)	0.0495 (19)	0.0010 (16)	−0.0182 (17)	−0.0208 (15)
C7b	0.0342 (17)	0.0259 (16)	0.0372 (15)	0.0013 (13)	−0.0187 (13)	−0.0117 (12)
C8b	0.0210 (13)	0.0253 (15)	0.0233 (12)	0.0048 (11)	−0.0117 (11)	−0.0092 (11)
C9b	0.0394 (17)	0.0260 (16)	0.0302 (14)	0.0045 (13)	−0.0166 (12)	−0.0103 (11)
C10b	0.0174 (13)	0.0271 (15)	0.0218 (12)	−0.0012 (11)	−0.0106 (10)	−0.0053 (11)
C11b	0.0314 (16)	0.0410 (18)	0.0248 (13)	0.0023 (14)	−0.0052 (12)	−0.0074 (12)
C12b	0.0359 (17)	0.0410 (19)	0.0222 (13)	−0.0049 (15)	−0.0067 (12)	0.0014 (12)
C13b	0.0395 (18)	0.0302 (17)	0.0328 (15)	−0.0074 (14)	−0.0192 (13)	0.0052 (12)
C14b	0.0416 (18)	0.0256 (16)	0.0328 (15)	0.0020 (14)	−0.0135 (13)	−0.0059 (12)
C15b	0.0317 (15)	0.0294 (16)	0.0220 (13)	−0.0006 (13)	−0.0094 (11)	−0.0054 (11)
C16b	0.0237 (14)	0.0383 (18)	0.0186 (12)	−0.0012 (13)	−0.0109 (11)	−0.0088 (11)
C17b	0.068 (3)	0.0351 (19)	0.0310 (16)	−0.0144 (18)	−0.0050 (16)	−0.0126 (13)
C18b	0.0238 (14)	0.0268 (16)	0.0217 (12)	0.0080 (12)	−0.0088 (11)	−0.0084 (11)
C19b	0.049 (2)	0.0337 (18)	0.0271 (14)	0.0092 (15)	−0.0220 (14)	−0.0099 (12)
C20b	0.072 (3)	0.0321 (19)	0.0264 (15)	0.0147 (18)	−0.0222 (16)	−0.0063 (13)
C21b	0.058 (2)	0.0265 (17)	0.0296 (15)	0.0093 (16)	−0.0053 (15)	0.0021 (12)
C22b	0.0350 (17)	0.0312 (18)	0.0418 (16)	0.0007 (15)	−0.0097 (14)	−0.0014 (14)
C23b	0.0264 (15)	0.0307 (17)	0.0286 (14)	0.0043 (13)	−0.0135 (12)	−0.0021 (12)

Geometric parameters (Å, º)

P1a—O1a	1.481 (2)	C17a—H2c17a	0.96
P1a—N1a	1.703 (2)	C17a—H3c17a	0.96
P1a—N2a	1.621 (2)	C18a—C19a	1.396 (5)
P1a—N3a	1.624 (2)	C18a—C23a	1.397 (4)
P1b—O1b	1.477 (2)	C19a—C20a	1.378 (4)
P1b—N1b	1.699 (3)	C19a—H1c19a	0.96
P1b—N2b	1.619 (3)	C20a—C21a	1.381 (5)
P1b—N3b	1.620 (2)	C20a—H1c20a	0.9599
F1a—C3a	1.361 (5)	C21a—C22a	1.393 (5)
F2a—C7a	1.351 (4)	C21a—H1c21a	0.96
F1b—C3b	1.359 (4)	C22a—C23a	1.375 (4)
F2b—C7b	1.355 (4)	C22a—H1c22a	0.96
O2a—C1a	1.232 (3)	C23a—H1c23a	0.9601
O2b—C1b	1.223 (3)	C1b—C2b	1.495 (4)
N1a—C1a	1.351 (4)	C2b—C3b	1.391 (4)
N1a—H1n1a	0.86 (2)	C2b—C7b	1.395 (5)
N2a—C8a	1.461 (3)	C3b—C4b	1.363 (4)
N2a—H1n2a	0.860 (9)	C4b—C5b	1.393 (5)
N3a—C16a	1.459 (4)	C4b—H1c4b	0.96
N3a—H1n3a	0.86 (2)	C5b—C6b	1.385 (6)
N1b—C1b	1.358 (4)	C5b—H1c5b	0.96
N1b—H1n1b	0.860 (17)	C6b—C7b	1.373 (5)
N2b—C8b	1.447 (3)	C6b—H1c6b	0.96
N2b—H1n2b	0.860 (14)	C8b—C9b	1.529 (5)
N3b—C16b	1.458 (4)	C8b—C10b	1.526 (4)
N3b—H1n3b	0.86 (2)	C8b—H1c8b	0.96
C1a—C2a	1.487 (4)	C9b—H1c9b	0.96
C2a—C3a	1.389 (5)	C9b—H2c9b	0.96
C2a—C7a	1.392 (5)	C9b—H3c9b	0.96
C3a—C4a	1.369 (5)	C10b—C11b	1.393 (4)
C4a—C5a	1.372 (7)	C10b—C15b	1.392 (4)
C4a—H1c4a	0.96	C11b—C12b	1.384 (4)
C5a—C6a	1.387 (7)	C11b—H1c11b	0.96
C5a—H1c5a	0.96	C12b—C13b	1.383 (5)
C6a—C7a	1.369 (5)	C12b—H1c12b	0.96
C6a—H1c6a	0.96	C13b—C14b	1.381 (4)
C8a—C9a	1.531 (5)	C13b—H1c13b	0.96
C8a—C10a	1.526 (4)	C14b—C15b	1.380 (4)
C8a—H1c8a	0.9601	C14b—H1c14b	0.96
C9a—H1c9a	0.96	C15b—H1c15b	0.96
C9a—H2c9a	0.96	C16b—C17b	1.526 (5)
C9a—H3c9a	0.9599	C16b—C18b	1.516 (4)
C10a—C11a	1.390 (4)	C16b—H1c16b	0.96
C10a—C15a	1.387 (4)	C17b—H1c17b	0.96
C11a—C12a	1.380 (5)	C17b—H2c17b	0.96
C11a—H1c11a	0.96	C17b—H3c17b	0.96

C12a—C13a	1.398 (5)	C18b—C19b	1.394 (4)
C12a—H1c12a	0.96	C18b—C23b	1.389 (5)
C13a—C14a	1.367 (4)	C19b—C20b	1.380 (4)
C13a—H1c13a	0.96	C19b—H1c19b	0.9601
C14a—C15a	1.391 (4)	C20b—C21b	1.382 (6)
C14a—H1c14a	0.96	C20b—H1c20b	0.96
C15a—H1c15a	0.96	C21b—C22b	1.395 (5)
C16a—C17a	1.532 (4)	C21b—H1c21b	0.96
C16a—C18a	1.528 (3)	C22b—C23b	1.381 (4)
C16a—H1c16a	0.9601	C22b—H1c22b	0.9599
C17a—H1c17a	0.96	C23b—H1c23b	0.96

