Crystal structure of the co-crystal of 5-amino-isophthalic acid and 1,2-bis(pyridin-4-yl)ethene

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In the title 1:1 co-crystal, $C_{12}H_{10}N_2 \cdot C_8H_7NO_4$, the bipyridine moiety shows whole-molecule disorder over two sets of sites in a 0.588 (3): 0.412 (3) ratio. In the crystal, the components form hydrogen-bonded sheets linked by N—H···O and O—H···N interactions, which stack along the a axis. A comparison to a related and previously published co-crystal of 5-amino-isophthalic acid and the shorter 4,4′-bipyridine is presented.

1. Chemical context

5-Amino-isophthalic acid (5AIA) is an emerging secondary building unit for a wide variety of metal–organic frameworks (MOFs). (Zeng et al., 2009; Wang et al., 2011; Cox et al., 2015) This compound is also a convenient precursor for the synthesis of azo-derivatized framework ligands, a key component in the rapidly evolving field of photochromic MOFs. (Brown et al., 2013; Castellanos et al., 2016; Walton et al., 2013; Patel et al., 2014). Similarly, 1,2-bis(pyridin-4-yl)ethene (BE) is also commonly used in MOF synthesis; however, it is routinely used in co-crystal engineering as well (Kongshaug & Fjellvag, 2003; MacGillivray et al., 2008; Desiraju, 1995) The 5AIA–BE co-crystal presented herein was produced as part of an undergraduate physical chemistry laboratory experiment developed by Jason Benedict.
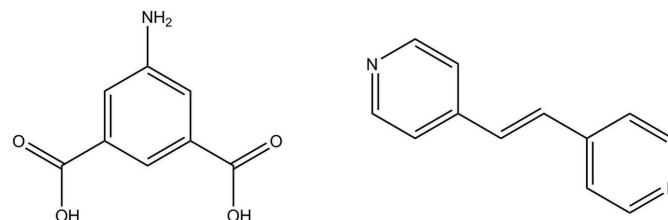
Recently, the co-crystal structure of 5AIA and 4,4′-bipyridine (BP), a shorter analogue of BE, was reported (Zhang et al., 2009). Unlike many MOFs in which different length linkers lead to isoreticular structures (Eddaoudi et al., 2002), the 5AIA–BP co-crystal exhibits several notable similarities and differences when compared to 5AIA–BE. As shown in Figs. 4, 5AIA forms hydrogen bonds with two 5AIA molecules and two BP molecules. The 5AIA–BP interactions and one of the 5AIA–5AIA interactions are similar to those found in 5AIA–BE. The remaining 5AIA–5AIA interaction in 5AIA–BP consists solely of an N(amine)–H···OH hydrogen bond, as opposed to the N(amine)—H···O=C interaction found in 5AIA–BP. Interestingly, this results in a total of five hydrogen
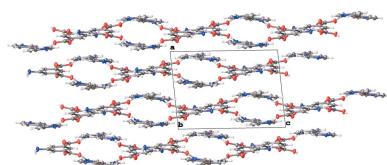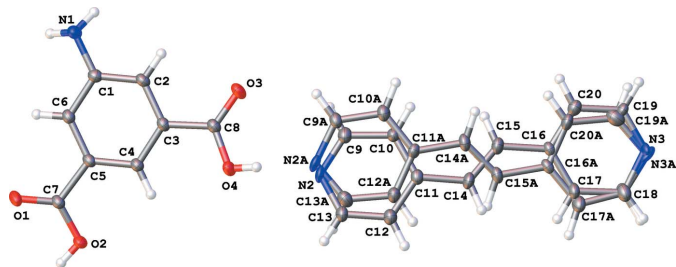
Figure 1
The asymmetric unit of the title compound, showing the numbering scheme. Displacement ellipsoids are shown at the 50% probability level.
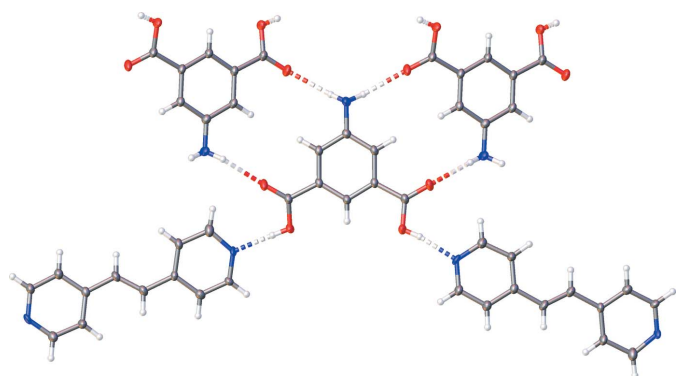

Figure 2
Diagram illustrating the hydrogen-bonding interactions present in the two-dimensional sheets found in the 5AIA–BE co-crystal.

