

Crystal structure of (1,4-diphenyl-4*H*-1,2,4-triazol-3-yl)phenylamine difluorophosphate, and a survey of the difluorophosphate anion (PO_2F_2^-)

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Nitron is the trivial name of (1,4-diphenyl-4*H*-1,2,4-triazol-3-yl)phenylamine ($\text{C}_{20}\text{H}_{16}\text{N}_4$), a triazole derivative used as an analytical reagent for gravimetric analysis of the nitrate anion. The crystal structure of the difluorophosphate salt of Nitron, 3-anilino-1,4-diphenyl-1*H*-1,2,4-triazol-4-ium difluorophosphate, $\text{C}_{20}\text{H}_{17}\text{N}_4^+\cdot\text{PO}_2\text{F}_2^-$, is reported here. Within the protonated Nitron molecule, the triazole ring, one of the phenyl rings and the NHPH moiety are virtually coplanar, with the third phenyl ring inclined to the least-squares plane of the other three rings by $56.07(3)^\circ$. Intermolecular $\text{N}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds between cations and difluorophosphate anions lead to the formation of a three-dimensional network that is consolidated by additional $\pi-\pi$ stacking interactions between the triazole ring and one of the phenyl rings. Database surveys on inorganic, metal-organic and organic structures comprising the tetrahedral PO_2F_2 group reveal mean bond lengths of $\text{P}-\text{O} = 1.459(27)$ Å, $\text{P}-\text{F} = 1.530(21)$ Å, and angles of $\text{O}-\text{P}-\text{O} = 121.2(2.9)^\circ$, $\text{O}-\text{P}-\text{F} = 108.7(6)^\circ$, and $\text{F}-\text{P}-\text{F} = 98.5(2.6)^\circ$, using a dataset of 67 independent PO_2F_2^- anions or PO_2F_2 entities.

1. Chemical context

Nitron is the trivial name for the triazole derivative (1,4-diphenyl-4*H*-1,2,4-triazol-3-yl)phenylamine, $\text{C}_{20}\text{H}_{16}\text{N}_4$, that shows tautomerism and can be present in its zwitterionic form (**I**) or its NHC-type carbenic form (**II**) (Fig. 1). Nitron has been utilized as a reagent for gravimetric analysis of the nitrate anion ('Busch's reagent'; Busch, 1905) from slightly acidic solutions under formation of the salt $\text{C}_{20}\text{H}_{17}\text{N}_4^+\cdot\text{NO}_3^-$. In recent years, inexpensive Nitron was rediscovered as a stable *N*-heterocyclic carbene (Färber *et al.*, 2012) that can be reacted with several coinage or other noble metals to yield corresponding metal complexes (Hitzel *et al.*, 2014; Thie *et al.*, 2016). The Nitron salt of difluorophosphoric acid, $\text{C}_{20}\text{H}_{17}\text{N}_4^+\cdot\text{PO}_2\text{F}_2^-$ (**III**) was reported by Lange more than 90

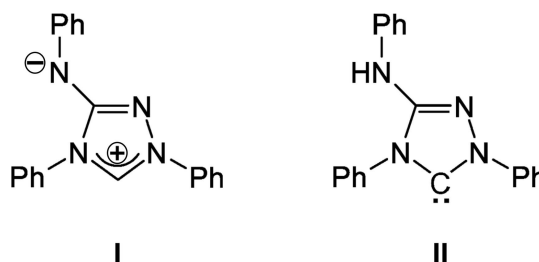
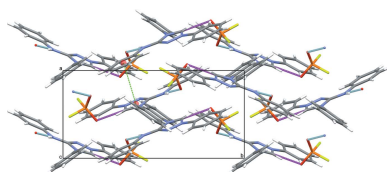
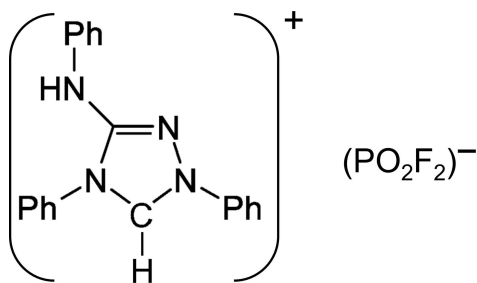


Figure 1
Structure of zwitterionic Nitron (**I**), and of its NHC-carbene tautomer (**II**).

years ago (Lange, 1929). It can be used as a precursor for obtaining difluorophosphates of several metals or other cations through metathesis reactions.