O1a—P1a—N1a	103.50 (12)	C18a—C19a—C20a	120.1 (3)
O1a—P1a—N2a	115.22 (11)	C18a—C19a—H1c19a	119.96
O1a—P1a—N3a	115.23 (13)	C20a—C19a—H1c19a	119.97
N1a—P1a—N2a	109.74 (13)	C19a—C20a—C21a	121.4 (3)
N1a—P1a—N3a	109.45 (11)	C19a—C20a—H1c20a	119.3
N2a—P1a—N3a	103.69 (12)	C21a—C20a—H1c20a	119.3
O1b—P1b—N1b	103.20 (12)	C20a—C21a—C22a	118.8 (3)
O1b—P1b—N2b	116.02 (11)	C20a—C21a—H1c21a	120.59
O1b—P1b—N3b	116.30 (13)	C22a—C21a—H1c21a	120.59
N1b—P1b—N2b	109.56 (14)	C21a—C22a—C23a	120.2 (3)
N1b—P1b—N3b	109.49 (12)	C21a—C22a—H1c22a	119.88
N2b—P1b—N3b	102.25 (12)	C23a—C22a—H1c22a	119.87
P1a—N1a—C1a	124.0 (2)	C18a—C23a—C22a	121.1 (3)
P1a—N1a—H1n1a	119 (2)	C18a—C23a—H1c23a	119.46
C1a—N1a—H1n1a	117 (2)	C22a—C23a—H1c23a	119.46
P1a—N2a—C8a	123.39 (19)	O2b—C1b—N1b	123.0 (3)
P1a—N2a—H1n2a	113 (2)	O2b—C1b—C2b	121.8 (3)
C8a—N2a—H1n2a	118 (2)	N1b—C1b—C2b	115.1 (2)
P1a—N3a—C16a	123.52 (19)	C1b—C2b—C3b	123.6 (3)
P1a—N3a—H1n3a	114 (2)	C1b—C2b—C7b	121.8 (3)
C16a—N3a—H1n3a	122 (2)	C3b—C2b—C7b	114.5 (3)
P1b—N1b—C1b	126.2 (2)	F1b—C3b—C2b	117.4 (3)
P1b—N1b—H1n1b	116 (2)	F1b—C3b—C4b	118.2 (3)
C1b—N1b—H1n1b	118 (2)	C2b—C3b—C4b	124.4 (3)
P1b—N2b—C8b	125.02 (19)	C3b—C4b—C5b	118.4 (3)
P1b—N2b—H1n2b	113 (2)	C3b—C4b—H1c4b	120.78
C8b—N2b—H1n2b	118 (2)	C5b—C4b—H1c4b	120.78
P1b—N3b—C16b	123.6 (2)	C4b—C5b—C6b	120.1 (3)
P1b—N3b—H1n3b	114 (2)	C4b—C5b—H1c5b	119.93
C16b—N3b—H1n3b	123 (2)	C6b—C5b—H1c5b	119.94
O2a—C1a—N1a	121.2 (3)	C5b—C6b—C7b	118.8 (4)
O2a—C1a—C2a	120.9 (3)	C5b—C6b—H1c6b	120.62
N1a—C1a—C2a	117.9 (2)	C7b—C6b—H1c6b	120.62
C1a—C2a—C3a	123.4 (3)	F2b—C7b—C2b	117.4 (3)
C1a—C2a—C7a	121.3 (3)	F2b—C7b—C6b	118.9 (3)
C3a—C2a—C7a	115.2 (3)	C2b—C7b—C6b	123.7 (3)

F1a—C3a—C2a	117.7 (3)	N2b—C8b—C9b	111.8 (2)
F1a—C3a—C4a	118.9 (3)	N2b—C8b—C10b	111.1 (2)
C2a—C3a—C4a	123.4 (4)	N2b—C8b—H1c8b	107.37
C3a—C4a—C5a	118.8 (4)	C9b—C8b—C10b	111.3 (2)
C3a—C4a—H1c4a	120.59	C9b—C8b—H1c8b	107.17
C5a—C4a—H1c4a	120.6	C10b—C8b—H1c8b	107.86
C4a—C5a—C6a	120.7 (4)	C8b—C9b—H1c9b	109.47
C4a—C5a—H1c5a	119.62	C8b—C9b—H2c9b	109.47
C6a—C5a—H1c5a	119.63	C8b—C9b—H3c9b	109.47
C5a—C6a—C7a	118.3 (4)	H1c9b—C9b—H2c9b	109.47
C5a—C6a—H1c6a	120.84	H1c9b—C9b—H3c9b	109.47
C7a—C6a—H1c6a	120.84	H2c9b—C9b—H3c9b	109.48
F2a—C7a—C2a	117.6 (3)	C8b—C10b—C11b	119.6 (3)
F2a—C7a—C6a	118.9 (4)	C8b—C10b—C15b	122.4 (2)
C2a—C7a—C6a	123.5 (3)	C11b—C10b—C15b	118.0 (3)
N2a—C8a—C9a	112.6 (2)	C10b—C11b—C12b	121.0 (3)
N2a—C8a—C10a	111.5 (2)	C10b—C11b—H1c11b	119.49
N2a—C8a—H1c8a	105.99	C12b—C11b—H1c11b	119.49
C9a—C8a—C10a	109.9 (2)	C11b—C12b—C13b	120.4 (3)
C9a—C8a—H1c8a	107.72	C11b—C12b—H1c12b	119.78
C10a—C8a—H1c8a	108.89	C13b—C12b—H1c12b	119.78
C8a—C9a—H1c9a	109.47	C12b—C13b—C14b	118.8 (3)
C8a—C9a—H2c9a	109.47	C12b—C13b—H1c13b	120.59
C8a—C9a—H3c9a	109.47	C14b—C13b—H1c13b	120.59
H1c9a—C9a—H2c9a	109.47	C13b—C14b—C15b	121.0 (3)
H1c9a—C9a—H3c9a	109.48	C13b—C14b—H1c14b	119.48
H2c9a—C9a—H3c9a	109.48	C15b—C14b—H1c14b	119.49
C8a—C10a—C11a	118.3 (2)	C10b—C15b—C14b	120.7 (2)
C8a—C10a—C15a	122.6 (2)	C10b—C15b—H1c15b	119.66
C11a—C10a—C15a	119.0 (3)	C14b—C15b—H1c15b	119.66
C10a—C11a—C12a	121.0 (3)	N3b—C16b—C17b	109.1 (2)
C10a—C11a—H1c11a	119.53	N3b—C16b—C18b	113.4 (3)
C12a—C11a—H1c11a	119.52	N3b—C16b—H1c16b	107.21
C11a—C12a—C13a	119.5 (3)	C17b—C16b—C18b	110.0 (2)
C11a—C12a—H1c12a	120.22	C17b—C16b—H1c16b	110.75
C13a—C12a—H1c12a	120.23	C18b—C16b—H1c16b	106.25
C12a—C13a—C14a	119.6 (3)	C16b—C17b—H1c17b	109.47
C12a—C13a—H1c13a	120.18	C16b—C17b—H2c17b	109.47
C14a—C13a—H1c13a	120.18	C16b—C17b—H3c17b	109.47
C13a—C14a—C15a	120.9 (3)	H1c17b—C17b—H2c17b	109.47
C13a—C14a—H1c14a	119.55	H1c17b—C17b—H3c17b	109.47
C15a—C14a—H1c14a	119.56	H2c17b—C17b—H3c17b	109.47
C10a—C15a—C14a	119.9 (2)	C16b—C18b—C19b	118.5 (3)
C10a—C15a—H1c15a	120.03	C16b—C18b—C23b	123.4 (3)
C14a—C15a—H1c15a	120.03	C19b—C18b—C23b	118.0 (3)
N3a—C16a—C17a	109.0 (2)	C18b—C19b—C20b	121.2 (4)
N3a—C16a—C18a	113.1 (2)	C18b—C19b—H1c19b	119.39
N3a—C16a—H1c16a	108.16	C20b—C19b—H1c19b	119.39