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O1[i]	0.899 (17)	2.062 (17)	2.9540 (13)	171.0 (15)
N1—H1B···O3[ii]	0.894 (17)	2.157 (17)	3.0500 (13)	178.6 (13)
O2—H2···N3[iii]	0.989 (19)	1.70 (2)	2.688 (8)	173.4 (18)
O2—H2···N3A[iii]	0.989 (19)	1.63 (2)	2.619 (12)	177 (2)
O4—H4···N2[iv]	0.98 (2)	1.72 (2)	2.702 (7)	173.2 (19)
O4—H4···N2A[iv]	0.98 (2)	1.59 (2)	2.566 (11)	175 (2)

Symmetry codes: (i) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (iii) $-x+1, -y+2, -z+1$; (iv) $x-\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$.

molecule disorder over two sets of sites, consistent with a local $C2$ rotation about the long axis of the molecule. The occupancy of the major and minor components was refined to be 0.588 (3) and 0.412 (3), respectively.

3. Supramolecular features

In this structure, the 5AIA molecule forms hydrogen bonds to both itself and the BE moiety, forming extended sheets (Table 1 and Fig. 2). The 5AIA–5AIA interactions consist of N(amine)—H···O=C hydrogen bonds where each 5AIA makes two hydrogen bonds with two neighboring 5AIA molecules. The 5AIA–BE interaction consists of an O—H···N(pyridyl) hydrogen bond such that each 5AIA makes one hydrogen bond with two neighboring BE molecules. The sheets formed by these interactions stack along the the a axis to produce a layered structure (Fig. 3).

4. Database survey

Recently, the co-crystal structure of 5AIA and 4,4′-bipyridine (BP), a shorter analogue of BE, was reported (Zhang *et al.*, 2009). Unlike many MOFs in which different length linkers lead to isoreticular structures (Eddaoudi *et al.*, 2002), the 5AIA–BP co-crystal exhibits several notable similarites and differences when compared to 5AIA–BE. As shown in Figs. 4,

bonds in the 5AIA–BP structure compared to the six hydrogen bonds observed in 5AIA–BE.

2. Structural commentary

The 5AIA–BE co-crystal crystallizes with one molecule of 5AIA and one molecule of BE in the asymmetric unit (Fig. 1). Both molecules are effectively planar in the solid state (r.m.s. deviation for 5AIA = 0.155 Å). The BE moiety shows whole
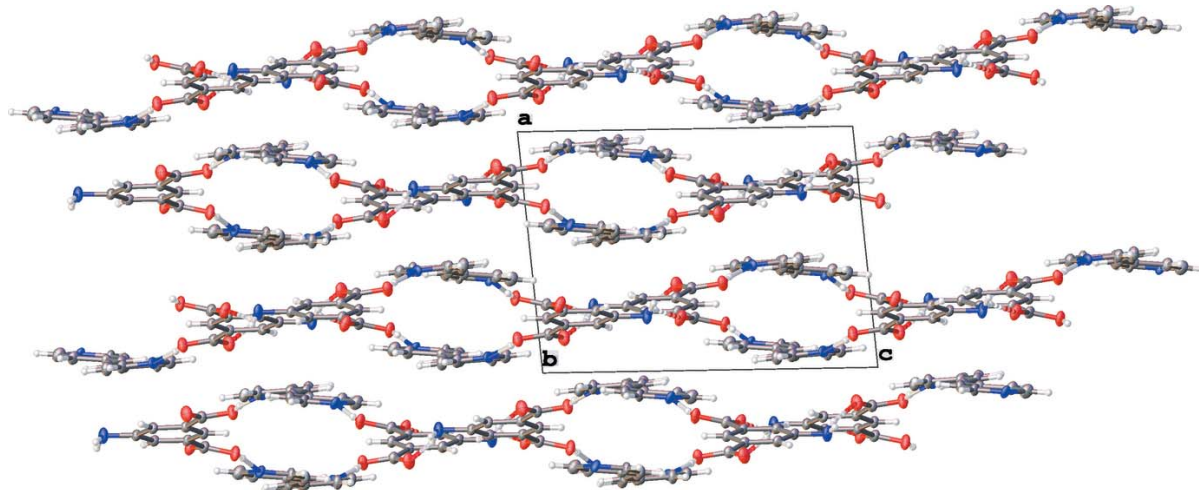