The synthesis, crystallization and structure analysis of **III** are reported here, together with a survey of the structural characteristics of the difluorophosphate anion present in inorganic, metal–organic and organic compounds.

2. Structural commentary

The asymmetric unit of **III** is composed of a Nitron molecule protonated at the C1 atom of the triazole ring, assuming the NHC-type tautomer **II** to be prevalent in Nitron itself, and a PO_2F_2^- anion (Fig. 2).

The central triazole ring (C1, C2, N1–N3), the phenyl ring attached to N2 (C9–C14) and the NPh moiety attached to C2 (N4, C15–C20) are virtually co-planar with the r.m.s. deviation of the 18 non-H atoms being 0.0666 Å [greatest deviation 0.1250 (13) Å for the phenyl C19 atom]. The third phenyl ring (C3–C8) is inclined to the least-squares plane of the three aforementioned rings by 56.07 (3)° (Fig. 2). A weak intra-

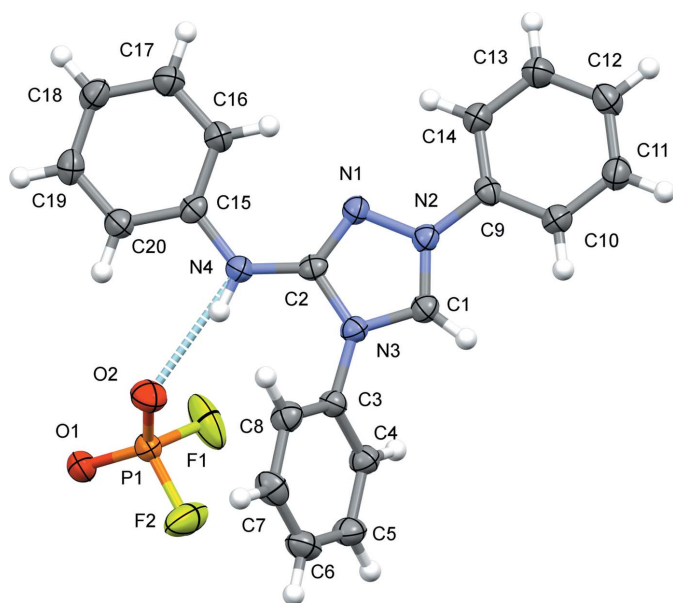


Figure 2
The asymmetric unit of **III**, showing the molecular components with displacement ellipsoids for non-H atoms drawn at the 75% probability level. H atoms are given as spheres of arbitrary radius; N–H...O hydrogen bonding between the organic cation and the inorganic anion is shown as a light-blue dashed line.

Table 1
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C1–H1...O1 ⁱ	0.95	2.02	2.9576 (17)	168
C20–H20...O2	0.95	2.44	3.2291 (17)	140
C16–H16...N1	0.95	2.22	2.8700 (18)	124
C10–H10...O1 ⁱ	0.95	2.45	3.3673 (17)	161
N4–H1N...O2	0.857 (19)	2.025 (19)	2.8614 (16)	165.0 (17)

Symmetry code: (i) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$.

Table 2
Selected geometric parameters (Å, °).

P1–O1	1.4684 (11)	P1–F2	1.5510 (10)
P1–O2	1.4686 (11)	P1–F1	1.5568 (10)
O1–P1–O2	123.22 (6)	O1–P1–F1	108.21 (6)
O1–P1–F2	107.75 (6)	O2–P1–F1	108.10 (6)
O2–P1–F2	109.20 (6)	F2–P1–F1	97.26 (7)

molecular hydrogen bond between a phenyl C–H group (C16–H16) and the free N atom (N1) of the triazole cycle stabilizes the conformation of the molecule (Table 1).

In **III**, the tetrahedral difluorophosphate anion shows the characteristic bond lengths distribution (Table 2) between two shorter P–O bonds (mean 1.468 Å) and two considerably longer P–F bonds (mean 1.554 Å). The distortion of the anion is evident not only by the two pairs of different bond lengths but even more so by the bond angles that partly deviate considerably from the ideal value of 109.47°. Whereas the O1–P–O2 angle is enlarged by about 14° relative to the ideal value, the F1–P–F2 angle is reduced by about 12°; the four O–P–F angles are rather similar, with a mean of 108.3°.