C17a—C16a—C18a	111.8 (2)	C19b—C20b—C21b	120.4 (3)
C17a—C16a—H1c16a	109.5	C19b—C20b—H1c20b	119.82
C18a—C16a—H1c16a	105.08	C21b—C20b—H1c20b	119.83
C16a—C17a—H1c17a	109.47	C20b—C21b—C22b	119.1 (3)
C16a—C17a—H2c17a	109.47	C20b—C21b—H1c21b	120.45
C16a—C17a—H3c17a	109.47	C22b—C21b—H1c21b	120.46
H1c17a—C17a—H2c17a	109.47	C21b—C22b—C23b	120.2 (4)
H1c17a—C17a—H3c17a	109.47	C21b—C22b—H1c22b	119.9
H2c17a—C17a—H3c17a	109.47	C23b—C22b—H1c22b	119.9
C16a—C18a—C19a	122.1 (3)	C18b—C23b—C22b	121.1 (3)
C16a—C18a—C23a	119.5 (3)	C18b—C23b—H1c23b	119.45
C19a—C18a—C23a	118.4 (2)	C22b—C23b—H1c23b	119.46
P1a—N2a—C8a—C9a	88.4 (3)	O1a—P1a—N3a—C16a	−25.2 (3)
P1b—N2b—C8b—C9b	100.4 (3)	O1b—P1b—N3b—C16b	−41.6 (3)
P1a—N3a—C16a—C17a	117.7 (2)	P1a—N1a—C1a—O2a	−2.2 (3)
P1b—N3b—C16b—C17b	121.6 (3)	P1b—N1b—C1b—O2b	1.0 (3)
O1a—P1a—N1a—C1a	−176.68 (19)	P1a—N2a—C8a—C10a	−147.5 (2)
O1b—P1b—N1b—C1b	−178.4 (2)	P1b—N2b—C8b—C10b	−134.6 (2)
O1a—P1a—N2a—C8a	51.6 (3)	P1a—N3a—C16a—C18a	−117.2 (2)
O1b—P1b—N2b—C8b	55.9 (3)	P1b—N3b—C16b—C18b	−115.4 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1*a*—H1*n*1*a*···O2*b*	0.86 (2)	2.019 (18)	2.874 (3)	172 (3)
N2*a*—H1*n*2*a*···O1*b*^{i}	0.860 (9)	2.111 (11)	2.919 (3)	156 (3)
N3*a*—H1*n*3*a*···O1*b*^{i}	0.86 (2)	2.12 (3)	2.942 (3)	160 (3)
N1*b*—H1*n*1*b*···O2*a*^{ii}	0.860 (17)	1.967 (15)	2.822 (3)	173 (3)
N2*b*—H1*n*2*b*···O1*a*	0.860 (14)	2.036 (13)	2.868 (3)	163 (3)
N3*b*—H1*n*3*b*···O1*a*	0.86 (2)	2.06 (3)	2.888 (3)	163 (3)
C5*a*—H1*c*5*a*···O1*a*^{iii}	0.96	2.35	3.278 (4)	162.01

Symmetry codes: (i) *x*−1, *y*, *z*; (ii) *x*+1, *y*, *z*; (iii) *x*, *y*−1, *z*.

N-(2,6-Difluorobenzoyl)-*N*′,*N*″-bis[(*R*)-(+)-α-methylbenzyl]phosphoric triamide (II)

Crystal data

$C_{23}H_{24}F_2N_3O_2P$
M_r = 443.4
Triclinic, *P*1
Hall symbol: P 1
a = 9.7524 (2) Å
b = 10.6117 (2) Å
c = 11.2510 (2) Å
α = 77.3381 (15)°
β = 75.6221 (16)°
γ = 87.7313 (16)°
V = 1100.33 (4) Å^3

Z = 2
F(000) = 464
D_x = 1.338 Mg m^{-3}
Cu *Kα* radiation, λ = 1.54184 Å
Cell parameters from 12269 reflections
θ = 4.1–69.2°
μ = 1.46 mm^{-1}
T = 95 K
Prism, colourless
0.29 × 0.09 × 0.07 mm

Data collection

Agilent SuperNova Dual Source diffractometer with an AtlasS2 detector
Radiation source: X-ray tube
Mirror monochromator
Detector resolution: 5.2027 pixels mm^{-1}
ω scans
Absorption correction: analytical (CrysAlis PRO; Rigaku OD, 2015)
T_{min} = 0.774, T_{max} = 0.917
16006 measured reflections
7660 independent reflections
7383 reflections with $I > 3\sigma(I)$
R_{int} = 0.034
θ_{max} = 69.4°, θ_{min} = 4.2°
h = −10→11
k = −12→12
l = −13→13