Figure 3
View down [001] showing the (100) sheets in the extended structure of the title compound.
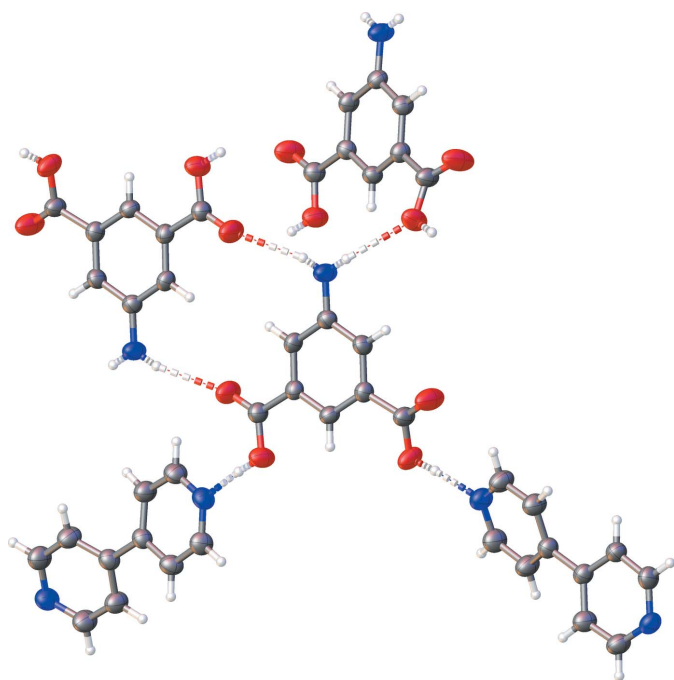
Figure 4
Diagram illustrating the hydrogen bonding interactions present in the previously reported 5AIA–BP co-crystal.

5AIA forms hydrogen bonds with two 5AIA molecules and two BP molecules. The 5AIA–BP interactions and one of the 5AIA–5AIA interactions are similar to those found in 5AIA–BE. The remaining 5AIA–5AIA interaction in 5AIA–BP consists solely of an N(amine)—H···OH hydrogen bond, as opposed to the N(amine)—H···O=C interaction found in 5AIA–BP. Interestingly, this results in a total of five hydrogen bonds in the 5AIA–BP structure compared to the six hydrogen bonds observed in 5AIA–BE.

5. Synthesis and crystallization

Solid BE (0.0119 g, 6.53×10^{-5} mol) and 5AIA (0.0109 g, 6.02×10^{-5} mol) were added to a 25 ml scintillation vial. To this was added approximately 15 ml of ethyl acetate followed by gentle heating. An additional 2 ml of methanol was added and all remaining solids dissolved. The loosely capped vial was then placed into a dark cabinet. After two weeks, yellow block-shaped crystals of the title compound suitable for single-crystal X-ray diffraction measurements were obtained.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Heteroatom hydrogen atoms were located in difference electron-density maps and freely refined. Hydrogen atoms attached to carbon atoms were refined using riding models with C—H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. The BE was found to be disordered over two sets of sites in a 0.588 (3): 0.412 (3) ratio.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{12}H_{10}N_2 \cdot C_8H_7NO_4$
M_r	363.36
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	90
a, b, c (Å)	10.1614 (10), 12.0782 (12), 14.0537 (14)
β (°)	95.027 (2)
V (Å^3)	1718.2 (3)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.10
Crystal size (mm)	$0.22 \times 0.2 \times 0.18$
Data collection	
Diffractometer	Bruker *SMART* APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2014)
T_{min}, T_{max}	0.683, 0.747
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	24372, 6546, 4519
R_{int}	0.033
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.771
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.047, 0.143, 1.02
No. of reflections	6546
No. of parameters	378
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.40, −0.24

Computer programs: *APEX2* and *SAINT* (Bruker, 2014), *SHELXT* (Sheldrick, 2015), *SHELXL2014* (Sheldrick, 2015b) and *OLEX2* (Dolomanov *et al.*, 2009).

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Crystal structure of the co-crystal of 5-aminoisophthalic acid and 1,2-bis-(pyridin-4-yl)ethene

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Computing details

Data collection: *APEX2* (Bruker, 2014); cell refinement: *SAINT* (Bruker, 2014); data reduction: *SAINT* (Bruker, 2014); program(s) used to solve structure: SHELXT (Sheldrick, 2015); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009).

5-Aminoisophthalic acid–1,2-bis(pyridin-4-yl)ethene (1/1)

Crystal data

$C_{12}H_{10}N_2 \cdot C_8H_7NO_4$	$F(000) = 760$
$M_r = 363.36$	$D_x = 1.405$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 10.1614$ (10) Å	Cell parameters from 428 reflections
$b = 12.0782$ (12) Å	$\theta = 2.8–22.0°$
$c = 14.0537$ (14) Å	$\mu = 0.10$ mm^{-1}
$\beta = 95.027$ (2)°	$T = 90$ K
$V = 1718.2$ (3) Å^3	Block, yellow
$Z = 4$	$0.22 \times 0.2 \times 0.18$ mm