3. Supramolecular features

Aside from Coulombic interactions, the cation is hydrogen-bonded by an N–H...O interaction of medium strength between the amino group (N4) of the NPh moiety and one of the O atoms (O2) of the difluorophosphate anion. The other O atom (O1) of the anion is the acceptor atom of a weak C–H...O hydrogen bond with the protonated carbene C1 atom as the donor group. F atoms are not involved in hydrogen bonding, as frequently observed for related compounds containing the monofluorophosphate anion PO_3F^{2-} (Weil *et al.*, 2015). The two types of hydrogen-bonding interactions link the cations and anions into a three-dimensional network structure. Additional π – π stacking between the triazole ring (Cg_1) and the phenyl ring C15–C20 (Cg_2) with a centroid-to-centroid distance of $Cg_1\cdots Cg_2(2-x, 1-y, 1-z) = 3.5378$ (9) Å and a slippage of 0.643 Å consolidates the packing (Fig. 3).

4. Database survey

A search of the Cambridge Structural Database (CSD; Version 5.41, last update November 2019; Groom *et al.*, 2016) for Nitron revealed 17 hits, including various coinage metal

Table 3

 Averaged bond lengths (Å) and angles (°) in PO₂F₂ tetrahedra present in several compounds.

Compound	Independent PO ₂ F ₂ groups	P–O	P–F	O–P–O	O–P–F	F–P–F
NH ₄ PO ₂ F ₂ ^a	1	1.457	1.541	118.7	109.5	98.6
KPO ₂ F ₂ ^b	1	1.470	1.575	122.4	108.7	97.1
CsPO ₂ F ₂ ^c	1	1.480	1.545	121.0	108.5	99.0
LiB(PO ₂ F ₂) ₄ ^d	4 (1 disordered)	1.483	1.520	119.7	108.6	100.5
AgPO ₂ F ₂ ^e	3	1.459	1.511	119.9	108.1	103.3
Ag ^I ₄ Ag ^{II} ₅ (PO ₂ F ₂) ₁₄ ^e	7	1.481	1.511	117.8	109.4	99.9
Cu(PO ₂ F ₂) ₂ ^f	3	1.450	1.496	119.1	109.5	97.6
Cs ₂ Fe ₂ F ₃ (PO ₃ F) ₂ (PO ₂ F ₂) ₂ ^g	1	1.512	1.555	117.8	108.2	106.2
KFe ₂ (PO ₂ F ₂)(PO ₃ F) ₂ F ₂ ^g	1	1.509	1.569	115.6	109.3	103.4
SbF ₄ (PO ₂ F ₂) ^h	1	1.500	1.500	117.4	108.5	104.6
(NH ₄)Mn ₃ (PO ₃ F) ₂ (PO ₂ F ₂) ₂ ⁱ	1	1.482	1.572	116.6	109.8	100.0
(NH ₄)Co ₃ (PO ₃ F) ₂ (PO ₂ F ₂) ₂ ⁱ	1	1.486	1.554	114.9	110.1	100.8
Organic and metal–organic compounds ^j	42	1.449	1.532	122.3	108.5	97.5

(a) Harrison & Trotter (1969); (b) Harrison *et al.* (1966); (c) Trotter & Whitlow (1967); (d) Schulz *et al.* (2015); (e) Malinowski *et al.* (2015); (f) Begley *et al.* (1985); (g) Keates *et al.* (2013); (h) Schneider *et al.* (2001); (i) Jiang *et al.* (2020); (j) A detailed list of entries for these compounds is given in Table S1 of the supporting information.

complexes of Nitron (EJEZOK, EJICEH, EJICOR, EJIPOE, EJIPUK, EJIQAR, EJIQEV, EJIXOM; Thie *et al.*, 2016), with selenium bonded to the carbene C atom (EJICIL; Thie *et al.*, 2016), rhodium complexes (NITLAF, NITLUZ, SAKNAV, SAKNEZ; Hitzel *et al.*, 2014, Färber *et al.*, 2012), with a carbodithioate group attached (SAKNID; Färber *et al.*, 2012), and isotopic ethylenediaminetetra-acetatoaluminate and -gallate complexes (FADJIE, FADJUQ; Ilyukhin & Petrosyant, 2001). The structure of the hydrochloride methanol solvate of Nitron (NITLEJ; Hitzel *et al.*, 2014) is the most similar in comparison to **I** because it shows no direct coordination to a metal and is not derivatized. In (Nitron)⁺Cl[−]·CH₃OH, the central triazole ring is co-planar with only one phenyl ring (attached to N2). The second phenyl ring (attached to N3) and the NPh moiety (attached to C2) are inclined to the mean plane by 48.13 (7) and 31.42 (6)°, respectively. The chloride anion is hydrogen-bonded through