Refinement

Refinement on F^2
$R[F > 3\sigma(F)]$ = 0.039
$wR(F)$ = 0.098
S = 1.50
7660 reflections
578 parameters
6 restraints
177 constraints
H atoms treated by a mixture of independent and constrained refinement
Weighting scheme based on measured s.u.'s $w = 1/(\sigma^2(I) + 0.0016I^2)$
$(\Delta/\sigma)_{max}$ = 0.030
$\Delta\rho_{max}$ = 0.17 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}
Absolute structure: 3604 of Friedel pairs used in the refinement
Absolute structure parameter: −0.014 (14)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
P1a	0.56995 (6)	0.29619 (5)	0.11407 (5)	0.01258 (15)
P1b	0.06956 (6)	0.29985 (5)	0.12175 (5)	0.01314 (15)
F1a	0.49063 (16)	0.69491 (13)	−0.06133 (13)	0.0322 (5)
F2a	0.64829 (18)	0.67228 (15)	0.30505 (13)	0.0384 (6)
F1b	−0.03241 (15)	0.67855 (12)	−0.06760 (12)	0.0244 (4)
F2b	0.14485 (18)	0.70701 (14)	0.27756 (15)	0.0376 (6)
O1a	0.43627 (16)	0.23908 (13)	0.10831 (13)	0.0161 (5)
O2a	0.74221 (16)	0.51377 (14)	0.12918 (15)	0.0215 (5)
O1b	−0.06848 (16)	0.23999 (13)	0.13222 (13)	0.0171 (5)
O2b	0.24662 (16)	0.53595 (14)	0.10757 (15)	0.0220 (5)
N1a	0.52918 (19)	0.45461 (16)	0.11171 (16)	0.0156 (5)
N2a	0.62725 (19)	0.23425 (16)	0.23755 (15)	0.0151 (5)
N3a	0.70464 (19)	0.28615 (17)	−0.00128 (16)	0.0161 (5)
N1b	0.02925 (19)	0.45795 (17)	0.11576 (17)	0.0170 (6)
N2b	0.14445 (19)	0.24619 (16)	0.23590 (16)	0.0156 (5)
N3b	0.1948 (2)	0.28665 (18)	0.00034 (16)	0.0175 (6)
C1a	0.6214 (2)	0.5421 (2)	0.12087 (19)	0.0164 (6)
C2a	0.5677 (2)	0.6759 (2)	0.1237 (2)	0.0201 (7)
C3a	0.5037 (3)	0.7481 (2)	0.0341 (2)	0.0263 (8)
C4a	0.4576 (3)	0.8722 (2)	0.0364 (3)	0.0398 (10)
C5a	0.4753 (3)	0.9279 (2)	0.1307 (3)	0.0465 (11)
C6a	0.5401 (3)	0.8611 (2)	0.2227 (3)	0.0404 (10)
C7a	0.5858 (3)	0.7377 (2)	0.2164 (2)	0.0283 (8)
C8a	0.5386 (2)	0.21972 (19)	0.36624 (18)	0.0171 (7)
C9a	0.5444 (3)	0.3396 (2)	0.4199 (2)	0.0258 (8)

C10a	0.5794 (2)	0.10097 (19)	0.45365 (18)	0.0173 (7)
C11a	0.4765 (3)	0.0426 (2)	0.5600 (2)	0.0256 (7)
C12a	0.5104 (3)	−0.0605 (2)	0.6464 (2)	0.0330 (8)
C13a	0.6473 (3)	−0.1063 (2)	0.6292 (2)	0.0312 (8)
C14a	0.7496 (3)	−0.0495 (2)	0.5234 (2)	0.0285 (8)
C15a	0.7155 (2)	0.0531 (2)	0.4358 (2)	0.0224 (7)
C16a	0.6926 (2)	0.27494 (19)	−0.12562 (18)	0.0167 (6)
C17a	0.7548 (3)	0.1462 (2)	−0.1518 (2)	0.0234 (7)
C18a	0.7592 (2)	0.38947 (19)	−0.22965 (19)	0.0176 (7)
C19a	0.8193 (2)	0.4951 (2)	−0.2049 (2)	0.0212 (7)
C20a	0.8750 (3)	0.5991 (2)	−0.3023 (2)	0.0275 (8)
C21a	0.8718 (3)	0.6005 (2)	−0.4246 (2)	0.0275 (8)
C22a	0.8103 (3)	0.4961 (2)	−0.4499 (2)	0.0272 (8)
C23a	0.7555 (2)	0.3923 (2)	−0.3536 (2)	0.0235 (7)
C1b	0.1223 (2)	0.5539 (2)	0.10859 (18)	0.0166 (7)
C2b	0.0578 (2)	0.68541 (19)	0.1059 (2)	0.0177 (7)
C3b	−0.0204 (2)	0.7421 (2)	0.02101 (19)	0.0187 (7)
C4b	−0.0835 (3)	0.8603 (2)	0.0210 (2)	0.0246 (7)
C5b	−0.0678 (3)	0.9280 (2)	0.1089 (2)	0.0281 (8)
C6b	0.0107 (3)	0.8774 (2)	0.1950 (2)	0.0327 (9)
C7b	0.0715 (3)	0.7579 (2)	0.1917 (2)	0.0246 (8)
C8b	0.0778 (2)	0.24297 (19)	0.36791 (18)	0.0178 (7)
C9b	0.1309 (3)	0.3555 (2)	0.4108 (2)	0.0253 (7)
C10b	0.1009 (2)	0.1136 (2)	0.45054 (19)	0.0178 (7)
C11b	0.0436 (3)	0.0910 (2)	0.5800 (2)	0.0260 (7)
C12b	0.0627 (3)	−0.0255 (2)	0.6578 (2)	0.0277 (8)
C13b	0.1401 (3)	−0.1223 (2)	0.6088 (2)	0.0270 (8)
C14b	0.1980 (3)	−0.1008 (2)	0.4801 (2)	0.0267 (8)
C15b	0.1790 (2)	0.0156 (2)	0.40209 (19)	0.0218 (7)
C16b	0.1742 (2)	0.3030 (2)	−0.12632 (19)	0.0214 (7)
C17b	0.2172 (3)	0.1792 (2)	−0.1735 (2)	0.0365 (9)
C18b	0.2550 (2)	0.4184 (2)	−0.21891 (19)	0.0196 (7)
C19b	0.2153 (3)	0.4637 (2)	−0.3311 (2)	0.0269 (8)
C20b	0.2915 (3)	0.5613 (2)	−0.4233 (2)	0.0337 (9)
C21b	0.4089 (3)	0.6167 (2)	−0.4052 (2)	0.0334 (9)
C22b	0.4476 (3)	0.5742 (2)	−0.2924 (2)	0.0298 (8)
C23b	0.3701 (3)	0.4758 (2)	−0.1995 (2)	0.0238 (7)
H1c4a	0.413696	0.919017	−0.027196	0.0478*
H1c5a	0.44259	1.013983	0.133401	0.0559*
H1c6a	0.552669	0.900101	0.288714	0.0484*
H1c8a	0.443119	0.208923	0.361198	0.0205*
H1c9a	0.487622	0.324487	0.504835	0.0309*
H2c9a	0.640552	0.357035	0.418827	0.0309*
H3c9a	0.508482	0.412272	0.36983	0.0309*
H1c11a	0.381568	0.074289	0.573319	0.0308*
H1c12a	0.438556	−0.100546	0.718595	0.0396*
H1c13a	0.671006	−0.17667	0.690061	0.0375*
H1c14a	0.844563	−0.081291	0.510522	0.0342*