Data collection

Bruker SMART APEXII CCD diffractometer	$T_{min} = 0.683$, $T_{max} = 0.747$
	24372 measured reflections
Radiation source: microfocus rotating anode, Incoatec Iμs	6546 independent reflections
	4519 reflections with $I > 2\sigma(I)$
Mirror optics monochromator	$R_{int} = 0.033$
Detector resolution: 7.9 pixels mm^{-1}	$\theta_{max} = 33.2°$, $\theta_{min} = 2.2°$
ω scans	$h = -15 \rightarrow 15$
Absorption correction: multi-scan (*SADABS*; Bruker, 2014)	$k = -16 \rightarrow 18$
	$l = -19 \rightarrow 21$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.047$	
$wR(F^2) = 0.143$	$w = 1/[\sigma^2(F_o^2) + (0.0727P)^2 + 0.2884P]$
$S = 1.02$	where $P = (F_o^2 + 2F_c^2)/3$
6546 reflections	$(\Delta/\sigma)_{max} < 0.001$
378 parameters	$\Delta\rho_{max} = 0.40$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.24$ 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 ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
O1	0.21821 (10)	0.91797 (6)	0.42759 (6)	0.0299 (2)	
O2	0.18838 (9)	0.81890 (6)	0.55840 (5)	0.02654 (18)	
H2	0.1646 (19)	0.8932 (16)	0.5810 (13)	0.058 (5)*	
O3	0.35542 (10)	0.33662 (6)	0.42624 (6)	0.0309 (2)	
O4	0.35891 (9)	0.43117 (6)	0.56369 (5)	0.02640 (18)	
H4	0.388 (2)	0.3606 (16)	0.5933 (14)	0.064 (6)*	
N1	0.27113 (12)	0.63283 (8)	0.17186 (7)	0.0291 (2)	
H1A	0.2656 (17)	0.5692 (14)	0.1385 (12)	0.043 (4)*	
H1B	0.2351 (16)	0.6925 (14)	0.1424 (11)	0.040 (4)*	
C1	0.27076 (11)	0.62966 (8)	0.26981 (7)	0.02010 (19)	
C2	0.29909 (11)	0.53166 (8)	0.32097 (7)	0.02032 (19)	
H2A	0.3164	0.4657	0.2874	0.024*	
C3	0.30223 (10)	0.52951 (8)	0.42012 (7)	0.01921 (19)	
C4	0.27368 (11)	0.62462 (8)	0.47130 (7)	0.01990 (19)	
H4A	0.2728	0.6226	0.5388	0.024*	
C5	0.24644 (10)	0.72289 (8)	0.42033 (7)	0.01881 (19)	
C6	0.24657 (10)	0.72561 (8)	0.32144 (7)	0.01947 (19)	
H6	0.2300	0.7935	0.2884	0.023*	
C7	0.21669 (11)	0.82903 (8)	0.46877 (7)	0.0211 (2)	
C8	0.34070 (11)	0.42315 (8)	0.46985 (7)	0.0215 (2)	
C18	0.89056 (13)	0.89912 (9)	0.43551 (9)	0.0306 (3)	
H18	0.8831	0.9091	0.5019	0.037*	0.588 (3)
H18A	0.8865	0.9167	0.5011	0.037*	0.412 (3)
N2	0.9309 (8)	0.2578 (6)	0.1571 (3)	0.0206 (8)	0.588 (3)
N3	0.8888 (10)	0.9864 (5)	0.3724 (9)	0.0203 (11)	0.588 (3)
C9	0.9283 (3)	0.3491 (2)	0.1046 (2)	0.0259 (5)	0.588 (3)
H9	0.9195	0.3426	0.0370	0.031*	0.588 (3)
C10	0.9382 (2)	0.45426 (16)	0.1453 (2)	0.0246 (4)	0.588 (3)
H10	0.9393	0.5181	0.1058	0.029*	0.588 (3)
C11	0.94634 (18)	0.46501 (16)	0.24375 (18)	0.0202 (4)	0.588 (3)
C12	0.9527 (2)	0.36771 (18)	0.29764 (18)	0.0260 (5)	0.588 (3)
H12	0.9624	0.3709	0.3654	0.031*	0.588 (3)
C13	0.9446 (4)	0.2666 (3)	0.2511 (2)	0.0240 (6)	0.588 (3)
H13	0.9491	0.2008	0.2883	0.029*	0.588 (3)
C14	0.9425 (2)	0.57258 (15)	0.29274 (13)	0.0245 (5)	0.588 (3)
H14	0.9538	0.5724	0.3606	0.029*	0.588 (3)
C15	0.9246 (2)	0.66976 (15)	0.24941 (15)	0.0241 (4)	0.588 (3)
H15	0.9170	0.6692	0.1816	0.029*	0.588 (3)
C16	0.9152 (3)	0.7790 (2)	0.2963 (2)	0.0182 (5)	0.588 (3)