N–H···Cl and O–H···Cl interactions to the protonated Nitron molecule and the methanol solvent molecule, respectively. In all structures comprising Nitron, the N atom (equivalent to N4 in the title structure) is protonated like in **II**.

A search of the Inorganic Crystal Structure Database (ICSD; Zagorac *et al.*, 2019) and the CSD for the difluorophosphate anion or the PO₂F₂ entity revealed the crystal structures of twelve inorganic and 30 metal–organic or organic compounds (Table 3). For a statistical analysis of bond lengths and angles within a PO₂F₂ tetrahedron, only ordered PO₂F₂ groups were considered. In summary, 67 independent PO₂F₂ tetrahedra were used, leading to the following averaged bond lengths and angles: P–O = 1.459 (27) Å, P–F = 1.530 (21) Å; O–P–O = 121.2 (2.9)°, O–P–F = 108.7 (6)°, F–P–F = 98.5 (2.6)°. It is evident that the bond lengths and angles observed in **III** (Table 2) fall within these limits.

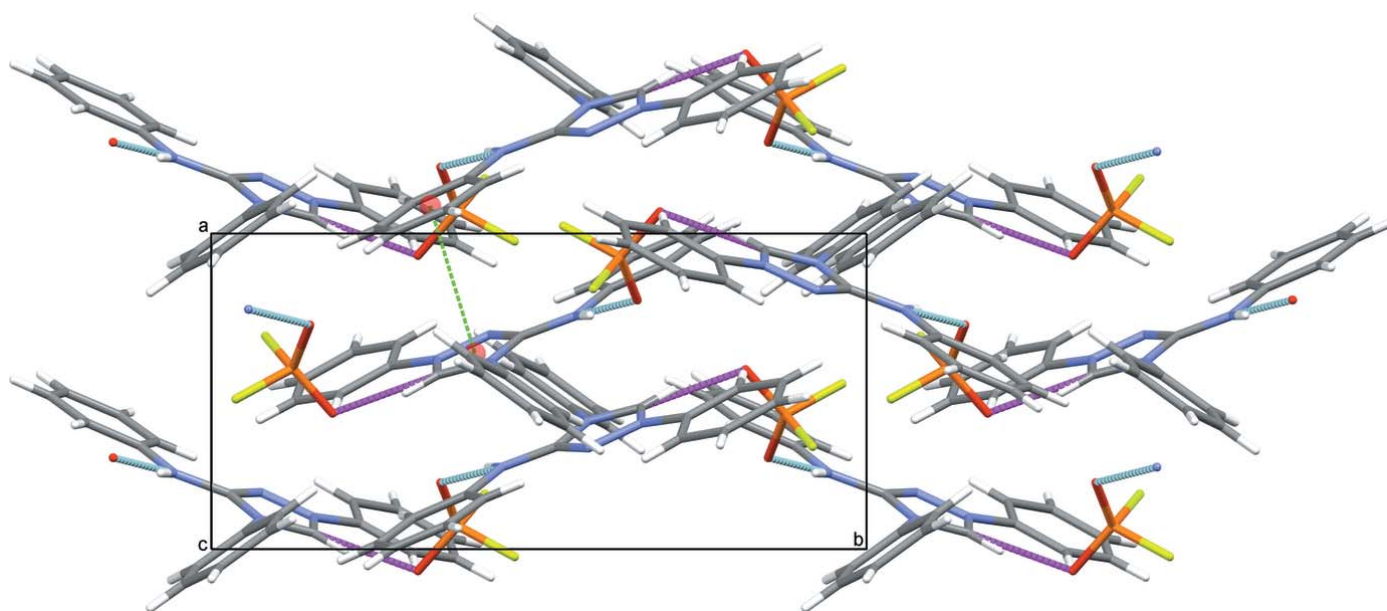


Figure 3

The packing of the organic cations and the inorganic anions in the crystal structure of **III** in a view along [001]. Intermolecular N–H···O and C–H···O bonds are shown as light-blue and magenta dashed lines, and π – π stacking interactions by green dashed lines.