H1c15a	0.786928	0.091158	0.362345	0.0269*
H1c16a	0.594075	0.276444	−0.12536	0.02*
H1c17a	0.742329	0.13601	−0.231136	0.028*
H2c17a	0.853919	0.145249	−0.154167	0.028*
H3c17a	0.707144	0.076649	−0.086357	0.028*
H1c19a	0.822149	0.496072	−0.12043	0.0254*
H1c20a	0.916377	0.671138	−0.284225	0.033*
H1c21a	0.911381	0.672317	−0.49121	0.033*
H1c22a	0.806024	0.496343	−0.53433	0.0327*
H1c23a	0.714082	0.320584	−0.372205	0.0282*
H1c4b	−0.13747	0.895182	−0.038952	0.0295*
H1c5b	−0.111496	1.010522	0.110254	0.0338*
H1c6b	0.022672	0.924411	0.255697	0.0392*
H1c8b	−0.022252	0.252785	0.37658	0.0214*
H1c9b	0.07756	0.357345	0.494463	0.0303*
H2c9b	0.229297	0.344342	0.409801	0.0303*
H3c9b	0.119049	0.435372	0.354842	0.0303*
H1c11b	−0.010042	0.157325	0.61581	0.0312*
H1c12b	0.021655	−0.039111	0.746554	0.0333*
H1c13b	0.153655	−0.202887	0.662869	0.0325*
H1c14b	0.251796	−0.167404	0.444865	0.0321*
H1c15b	0.220237	0.028844	0.31336	0.0262*
H1c16b	0.07572	0.319982	−0.121146	0.0257*
H1c17b	0.206173	0.190041	−0.257602	0.0438*
H2c17b	0.314294	0.16119	−0.172967	0.0438*
H3c17b	0.158091	0.108701	−0.119636	0.0438*
H1c19b	0.133719	0.426594	−0.344647	0.0323*
H1c20b	0.262897	0.590967	−0.500341	0.0404*
H1c21b	0.462776	0.683548	−0.469753	0.0401*
H1c22b	0.528053	0.612603	−0.278421	0.0358*
H1c23b	0.396857	0.447694	−0.121396	0.0286*
H1n1a	0.4466 (15)	0.481 (2)	0.103 (3)	0.0187*
H1n2a	0.7166 (11)	0.244 (3)	0.228 (2)	0.0182*
H1n3a	0.7867 (15)	0.281 (3)	0.015 (2)	0.0193*
H1n1b	−0.0566 (14)	0.481 (3)	0.115 (3)	0.0204*
H1n2b	0.2351 (10)	0.246 (3)	0.217 (2)	0.0187*
H1n3b	0.2793 (15)	0.274 (3)	0.011 (3)	0.021*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P1a	0.0123 (2)	0.0121 (2)	0.0137 (2)	0.00083 (16)	−0.00338 (18)	−0.00343 (17)
P1b	0.0126 (2)	0.0130 (2)	0.0142 (2)	0.00084 (17)	−0.00369 (18)	−0.00329 (17)
F1a	0.0372 (8)	0.0269 (7)	0.0317 (7)	−0.0001 (6)	−0.0154 (6)	0.0032 (6)
F2a	0.0520 (10)	0.0373 (8)	0.0316 (8)	−0.0070 (7)	−0.0123 (7)	−0.0156 (6)
F1b	0.0331 (8)	0.0215 (6)	0.0225 (6)	0.0036 (5)	−0.0126 (5)	−0.0070 (5)
F2b	0.0508 (10)	0.0352 (8)	0.0397 (8)	0.0061 (7)	−0.0294 (7)	−0.0157 (6)
O1a	0.0147 (7)	0.0156 (7)	0.0189 (7)	0.0006 (5)	−0.0045 (6)	−0.0053 (5)