C17	0.9045 (7)	0.7916 (5)	0.3934 (2)	0.0242 (8)	0.588 (3)
H17	0.9064	0.7278	0.4330	0.029*	0.588 (3)
C19	0.9010 (9)	0.9740 (6)	0.2814 (5)	0.0214 (8)	0.588 (3)
H19	0.8997	1.0381	0.2422	0.026*	0.588 (3)
C20	0.9153 (4)	0.8733 (3)	0.2402 (3)	0.0244 (6)	0.588 (3)
H20	0.9254	0.8678	0.1738	0.029*	0.588 (3)
C17A	0.9027 (10)	0.7907 (7)	0.4220 (4)	0.0258 (10)	0.412 (3)
H17A	0.9026	0.7388	0.4728	0.031*	0.412 (3)
C9A	0.9486 (4)	0.3433 (3)	0.0717 (3)	0.0219 (7)	0.412 (3)
H9A	0.9550	0.3259	0.0064	0.026*	0.412 (3)
C20A	0.9161 (6)	0.8429 (4)	0.2607 (4)	0.0260 (11)	0.412 (3)
H20A	0.9275	0.8265	0.1958	0.031*	0.412 (3)
N2A	0.9319 (11)	0.2579 (10)	0.1328 (4)	0.0202 (10)	0.412 (3)
N3A	0.8830 (15)	0.9861 (9)	0.3829 (13)	0.025 (2)	0.412 (3)
C19A	0.8995 (15)	0.9532 (9)	0.2902 (9)	0.034 (2)	0.412 (3)
H19A	0.8996	1.0094	0.2428	0.040*	0.412 (3)
C10A	0.9569 (3)	0.4532 (2)	0.0982 (3)	0.0243 (6)	0.412 (3)
H10A	0.9663	0.5087	0.0514	0.029*	0.412 (3)
C11A	0.9515 (3)	0.4826 (2)	0.1934 (3)	0.0195 (6)	0.412 (3)
C12A	0.9434 (3)	0.3974 (3)	0.2586 (3)	0.0250 (6)	0.412 (3)
H12A	0.9448	0.4125	0.3250	0.030*	0.412 (3)
C13A	0.9330 (6)	0.2880 (4)	0.2245 (4)	0.0293 (10)	0.412 (3)
H13A	0.9262	0.2309	0.2703	0.035*	0.412 (3)
C14A	0.9493 (3)	0.6007 (2)	0.21878 (19)	0.0235 (6)	0.412 (3)
H14A	0.9676	0.6526	0.1709	0.028*	0.412 (3)
C15A	0.9237 (3)	0.6405 (2)	0.3033 (2)	0.0226 (6)	0.412 (3)
H15A	0.9095	0.5884	0.3521	0.027*	0.412 (3)
C16A	0.9155 (4)	0.7585 (4)	0.3276 (3)	0.0186 (7)	0.412 (3)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0508 (6)	0.0126 (3)	0.0286 (4)	0.0008 (3)	0.0170 (4)	−0.0002 (3)
O2	0.0459 (5)	0.0155 (3)	0.0195 (3)	0.0059 (3)	0.0096 (3)	−0.0016 (3)
O3	0.0510 (6)	0.0143 (3)	0.0270 (4)	0.0041 (3)	0.0012 (4)	−0.0046 (3)
O4	0.0438 (5)	0.0149 (3)	0.0201 (3)	0.0063 (3)	0.0006 (3)	−0.0003 (3)
N1	0.0510 (7)	0.0180 (4)	0.0186 (4)	0.0067 (4)	0.0058 (4)	−0.0018 (3)
C1	0.0246 (5)	0.0175 (4)	0.0187 (4)	0.0010 (4)	0.0046 (4)	−0.0022 (3)
C2	0.0255 (5)	0.0148 (4)	0.0210 (4)	0.0017 (4)	0.0039 (4)	−0.0038 (3)
C3	0.0242 (5)	0.0130 (4)	0.0206 (4)	0.0003 (3)	0.0030 (4)	−0.0012 (3)
C4	0.0269 (5)	0.0142 (4)	0.0191 (4)	0.0002 (4)	0.0047 (4)	−0.0016 (3)
C5	0.0235 (5)	0.0130 (4)	0.0206 (4)	−0.0001 (3)	0.0056 (4)	−0.0026 (3)
C6	0.0236 (5)	0.0140 (4)	0.0213 (4)	0.0010 (3)	0.0050 (4)	−0.0006 (3)
C7	0.0285 (5)	0.0142 (4)	0.0214 (4)	0.0004 (4)	0.0069 (4)	−0.0025 (3)
C8	0.0285 (5)	0.0145 (4)	0.0217 (5)	−0.0002 (4)	0.0025 (4)	−0.0023 (3)
C18	0.0394 (7)	0.0178 (5)	0.0360 (6)	0.0017 (4)	0.0118 (5)	−0.0001 (4)
N2	0.0261 (11)	0.0147 (9)	0.021 (2)	−0.0007 (7)	0.0014 (18)	−0.0088 (18)
N3	0.0306 (19)	0.0099 (16)	0.022 (3)	0.0050 (11)	0.0112 (14)	−0.0001 (12)