Table 4
Experimental details.

Crystal data	
Chemical formula	C ₂₀ H ₁₇ N ₄ ⁺ ·PO ₂ F ₂ ⁻
<i>M</i> _r	414.35
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.3811 (5), 14.9963 (9), 16.9217 (10)
β (°)	102.138 (2)
<i>V</i> (Å ³)	1831.2 (2)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.20
Crystal size (mm)	0.50 × 0.10 × 0.10
Data collection	
Diffraction	Bruker APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T</i> _{min} , <i>T</i> _{max}	0.701, 0.746
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	30253, 5325, 4077
<i>R</i> _{int}	0.046
(sin θ/λ) _{max} (Å ⁻¹)	0.703
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.039, 0.100, 1.03
No. of reflections	5325
No. of parameters	266
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.38, -0.36

Computer programs: *APEX2* and *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b), *Mercury* (Macrae *et al.*, 2020) and *pubCIF* (Westrip, 2010).

5. Synthesis and crystallization

In a nickel crucible, P₂O₅ (2.67 g) and NH₄F (1.86 g) were thoroughly mixed. The open crucible was placed on a hot plate (≈ 420 K) where a vehement reaction took place within a few seconds. The crucible was then taken from the plate and cooled to room temperature. The obtained solid was dissolved in 50 ml water to which ammonia solution (25%_{w/v}) was added until neutralisation. Subsequently, the pH was adjusted to *ca.* 5 with a few drops of glacial acetic acid. Nitron (3 g) was then added in small portions to the cooled (273 K) acetic solution under constant stirring for about two h. The formed solid was separated by suction filtration and recrystallized from diluted acetic acid solution. Storing the solution in a refrigerator at 280 K overnight resulted in the formation of light-brown crystals of the title compound with a rod-like form; yield 60%.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. The H atom attached to N1 was discernible in a difference-Fourier map and was refined freely.

Acknowledgements

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supporting information

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Crystal structure of (1,4-diphenyl-4*H*-1,2,4-triazol-3-yl)phenylamine difluorophosphate, and a survey of the difluorophosphate anion (PO_2F_2^-)

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Computing details

Data collection: *APEX2* (Bruker, 2016); cell refinement: *SAINTE* (Bruker, 2016); data reduction: *SAINTE* (Bruker, 2016); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015b); molecular graphics: *Mercury* (Macrae *et al.*, 2020); software used to prepare material for publication: *publCIF* (Westrip, 2010).

3-Anilino-1,4-diphenyl-1*H*-1,2,4-triazol-4-ium difluorophosphate

Crystal data

$\text{C}_{20}\text{H}_{17}\text{N}_4^+\cdot\text{PO}_2\text{F}_2^-$

$M_r = 414.35$

Monoclinic, $P2_1/n$

$a = 7.3811$ (5) Å

$b = 14.9963$ (9) Å

$c = 16.9217$ (10) Å

$\beta = 102.138$ (2)°

$V = 1831.2$ (2) Å³

$Z = 4$

$F(000) = 856$

$D_x = 1.503$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 7088 reflections

$\theta = 2.5$ – 29.9 °

$\mu = 0.20$ mm⁻¹

$T = 100$ K

Bar, light-brown

$0.50 \times 0.10 \times 0.10$ mm

Data collection

Bruker APEXII CCD
diffractometer

ω - and ϕ -scans

Absorption correction: multi-scan
(*SADABS*; Krause *et al.*, 2015)

$T_{\min} = 0.701$, $T_{\max} = 0.746$

30253 measured reflections

5325 independent reflections

4077 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.046$

$\theta_{\max} = 30.0$ °, $\theta_{\min} = 2.5$ °

$h = -10 \rightarrow 10$

$k = -21 \rightarrow 21$

$l = -23 \rightarrow 23$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.039$

$wR(F^2) = 0.100$

$S = 1.03$

5325 reflections

266 parameters

0 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0405P)^2 + 0.7893P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.38$ e Å⁻³