O2a	0.0150 (8)	0.0206 (7)	0.0311 (8)	0.0015 (6)	−0.0076 (6)	−0.0082 (6)
O1b	0.0155 (7)	0.0160 (7)	0.0205 (7)	0.0007 (5)	−0.0050 (6)	−0.0047 (5)
O2b	0.0155 (8)	0.0214 (8)	0.0301 (8)	−0.0001 (6)	−0.0071 (6)	−0.0060 (6)
N1a	0.0123 (9)	0.0147 (8)	0.0208 (8)	0.0016 (6)	−0.0055 (7)	−0.0047 (6)
N2a	0.0124 (9)	0.0176 (8)	0.0146 (8)	0.0003 (6)	−0.0027 (7)	−0.0026 (6)
N3a	0.0134 (9)	0.0203 (8)	0.0157 (8)	0.0024 (7)	−0.0048 (7)	−0.0055 (6)
N1b	0.0115 (9)	0.0162 (8)	0.0242 (8)	0.0008 (7)	−0.0062 (7)	−0.0047 (7)
N2b	0.0122 (9)	0.0200 (8)	0.0145 (8)	0.0018 (7)	−0.0027 (7)	−0.0045 (6)
N3b	0.0139 (9)	0.0251 (9)	0.0144 (8)	0.0017 (7)	−0.0049 (7)	−0.0047 (7)
C1a	0.0167 (11)	0.0160 (9)	0.0157 (9)	0.0005 (8)	−0.0032 (8)	−0.0022 (7)
C2a	0.0172 (11)	0.0145 (10)	0.0261 (11)	−0.0016 (8)	0.0008 (8)	−0.0059 (8)
C3a	0.0219 (12)	0.0180 (10)	0.0337 (12)	−0.0011 (9)	−0.0025 (10)	0.0009 (9)
C4a	0.0305 (15)	0.0163 (12)	0.0611 (18)	0.0017 (10)	−0.0012 (13)	0.0042 (11)
C5a	0.0372 (16)	0.0127 (11)	0.073 (2)	0.0004 (10)	0.0163 (14)	−0.0083 (12)
C6a	0.0393 (16)	0.0259 (13)	0.0505 (17)	−0.0107 (11)	0.0131 (13)	−0.0226 (12)
C7a	0.0271 (13)	0.0231 (11)	0.0310 (12)	−0.0069 (9)	0.0041 (10)	−0.0096 (9)
C8a	0.0160 (11)	0.0189 (10)	0.0162 (10)	0.0015 (8)	−0.0036 (8)	−0.0042 (8)
C9a	0.0404 (14)	0.0202 (11)	0.0187 (10)	0.0051 (9)	−0.0088 (9)	−0.0074 (8)
C10a	0.0206 (11)	0.0170 (10)	0.0159 (9)	−0.0007 (8)	−0.0064 (8)	−0.0046 (8)
C11a	0.0238 (12)	0.0271 (11)	0.0221 (10)	−0.0008 (9)	−0.0016 (9)	−0.0016 (8)
C12a	0.0342 (15)	0.0308 (13)	0.0250 (12)	−0.0021 (10)	−0.0008 (10)	0.0059 (9)
C13a	0.0369 (14)	0.0241 (12)	0.0300 (12)	−0.0001 (10)	−0.0133 (11)	0.0056 (9)
C14a	0.0257 (13)	0.0235 (11)	0.0340 (12)	0.0001 (9)	−0.0103 (10)	0.0020 (9)
C15a	0.0205 (11)	0.0205 (10)	0.0239 (11)	0.0001 (8)	−0.0054 (9)	0.0001 (8)
C16a	0.0163 (11)	0.0197 (10)	0.0154 (9)	0.0004 (8)	−0.0052 (8)	−0.0053 (8)
C17a	0.0303 (13)	0.0169 (10)	0.0200 (10)	−0.0007 (9)	0.0003 (9)	−0.0051 (8)
C18a	0.0173 (11)	0.0169 (10)	0.0178 (10)	0.0039 (8)	−0.0045 (8)	−0.0030 (8)
C19a	0.0221 (11)	0.0216 (10)	0.0199 (10)	−0.0005 (8)	−0.0055 (9)	−0.0043 (8)
C20a	0.0306 (13)	0.0225 (11)	0.0284 (12)	−0.0042 (9)	−0.0055 (10)	−0.0045 (9)
C21a	0.0296 (13)	0.0227 (11)	0.0244 (11)	0.0003 (9)	−0.0035 (9)	0.0034 (9)
C22a	0.0339 (13)	0.0281 (11)	0.0182 (10)	0.0015 (9)	−0.0072 (9)	−0.0011 (9)
C23a	0.0279 (12)	0.0229 (11)	0.0208 (10)	−0.0008 (9)	−0.0085 (9)	−0.0036 (8)
C1b	0.0162 (11)	0.0170 (10)	0.0169 (9)	0.0003 (8)	−0.0044 (8)	−0.0037 (8)
C2b	0.0165 (11)	0.0153 (10)	0.0210 (10)	−0.0016 (8)	−0.0034 (8)	−0.0040 (8)
C3b	0.0205 (11)	0.0163 (10)	0.0187 (10)	−0.0025 (8)	−0.0033 (8)	−0.0035 (8)
C4b	0.0262 (13)	0.0167 (10)	0.0277 (11)	0.0014 (8)	−0.0058 (9)	0.0006 (8)
C5b	0.0312 (14)	0.0148 (10)	0.0355 (12)	0.0013 (9)	−0.0024 (10)	−0.0060 (9)
C6b	0.0413 (15)	0.0239 (12)	0.0362 (13)	−0.0004 (10)	−0.0082 (11)	−0.0150 (10)
C7b	0.0291 (13)	0.0215 (11)	0.0266 (11)	−0.0016 (9)	−0.0108 (10)	−0.0076 (9)
C8b	0.0174 (11)	0.0214 (10)	0.0152 (9)	0.0030 (8)	−0.0028 (8)	−0.0068 (8)
C9b	0.0348 (14)	0.0224 (11)	0.0218 (10)	0.0042 (9)	−0.0100 (9)	−0.0086 (8)
C10b	0.0147 (10)	0.0232 (11)	0.0168 (10)	−0.0027 (8)	−0.0060 (8)	−0.0041 (8)
C11b	0.0257 (12)	0.0324 (12)	0.0180 (10)	0.0021 (9)	−0.0011 (9)	−0.0065 (9)
C12b	0.0297 (13)	0.0342 (12)	0.0160 (10)	−0.0052 (10)	−0.0030 (9)	−0.0004 (9)
C13b	0.0306 (13)	0.0245 (11)	0.0251 (11)	−0.0062 (9)	−0.0110 (10)	0.0025 (9)
C14b	0.0350 (14)	0.0210 (11)	0.0238 (11)	0.0007 (9)	−0.0062 (10)	−0.0053 (8)
C15b	0.0263 (12)	0.0216 (10)	0.0173 (10)	−0.0013 (8)	−0.0037 (8)	−0.0052 (8)
C16b	0.0211 (11)	0.0300 (12)	0.0155 (10)	−0.0014 (9)	−0.0064 (8)	−0.0071 (8)

C17b	0.0572 (18)	0.0270 (12)	0.0246 (12)	−0.0130 (11)	−0.0025 (11)	−0.0104 (9)
C18b	0.0225 (12)	0.0200 (10)	0.0174 (10)	0.0066 (8)	−0.0055 (8)	−0.0070 (8)
C19b	0.0393 (15)	0.0257 (11)	0.0202 (10)	0.0065 (10)	−0.0127 (10)	−0.0094 (9)
C20b	0.0564 (18)	0.0265 (12)	0.0196 (11)	0.0109 (11)	−0.0132 (11)	−0.0054 (9)
C21b	0.0483 (17)	0.0204 (11)	0.0224 (11)	0.0043 (10)	0.0021 (11)	0.0017 (9)
C22b	0.0282 (13)	0.0240 (11)	0.0323 (12)	0.0013 (10)	−0.0036 (10)	−0.0002 (9)
C23b	0.0249 (12)	0.0247 (11)	0.0194 (10)	0.0021 (9)	−0.0067 (9)	0.0017 (8)

Geometric parameters (Å, º)

P1a—O1a	1.4808 (17)	C17a—H2c17a	0.9599
P1a—N1a	1.7081 (18)	C17a—H3c17a	0.96
P1a—N2a	1.6219 (19)	C18a—C19a	1.396 (3)
P1a—N3a	1.6199 (17)	C18a—C23a	1.398 (3)
P1b—O1b	1.4784 (17)	C19a—C20a	1.391 (3)
P1b—N1b	1.6986 (19)	C19a—H1c19a	0.9599
P1b—N2b	1.618 (2)	C20a—C21a	1.380 (4)
P1b—N3b	1.6181 (17)	C20a—H1c20a	0.9599
F1a—C3a	1.352 (3)	C21a—C22a	1.395 (4)
F2a—C7a	1.346 (3)	C21a—H1c21a	0.96
F1b—C3b	1.349 (3)	C22a—C23a	1.382 (3)
F2b—C7b	1.349 (3)	C22a—H1c22a	0.9601
O2a—C1a	1.225 (3)	C23a—H1c23a	0.9601
O2b—C1b	1.218 (3)	C1b—C2b	1.505 (3)
N1a—C1a	1.355 (3)	C2b—C3b	1.390 (3)
N1a—H1n1a	0.862 (18)	C2b—C7b	1.392 (4)
N2a—C8a	1.469 (2)	C3b—C4b	1.375 (3)
N2a—H1n2a	0.859 (12)	C4b—C5b	1.383 (4)
N3a—C16a	1.463 (3)	C4b—H1c4b	0.9601
N3a—H1n3a	0.861 (19)	C5b—C6b	1.386 (4)
N1b—C1b	1.367 (3)	C5b—H1c5b	0.96
N1b—H1n1b	0.865 (16)	C6b—C7b	1.383 (3)
N2b—C8b	1.459 (3)	C6b—H1c6b	0.9599
N2b—H1n2b	0.856 (10)	C8b—C9b	1.534 (3)
N3b—C16b	1.460 (3)	C8b—C10b	1.523 (3)
N3b—H1n3b	0.861 (17)	C8b—H1c8b	0.9601
C1a—C2a	1.498 (3)	C9b—H1c9b	0.96
C2a—C3a	1.389 (3)	C9b—H2c9b	0.9599
C2a—C7a	1.396 (4)	C9b—H3c9b	0.96
C3a—C4a	1.378 (3)	C10b—C11b	1.395 (3)
C4a—C5a	1.370 (5)	C10b—C15b	1.393 (3)
C4a—H1c4a	0.9601	C11b—C12b	1.384 (3)
C5a—C6a	1.393 (5)	C11b—H1c11b	0.96
C5a—H1c5a	0.96	C12b—C13b	1.382 (4)
C6a—C7a	1.377 (4)	C12b—H1c12b	0.96
C6a—H1c6a	0.9599	C13b—C14b	1.388 (3)
C8a—C9a	1.531 (3)	C13b—H1c13b	0.96
C8a—C10a	1.525 (3)	C14b—C15b	1.385 (3)