C9	0.0351 (14)	0.0194 (9)	0.0238 (13)	−0.0024 (8)	0.0066 (10)	−0.0027 (10)
C10	0.0400 (12)	0.0158 (8)	0.0182 (11)	−0.0012 (7)	0.0044 (9)	−0.0006 (8)
C11	0.0232 (9)	0.0158 (10)	0.0219 (11)	−0.0012 (6)	0.0037 (7)	−0.0024 (7)
C12	0.0388 (12)	0.0170 (9)	0.0225 (10)	0.0016 (8)	0.0038 (9)	−0.0012 (8)
C13	0.0341 (13)	0.0160 (13)	0.0225 (15)	0.0007 (10)	0.0055 (12)	−0.0034 (9)
C14	0.0348 (11)	0.0173 (9)	0.0218 (8)	0.0012 (7)	0.0053 (7)	−0.0064 (6)
C15	0.0325 (10)	0.0176 (8)	0.0223 (9)	−0.0004 (7)	0.0021 (7)	−0.0056 (7)
C16	0.0226 (9)	0.0109 (14)	0.0211 (13)	0.0001 (8)	0.0021 (10)	0.0004 (10)
C17	0.0346 (13)	0.0133 (9)	0.026 (2)	0.0011 (8)	0.0086 (18)	−0.0038 (17)
C19	0.0301 (15)	0.0192 (19)	0.0155 (15)	0.0019 (14)	0.0054 (11)	−0.0047 (15)
C20	0.0324 (12)	0.0204 (16)	0.0205 (14)	0.0012 (12)	0.0019 (10)	−0.0034 (10)
C17A	0.0330 (18)	0.0195 (15)	0.027 (3)	0.0003 (12)	0.011 (3)	−0.005 (2)
C9A	0.0281 (17)	0.0136 (11)	0.0247 (18)	−0.0015 (10)	0.0065 (14)	−0.0010 (13)
C20A	0.0378 (18)	0.019 (3)	0.021 (2)	0.0028 (19)	0.0022 (17)	−0.0085 (17)
N2A	0.0234 (15)	0.0201 (13)	0.017 (3)	0.0010 (10)	−0.001 (2)	−0.010 (2)
N3A	0.026 (3)	0.033 (4)	0.016 (3)	−0.001 (2)	0.008 (2)	−0.011 (2)
C19A	0.039 (3)	0.029 (4)	0.032 (3)	−0.002 (3)	0.0015 (19)	0.006 (2)
C10A	0.0320 (15)	0.0166 (11)	0.0243 (15)	−0.0019 (10)	0.0035 (12)	−0.0024 (10)
C11A	0.0250 (13)	0.0163 (11)	0.0170 (15)	−0.0012 (9)	0.0008 (10)	−0.0038 (11)
C12A	0.0386 (17)	0.0155 (16)	0.0209 (15)	0.0010 (11)	0.0017 (12)	−0.0020 (11)
C13A	0.041 (2)	0.019 (2)	0.027 (3)	0.0004 (15)	0.0012 (19)	0.0024 (15)
C14A	0.0299 (14)	0.0125 (10)	0.0283 (13)	−0.0003 (9)	0.0033 (10)	−0.0035 (9)
C15A	0.0308 (14)	0.0119 (12)	0.0251 (14)	0.0007 (9)	0.0020 (10)	−0.0013 (9)
C16A	0.0207 (13)	0.0107 (14)	0.024 (2)	0.0002 (10)	0.0012 (14)	0.0033 (15)

Geometric parameters (Å, º)

O1—C7	1.2209 (12)	C12—H12	0.9500
O2—H2	0.990 (19)	C12—C13	1.385 (4)
O2—C7	1.3222 (12)	C13—H13	0.9500
O3—C8	1.2274 (12)	C14—H14	0.9500
O4—H4	0.98 (2)	C14—C15	1.327 (3)
O4—C8	1.3191 (12)	C15—H15	0.9500
N1—H1A	0.899 (17)	C15—C16	1.482 (3)
N1—H1B	0.894 (17)	C16—C17	1.387 (4)
N1—C1	1.3775 (13)	C16—C20	1.385 (3)
C1—C2	1.4017 (14)	C17—H17	0.9500
C1—C6	1.4005 (13)	C19—H19	0.9500
C2—H2A	0.9500	C19—C20	1.360 (7)
C2—C3	1.3912 (14)	C20—H20	0.9500
C3—C4	1.3991 (13)	C17A—H17A	0.9500
C3—C8	1.4979 (14)	C17A—C16A	1.399 (6)
C4—H4A	0.9500	C9A—H9A	0.9500
C4—C5	1.4014 (13)	C9A—N2A	1.361 (10)
C5—C6	1.3902 (14)	C9A—C10A	1.379 (4)
C5—C7	1.4948 (13)	C20A—H20A	0.9500
C6—H6	0.9500	C20A—C19A	1.410 (11)
C18—H18	0.9500	C20A—C16A	1.388 (5)