$\Delta\rho_{\min} = -0.36$ e Å⁻³

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
P1	0.92663 (5)	0.62394 (2)	0.23419 (2)	0.01781 (9)
F1	1.02420 (15)	0.53730 (7)	0.27209 (7)	0.0427 (3)
F2	0.82504 (15)	0.58249 (8)	0.15294 (6)	0.0399 (3)
O1	1.06913 (14)	0.68482 (7)	0.21683 (6)	0.0215 (2)
O2	0.78943 (15)	0.65005 (7)	0.28139 (6)	0.0256 (2)
N1	0.67953 (16)	0.42442 (7)	0.49191 (7)	0.0167 (2)
N2	0.60128 (16)	0.34410 (7)	0.46219 (7)	0.0159 (2)
N3	0.59412 (16)	0.42525 (7)	0.35731 (7)	0.0160 (2)
N4	0.74014 (17)	0.55678 (8)	0.42288 (7)	0.0172 (2)
C1	0.55145 (19)	0.34448 (9)	0.38303 (8)	0.0173 (3)
H1	0.495559	0.296572	0.349946	0.021*
C2	0.67538 (18)	0.47308 (9)	0.42636 (8)	0.0154 (3)
C3	0.55076 (19)	0.45013 (9)	0.27301 (8)	0.0164 (3)
C4	0.6100 (2)	0.39458 (9)	0.21783 (8)	0.0192 (3)
H4	0.686529	0.344484	0.235566	0.023*
C5	0.5545 (2)	0.41403 (10)	0.13613 (8)	0.0223 (3)
H5	0.592902	0.376766	0.097312	0.027*
C6	0.4434 (2)	0.48749 (10)	0.11080 (9)	0.0234 (3)
H6	0.405364	0.500038	0.054732	0.028*
C7	0.3878 (2)	0.54265 (10)	0.16687 (9)	0.0228 (3)
H7	0.313089	0.593352	0.149122	0.027*
C8	0.4405 (2)	0.52423 (9)	0.24886 (8)	0.0201 (3)
H8	0.402026	0.561559	0.287605	0.024*
C9	0.58060 (18)	0.27329 (9)	0.51670 (8)	0.0161 (3)
C10	0.4911 (2)	0.19539 (9)	0.48580 (8)	0.0199 (3)
H10	0.445350	0.188499	0.429318	0.024*
C11	0.4701 (2)	0.12795 (10)	0.53908 (9)	0.0221 (3)
H11	0.410626	0.073931	0.518867	0.027*
C12	0.5349 (2)	0.13848 (10)	0.62172 (9)	0.0221 (3)
H12	0.517537	0.092364	0.657898	0.026*
C13	0.6250 (2)	0.21647 (10)	0.65123 (9)	0.0242 (3)
H13	0.670021	0.223552	0.707742	0.029*
C14	0.6498 (2)	0.28444 (10)	0.59862 (8)	0.0210 (3)
H14	0.713296	0.337592	0.618605	0.025*
C15	0.82708 (19)	0.60945 (9)	0.48991 (8)	0.0162 (3)
C16	0.8404 (2)	0.58403 (9)	0.57031 (8)	0.0200 (3)
H16	0.792304	0.528252	0.582833	0.024*
C17	0.9249 (2)	0.64124 (10)	0.63198 (9)	0.0226 (3)
H17	0.933453	0.623820	0.686619	0.027*