C8a—H1c8a	0.9601	C14b—H1c14b	0.96
C9a—H1c9a	0.96	C15b—H1c15b	0.96
C9a—H2c9a	0.9599	C16b—C17b	1.528 (4)
C9a—H3c9a	0.96	C16b—C18b	1.521 (3)
C10a—C11a	1.397 (3)	C16b—H1c16b	0.9601
C10a—C15a	1.385 (3)	C17b—H1c17b	0.9601
C11a—C12a	1.384 (3)	C17b—H2c17b	0.9599
C11a—H1c11a	0.9601	C17b—H3c17b	0.9601
C12a—C13a	1.384 (4)	C18b—C19b	1.392 (3)
C12a—H1c12a	0.9601	C18b—C23b	1.383 (4)
C13a—C14a	1.385 (3)	C19b—C20b	1.381 (3)
C13a—H1c13a	0.96	C19b—H1c19b	0.9601
C14a—C15a	1.390 (3)	C20b—C21b	1.385 (4)
C14a—H1c14a	0.9599	C20b—H1c20b	0.9601
C15a—H1c15a	0.9599	C21b—C22b	1.389 (4)
C16a—C17a	1.530 (3)	C21b—H1c21b	0.96
C16a—C18a	1.526 (2)	C22b—C23b	1.395 (3)
C16a—H1c16a	0.9601	C22b—H1c22b	0.9599
C17a—H1c17a	0.9601	C23b—H1c23b	0.9599

O1a—P1a—N1a	103.29 (9)	C18a—C19a—C20a	120.2 (2)
O1a—P1a—N2a	115.49 (8)	C18a—C19a—H1c19a	119.9
O1a—P1a—N3a	115.08 (10)	C20a—C19a—H1c19a	119.91
N1a—P1a—N2a	109.87 (10)	C19a—C20a—C21a	121.1 (2)
N1a—P1a—N3a	109.77 (8)	C19a—C20a—H1c20a	119.45
N2a—P1a—N3a	103.37 (9)	C21a—C20a—H1c20a	119.45
O1b—P1b—N1b	102.89 (9)	C20a—C21a—C22a	119.1 (2)
O1b—P1b—N2b	116.28 (8)	C20a—C21a—H1c21a	120.44
O1b—P1b—N3b	116.30 (10)	C22a—C21a—H1c21a	120.43
N1b—P1b—N2b	109.74 (10)	C21a—C22a—C23a	120.0 (2)
N1b—P1b—N3b	109.71 (9)	C21a—C22a—H1c22a	120.01
N2b—P1b—N3b	101.94 (10)	C23a—C22a—H1c22a	120
P1a—N1a—C1a	123.03 (15)	C18a—C23a—C22a	121.4 (2)
P1a—N1a—H1n1a	118.7 (18)	C18a—C23a—H1c23a	119.33
C1a—N1a—H1n1a	118.3 (18)	C22a—C23a—H1c23a	119.32
P1a—N2a—C8a	122.96 (14)	O2b—C1b—N1b	123.66 (19)
P1a—N2a—H1n2a	114.9 (17)	O2b—C1b—C2b	121.8 (2)
C8a—N2a—H1n2a	116.2 (18)	N1b—C1b—C2b	114.51 (19)
P1a—N3a—C16a	123.75 (16)	C1b—C2b—C3b	123.3 (2)
P1a—N3a—H1n3a	116.7 (17)	C1b—C2b—C7b	121.3 (2)
C16a—N3a—H1n3a	119.4 (18)	C3b—C2b—C7b	115.4 (2)
P1b—N1b—C1b	125.57 (16)	F1b—C3b—C2b	118.00 (19)
P1b—N1b—H1n1b	118.1 (18)	F1b—C3b—C4b	118.5 (2)
C1b—N1b—H1n1b	116.3 (18)	C2b—C3b—C4b	123.5 (2)
P1b—N2b—C8b	124.36 (15)	C3b—C4b—C5b	118.9 (2)
P1b—N2b—H1n2b	116.7 (17)	C3b—C4b—H1c4b	120.55
C8b—N2b—H1n2b	115.1 (18)	C5b—C4b—H1c4b	120.55
P1b—N3b—C16b	123.82 (16)	C4b—C5b—C6b	120.3 (2)