C18—H18A	0.9500	N2A—C13A	1.338 (7)
C18—N3	1.376 (9)	N3A—C19A	1.39 (2)
C18—C17	1.439 (5)	C19A—H19A	0.9500
C18—C17A	1.331 (9)	C10A—H10A	0.9500
C18—N3A	1.283 (13)	C10A—C11A	1.390 (5)
N2—C9	1.326 (7)	C11A—C12A	1.385 (4)
N2—C13	1.320 (5)	C11A—C14A	1.472 (4)
N3—C19	1.305 (13)	C12A—H12A	0.9500
C9—H9	0.9500	C12A—C13A	1.406 (6)
C9—C10	1.392 (3)	C13A—H13A	0.9500
C10—H10	0.9500	C14A—H14A	0.9500
C10—C11	1.386 (3)	C14A—C15A	1.329 (4)
C11—C12	1.397 (3)	C15A—H15A	0.9500
C11—C14	1.472 (2)	C15A—C16A	1.469 (5)
C7—O2—H2	107.5 (11)	C15—C14—C11	125.02 (18)
C8—O4—H4	111.7 (11)	C15—C14—H14	117.5
H1A—N1—H1B	116.4 (15)	C14—C15—H15	116.7
C1—N1—H1A	119.4 (11)	C14—C15—C16	126.5 (2)
C1—N1—H1B	116.6 (10)	C16—C15—H15	116.7
N1—C1—C2	121.17 (9)	C17—C16—C15	123.3 (3)
N1—C1—C6	120.72 (9)	C20—C16—C15	118.4 (3)
C6—C1—C2	118.07 (9)	C20—C16—C17	118.3 (4)
C1—C2—H2A	119.5	C18—C17—H17	119.2
C3—C2—C1	121.01 (9)	C16—C17—C18	121.5 (4)
C3—C2—H2A	119.5	C16—C17—H17	119.2
C2—C3—C4	120.80 (9)	N3—C19—H19	118.6
C2—C3—C8	117.74 (8)	N3—C19—C20	122.9 (6)
C4—C3—C8	121.44 (9)	C20—C19—H19	118.6
C3—C4—H4A	120.9	C16—C20—H20	120.4
C3—C4—C5	118.24 (9)	C19—C20—C16	119.2 (4)
C5—C4—H4A	120.9	C19—C20—H20	120.4
C4—C5—C7	122.17 (9)	C18—C17A—H17A	122.4
C6—C5—C4	120.90 (9)	C18—C17A—C16A	115.3 (5)
C6—C5—C7	116.93 (8)	C16A—C17A—H17A	122.4
C1—C6—H6	119.5	N2A—C9A—H9A	117.7
C5—C6—C1	120.93 (9)	N2A—C9A—C10A	124.5 (5)
C5—C6—H6	119.5	C10A—C9A—H9A	117.7
O1—C7—O2	123.09 (9)	C19A—C20A—H20A	120.4
O1—C7—C5	121.82 (9)	C16A—C20A—H20A	120.4
O2—C7—C5	115.09 (8)	C16A—C20A—C19A	119.2 (6)
O3—C8—O4	123.31 (9)	C13A—N2A—C9A	114.3 (9)
O3—C8—C3	122.38 (9)	C18—N3A—C19A	107.5 (10)
O4—C8—C3	114.30 (8)	C20A—C19A—H19A	117.5
N3—C18—H18	122.5	N3A—C19A—C20A	125.0 (9)
N3—C18—C17	115.0 (5)	N3A—C19A—H19A	117.5
C17—C18—H18	122.5	C9A—C10A—H10A	120.1
C17A—C18—H18A	111.8	C9A—C10A—C11A	119.9 (3)