C18	0.9968 (2)	0.72284 (9)	0.61568 (9)	0.0214 (3)
H18	1.052684	0.761540	0.658329	0.026*
C19	0.9854 (2)	0.74688 (10)	0.53521 (9)	0.0211 (3)
H19	1.036019	0.802151	0.522932	0.025*
C20	0.9009 (2)	0.69113 (9)	0.47280 (8)	0.0198 (3)
H20	0.893375	0.708627	0.418243	0.024*
H1N	0.741 (3)	0.5776 (12)	0.3758 (11)	0.031 (5)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P1	0.02253 (19)	0.01490 (16)	0.01649 (17)	-0.00094 (14)	0.00522 (14)	0.00142 (13)
F1	0.0456 (6)	0.0255 (5)	0.0631 (7)	0.0121 (5)	0.0255 (6)	0.0221 (5)
F2	0.0414 (6)	0.0531 (7)	0.0280 (5)	-0.0244 (5)	0.0132 (4)	-0.0184 (5)
O1	0.0245 (5)	0.0200 (5)	0.0200 (5)	-0.0034 (4)	0.0045 (4)	0.0023 (4)
O2	0.0291 (6)	0.0270 (6)	0.0231 (5)	0.0005 (5)	0.0110 (5)	0.0005 (4)
N1	0.0190 (6)	0.0140 (5)	0.0175 (5)	-0.0006 (4)	0.0049 (5)	-0.0010 (4)
N2	0.0175 (6)	0.0137 (5)	0.0169 (5)	0.0000 (4)	0.0043 (4)	-0.0015 (4)
N3	0.0184 (6)	0.0155 (5)	0.0144 (5)	0.0009 (4)	0.0040 (4)	-0.0012 (4)
N4	0.0225 (6)	0.0151 (5)	0.0147 (5)	-0.0011 (5)	0.0056 (5)	0.0001 (4)
C1	0.0187 (6)	0.0160 (6)	0.0178 (6)	0.0007 (5)	0.0049 (5)	-0.0010 (5)
C2	0.0151 (6)	0.0168 (6)	0.0148 (6)	0.0020 (5)	0.0044 (5)	-0.0019 (5)
C3	0.0173 (6)	0.0173 (6)	0.0145 (6)	-0.0011 (5)	0.0033 (5)	0.0008 (5)
C4	0.0216 (7)	0.0184 (6)	0.0178 (6)	0.0015 (5)	0.0049 (5)	-0.0010 (5)
C5	0.0253 (7)	0.0255 (7)	0.0170 (6)	-0.0019 (6)	0.0066 (6)	-0.0028 (5)
C6	0.0222 (7)	0.0305 (8)	0.0168 (6)	-0.0036 (6)	0.0025 (6)	0.0034 (6)
C7	0.0198 (7)	0.0235 (7)	0.0239 (7)	0.0033 (6)	0.0020 (6)	0.0063 (6)
C8	0.0203 (7)	0.0195 (7)	0.0208 (7)	0.0020 (5)	0.0054 (6)	-0.0015 (5)
C9	0.0160 (6)	0.0149 (6)	0.0184 (6)	0.0011 (5)	0.0064 (5)	0.0015 (5)
C10	0.0232 (7)	0.0191 (7)	0.0174 (6)	-0.0025 (5)	0.0045 (5)	-0.0016 (5)
C11	0.0242 (7)	0.0184 (7)	0.0243 (7)	-0.0033 (6)	0.0062 (6)	-0.0017 (5)
C12	0.0235 (7)	0.0209 (7)	0.0221 (7)	-0.0018 (6)	0.0057 (6)	0.0052 (5)
C13	0.0289 (8)	0.0243 (7)	0.0184 (7)	-0.0047 (6)	0.0026 (6)	0.0012 (5)
C14	0.0255 (7)	0.0183 (7)	0.0188 (7)	-0.0041 (6)	0.0038 (6)	-0.0014 (5)
C15	0.0152 (6)	0.0157 (6)	0.0179 (6)	0.0022 (5)	0.0037 (5)	-0.0019 (5)
C16	0.0251 (7)	0.0163 (6)	0.0185 (6)	-0.0010 (6)	0.0042 (6)	0.0011 (5)
C17	0.0287 (8)	0.0201 (7)	0.0180 (6)	0.0005 (6)	0.0027 (6)	0.0004 (5)
C18	0.0234 (7)	0.0168 (6)	0.0219 (7)	0.0013 (6)	0.0002 (6)	-0.0034 (5)
C19	0.0225 (7)	0.0149 (6)	0.0256 (7)	-0.0012 (5)	0.0044 (6)	0.0001 (5)
C20	0.0232 (7)	0.0182 (6)	0.0190 (7)	0.0001 (5)	0.0064 (6)	0.0008 (5)

Geometric parameters (Å, °)

P1—O1	1.4684 (11)	C7—H7	0.9500
P1—O2	1.4686 (11)	C8—H8	0.9500
P1—F2	1.5510 (10)	C9—C14	1.3832 (18)
P1—F1	1.5568 (10)	C9—C10	1.3890 (19)
N1—C2	1.3227 (17)	C10—C11	1.385 (2)