P1b—N3b—H1n3b	117.7 (19)	C4b—C5b—H1c5b	119.82
C16b—N3b—H1n3b	118.4 (18)	C6b—C5b—H1c5b	119.83
O2a—C1a—N1a	122.3 (2)	C5b—C6b—C7b	118.6 (3)
O2a—C1a—C2a	120.9 (2)	C5b—C6b—H1c6b	120.69
N1a—C1a—C2a	116.76 (19)	C7b—C6b—H1c6b	120.7
C1a—C2a—C3a	123.5 (2)	F2b—C7b—C2b	118.1 (2)
C1a—C2a—C7a	120.6 (2)	F2b—C7b—C6b	118.7 (2)
C3a—C2a—C7a	115.8 (2)	C2b—C7b—C6b	123.2 (2)
F1a—C3a—C2a	118.0 (2)	N2b—C8b—C9b	111.10 (16)
F1a—C3a—C4a	119.0 (2)	N2b—C8b—C10b	110.97 (17)
C2a—C3a—C4a	122.9 (3)	N2b—C8b—H1c8b	107.94
C3a—C4a—C5a	119.1 (3)	C9b—C8b—C10b	111.28 (19)
C3a—C4a—H1c4a	120.45	C9b—C8b—H1c8b	107.62
C5a—C4a—H1c4a	120.46	C10b—C8b—H1c8b	107.75
C4a—C5a—C6a	120.8 (2)	C8b—C9b—H1c9b	109.47
C4a—C5a—H1c5a	119.58	C8b—C9b—H2c9b	109.47
C6a—C5a—H1c5a	119.59	C8b—C9b—H3c9b	109.47
C5a—C6a—C7a	118.2 (3)	H1c9b—C9b—H2c9b	109.48
C5a—C6a—H1c6a	120.88	H1c9b—C9b—H3c9b	109.47
C7a—C6a—H1c6a	120.88	H2c9b—C9b—H3c9b	109.48
F2a—C7a—C2a	118.2 (2)	C8b—C10b—C11b	119.68 (19)
F2a—C7a—C6a	118.7 (3)	C8b—C10b—C15b	122.50 (17)
C2a—C7a—C6a	123.1 (3)	C11b—C10b—C15b	117.82 (19)
N2a—C8a—C9a	112.49 (16)	C10b—C11b—C12b	121.1 (2)
N2a—C8a—C10a	111.31 (16)	C10b—C11b—H1c11b	119.44
N2a—C8a—H1c8a	106.17	C12b—C11b—H1c11b	119.44
C9a—C8a—C10a	109.74 (18)	C11b—C12b—C13b	120.6 (2)
C9a—C8a—H1c8a	107.86	C11b—C12b—H1c12b	119.67
C10a—C8a—H1c8a	109.12	C13b—C12b—H1c12b	119.68
C8a—C9a—H1c9a	109.47	C12b—C13b—C14b	118.8 (2)
C8a—C9a—H2c9a	109.47	C12b—C13b—H1c13b	120.61
C8a—C9a—H3c9a	109.47	C14b—C13b—H1c13b	120.61
H1c9a—C9a—H2c9a	109.48	C13b—C14b—C15b	120.7 (2)
H1c9a—C9a—H3c9a	109.47	C13b—C14b—H1c14b	119.66
H2c9a—C9a—H3c9a	109.48	C15b—C14b—H1c14b	119.66
C8a—C10a—C11a	118.23 (19)	C10b—C15b—C14b	120.92 (19)
C8a—C10a—C15a	122.90 (16)	C10b—C15b—H1c15b	119.54
C11a—C10a—C15a	118.77 (19)	C14b—C15b—H1c15b	119.54
C10a—C11a—C12a	120.5 (2)	N3b—C16b—C17b	108.99 (18)
C10a—C11a—H1c11a	119.75	N3b—C16b—C18b	113.5 (2)
C12a—C11a—H1c11a	119.75	N3b—C16b—H1c16b	107.25
C11a—C12a—C13a	120.4 (2)	C17b—C16b—C18b	110.12 (17)
C11a—C12a—H1c12a	119.79	C17b—C16b—H1c16b	110.84
C13a—C12a—H1c12a	119.8	C18b—C16b—H1c16b	106.06
C12a—C13a—C14a	119.4 (2)	C16b—C17b—H1c17b	109.47
C12a—C13a—H1c13a	120.29	C16b—C17b—H2c17b	109.47
C14a—C13a—H1c13a	120.3	C16b—C17b—H3c17b	109.47
C13a—C14a—C15a	120.3 (2)	H1c17b—C17b—H2c17b	109.48

C13a—C14a—H1c14a	119.85	H1c17b—C17b—H3c17b	109.46
C15a—C14a—H1c14a	119.85	H2c17b—C17b—H3c17b	109.47
C10a—C15a—C14a	120.59 (18)	C16b—C18b—C19b	118.2 (2)
C10a—C15a—H1c15a	119.7	C16b—C18b—C23b	123.1 (2)
C14a—C15a—H1c15a	119.71	C19b—C18b—C23b	118.69 (19)
N3a—C16a—C17a	109.06 (17)	C18b—C19b—C20b	120.9 (3)
N3a—C16a—C18a	113.06 (18)	C18b—C19b—H1c19b	119.53
N3a—C16a—H1c16a	108.25	C20b—C19b—H1c19b	119.53
C17a—C16a—C18a	112.13 (16)	C19b—C20b—C21b	120.4 (2)
C17a—C16a—H1c16a	109.25	C19b—C20b—H1c20b	119.8
C18a—C16a—H1c16a	104.91	C21b—C20b—H1c20b	119.81
C16a—C17a—H1c17a	109.47	C20b—C21b—C22b	119.2 (2)
C16a—C17a—H2c17a	109.47	C20b—C21b—H1c21b	120.42
C16a—C17a—H3c17a	109.47	C22b—C21b—H1c21b	120.43
H1c17a—C17a—H2c17a	109.47	C21b—C22b—C23b	120.2 (3)
H1c17a—C17a—H3c17a	109.46	C21b—C22b—H1c22b	119.88
H2c17a—C17a—H3c17a	109.48	C23b—C22b—H1c22b	119.88
C16a—C18a—C19a	122.2 (2)	C18b—C23b—C22b	120.5 (2)
C16a—C18a—C23a	119.5 (2)	C18b—C23b—H1c23b	119.72
C19a—C18a—C23a	118.25 (18)	C22b—C23b—H1c23b	119.74
P1a—N2a—C8a—C9a	−88.5 (2)	O1a—P1a—N3a—C16a	25.1 (2)
P1b—N2b—C8b—C9b	−101.0 (2)	O1b—P1b—N3b—C16b	42.1 (2)
P1a—N3a—C16a—C17a	−117.68 (19)	P1a—N1a—C1a—O2a	1.4 (3)
P1b—N3b—C16b—C17b	−121.47 (19)	P1b—N1b—C1b—O2b	−1.2 (3)
O1a—P1a—N1a—C1a	177.16 (16)	P1a—N2a—C8a—C10a	147.93 (15)
O1b—P1b—N1b—C1b	178.46 (17)	P1b—N2b—C8b—C10b	134.66 (16)
O1a—P1a—N2a—C8a	−51.78 (19)	P1a—N3a—C16a—C18a	116.90 (18)
O1b—P1b—N2b—C8b	−55.44 (19)	P1b—N3b—C16b—C18b	115.40 (19)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5*a*—H1*c*5*a*···O1*a*^{i}	0.96	2.34	3.271 (3)	162.23
N1*a*—H1*n*1*a*···O2*b*	0.862 (18)	2.006 (16)	2.863 (2)	173 (3)
N2*a*—H1*n*2*a*···O1*b*^{ii}	0.859 (12)	2.110 (12)	2.907 (2)	154 (3)
N3*a*—H1*n*3*a*···O1*b*^{ii}	0.861 (19)	2.13 (2)	2.938 (3)	155 (2)
N1*b*—H1*n*1*b*···O2*a*^{iii}	0.865 (16)	1.951 (14)	2.812 (2)	173 (2)
N2*b*—H1*n*2*b*···O1*a*	0.856 (10)	2.046 (13)	2.858 (2)	158 (3)
N3*b*—H1*n*3*b*···O1*a*	0.861 (17)	2.07 (2)	2.887 (3)	157 (2)

Symmetry codes: (i) *x*, *y*+1, *z*; (ii) *x*+1, *y*, *z*; (iii) *x*−1, *y*, *z*.