N3A—C18—H18A	111.8	C11A—C10A—H10A	120.1
N3A—C18—C17A	136.5 (8)	C10A—C11A—C14A	118.9 (3)
C13—N2—C9	119.0 (5)	C12A—C11A—C10A	117.2 (2)
C19—N3—C18	123.1 (6)	C12A—C11A—C14A	123.8 (3)
N2—C9—H9	118.9	C11A—C12A—H12A	120.7
N2—C9—C10	122.3 (3)	C11A—C12A—C13A	118.6 (3)
C10—C9—H9	118.9	C13A—C12A—H12A	120.7
C9—C10—H10	120.3	N2A—C13A—C12A	125.3 (6)
C11—C10—C9	119.4 (2)	N2A—C13A—H13A	117.4
C11—C10—H10	120.3	C12A—C13A—H13A	117.4
C10—C11—C12	117.31 (16)	C11A—C14A—H14A	117.4
C10—C11—C14	123.2 (2)	C15A—C14A—C11A	125.2 (3)
C12—C11—C14	119.4 (2)	C15A—C14A—H14A	117.4
C11—C12—H12	120.4	C14A—C15A—H15A	117.3
C13—C12—C11	119.2 (2)	C14A—C15A—C16A	125.3 (3)
C13—C12—H12	120.4	C16A—C15A—H15A	117.3
N2—C13—C12	122.7 (4)	C17A—C16A—C15A	120.1 (5)
N2—C13—H13	118.6	C20A—C16A—C17A	116.4 (5)
C12—C13—H13	118.6	C20A—C16A—C15A	123.5 (4)
C11—C14—H14	117.5		
N1—C1—C2—C3	178.19 (10)	C11—C14—C15—C16	177.6 (2)
N1—C1—C6—C5	−179.82 (10)	C12—C11—C14—C15	−173.6 (2)
C1—C2—C3—C4	1.71 (16)	C13—N2—C9—C10	−0.7 (9)
C1—C2—C3—C8	−176.64 (10)	C14—C11—C12—C13	174.4 (3)
C2—C1—C6—C5	−2.05 (16)	C14—C15—C16—C17	−10.0 (5)
C2—C3—C4—C5	−2.20 (16)	C14—C15—C16—C20	170.8 (3)
C2—C3—C8—O3	−7.84 (17)	C15—C16—C17—C18	−177.6 (3)
C2—C3—C8—O4	171.27 (10)	C15—C16—C20—C19	177.1 (5)
C3—C4—C5—C6	0.59 (16)	C17—C18—N3—C19	−1.1 (12)
C3—C4—C5—C7	−179.15 (10)	C17—C18—C17A—C16A	1.4 (17)
C4—C3—C8—O3	173.81 (11)	C17—C18—N3A—C19A	−3.8 (15)
C4—C3—C8—O4	−7.07 (15)	C17—C16—C20—C19	−2.0 (7)
C4—C5—C6—C1	1.56 (16)	C20—C16—C17—C18	1.5 (7)
C4—C5—C7—O1	165.59 (11)	C17A—C18—N3—C19	−0.5 (14)
C4—C5—C7—O2	−14.70 (15)	C17A—C18—C17—C16	−179 (3)
C6—C1—C2—C3	0.43 (16)	C17A—C18—N3A—C19A	−4.3 (18)
C6—C5—C7—O1	−14.15 (16)	C9A—N2A—C13A—C12A	3.1 (13)
C6—C5—C7—O2	165.55 (10)	C9A—C10A—C11A—C12A	2.7 (4)
C7—C5—C6—C1	−178.69 (10)	C9A—C10A—C11A—C14A	−174.9 (3)
C8—C3—C4—C5	176.09 (10)	N2A—C9A—C10A—C11A	1.6 (8)
C18—N3—C19—C20	0.6 (15)	N3A—C18—N3—C19	−159 (11)
C18—C17A—C16A—C20A	0.9 (9)	N3A—C18—C17—C16	2.5 (10)
C18—C17A—C16A—C15A	−177.3 (5)	N3A—C18—C17A—C16A	2.8 (15)
C18—N3A—C19A—C20A	2 (2)	C19A—C20A—C16A—C17A	−2.1 (11)
N2—C9—C10—C11	−2.3 (6)	C19A—C20A—C16A—C15A	176.0 (8)
N3—C18—C17—C16	0.0 (8)	C10A—C9A—N2A—C13A	−4.4 (12)
N3—C18—C17A—C16A	−0.3 (12)	C10A—C11A—C12A—C13A	−3.8 (5)

N3—C18—N3A—C19A	19 (9)	C10A—C11A—C14A—C15A	168.9 (3)
N3—C19—C20—C16	1.0 (12)	C11A—C12A—C13A—N2A	0.9 (9)
C9—N2—C13—C12	1.9 (9)	C11A—C14A—C15A—C16A	−177.1 (3)
C9—C10—C11—C12	4.0 (3)	C12A—C11A—C14A—C15A	−8.5 (5)
C9—C10—C11—C14	−173.2 (2)	C14A—C11A—C12A—C13A	173.6 (4)
C10—C11—C12—C13	−2.9 (3)	C14A—C15A—C16A—C17A	−172.8 (5)
C10—C11—C14—C15	3.5 (3)	C14A—C15A—C16A—C20A	9.1 (6)
C11—C12—C13—N2	−0.1 (6)	C16A—C20A—C19A—N3A	0.5 (19)

Hydrogen-bond geometry (Å, º)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1A⋯O1[i]	0.899 (17)	2.062 (17)	2.9540 (13)	171.0 (15)
N1—H1B⋯O3[ii]	0.894 (17)	2.157 (17)	3.0500 (13)	178.6 (13)
O2—H2⋯N3[iii]	0.989 (19)	1.70 (2)	2.688 (8)	173.4 (18)
O2—H2⋯N3A[iii]	0.989 (19)	1.63 (2)	2.619 (12)	177 (2)
O4—H4⋯N2[iv]	0.98 (2)	1.72 (2)	2.702 (7)	173.2 (19)
O4—H4⋯N2A[iv]	0.98 (2)	1.59 (2)	2.566 (11)	175 (2)

Symmetry codes: (i) −x+1/2, y−1/2, −z+1/2; (ii) −x+1/2, y+1/2, −z+1/2; (iii) −x+1, −y+2, −z+1; (iv) x−1/2, −y+1/2, z+1/2.