N1—N2	1.3840 (15)	C10—H10	0.9500
N2—C1	1.3124 (17)	C11—C12	1.389 (2)
N2—C9	1.4356 (17)	C11—H11	0.9500
N3—C1	1.3467 (17)	C12—C13	1.386 (2)
N3—C2	1.3944 (16)	C12—H12	0.9500
N3—C3	1.4439 (16)	C13—C14	1.391 (2)
N4—C2	1.3488 (17)	C13—H13	0.9500
N4—C15	1.4200 (17)	C14—H14	0.9500
N4—H1N	0.857 (19)	C15—C20	1.3957 (19)
C1—H1	0.9500	C15—C16	1.3962 (18)
C3—C8	1.3870 (19)	C16—C17	1.3930 (19)
C3—C4	1.3887 (19)	C16—H16	0.9500
C4—C5	1.3877 (19)	C17—C18	1.385 (2)
C4—H4	0.9500	C17—H17	0.9500
C5—C6	1.386 (2)	C18—C19	1.394 (2)
C5—H5	0.9500	C18—H18	0.9500
C6—C7	1.385 (2)	C19—C20	1.3878 (19)
C6—H6	0.9500	C19—H19	0.9500
C7—C8	1.3877 (19)	C20—H20	0.9500
O1—P1—O2	123.22 (6)	C3—C8—H8	120.7
O1—P1—F2	107.75 (6)	C7—C8—H8	120.7
O2—P1—F2	109.20 (6)	C14—C9—C10	121.68 (13)
O1—P1—F1	108.21 (6)	C14—C9—N2	119.20 (12)
O2—P1—F1	108.10 (6)	C10—C9—N2	119.12 (12)
F2—P1—F1	97.26 (7)	C11—C10—C9	118.60 (13)
C2—N1—N2	103.95 (10)	C11—C10—H10	120.7
C1—N2—N1	111.91 (11)	C9—C10—H10	120.7
C1—N2—C9	127.89 (12)	C10—C11—C12	120.69 (14)
N1—N2—C9	120.19 (11)	C10—C11—H11	119.7
C1—N3—C2	106.29 (11)	C12—C11—H11	119.7
C1—N3—C3	122.23 (11)	C13—C12—C11	119.78 (13)
C2—N3—C3	131.44 (11)	C13—C12—H12	120.1
C2—N4—C15	125.98 (12)	C11—C12—H12	120.1
C2—N4—H1N	116.8 (12)	C12—C13—C14	120.39 (13)
C15—N4—H1N	116.7 (12)	C12—C13—H13	119.8
N2—C1—N3	107.41 (12)	C14—C13—H13	119.8
N2—C1—H1	126.3	C9—C14—C13	118.84 (13)
N3—C1—H1	126.3	C9—C14—H14	120.6
N1—C2—N4	127.16 (12)	C13—C14—H14	120.6
N1—C2—N3	110.42 (11)	C20—C15—C16	119.42 (12)
N4—C2—N3	122.41 (12)	C20—C15—N4	116.94 (12)
C8—C3—C4	122.04 (13)	C16—C15—N4	123.64 (12)
C8—C3—N3	119.51 (12)	C17—C16—C15	119.38 (13)
C4—C3—N3	118.27 (12)	C17—C16—H16	120.3
C5—C4—C3	118.36 (13)	C15—C16—H16	120.3
C5—C4—H4	120.8	C18—C17—C16	121.67 (13)
C3—C4—H4	120.8	C18—C17—H17	119.2

C6—C5—C4	120.43 (14)	C16—C17—H17	119.2
C6—C5—H5	119.8	C17—C18—C19	118.44 (13)
C4—C5—H5	119.8	C17—C18—H18	120.8
C7—C6—C5	120.29 (13)	C19—C18—H18	120.8
C7—C6—H6	119.9	C20—C19—C18	120.86 (13)
C5—C6—H6	119.9	C20—C19—H19	119.6
C6—C7—C8	120.31 (14)	C18—C19—H19	119.6
C6—C7—H7	119.8	C19—C20—C15	120.22 (13)
C8—C7—H7	119.8	C19—C20—H20	119.9
C3—C8—C7	118.56 (13)	C15—C20—H20	119.9

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C1—H1 \cdots O1 ⁱ	0.95	2.02	2.9576 (17)	168
C20—H20 \cdots O2	0.95	2.44	3.2291 (17)	140
C16—H16 \cdots N1	0.95	2.22	2.8700 (18)	124
C10—H10 \cdots O1 ⁱ	0.95	2.45	3.3673 (17)	161
N4—H1N \cdots O2	0.857 (19)	2.025 (19)	2.8614 (16)	165.0 (17)

Symmetry code: (i) $-x+3/2, y-1/2, -z+1/2$.