organic compounds

2-Aminobenzoic acid–4-[2-(pyridin-4-yl)ethyl]pyridine (2/1)

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The asymmetric unit of the title co-crystal, $C_{12}H_{12}N_2$·$2C_7H_7NO_2$, comprises a centrosymmetric 4-[2-(pyridin-4-yl)ethyl]pyridine molecule and a 2-aminobenzoic acid molecule in a general position. The acid has a small twist between the carboxylic acid residue and the ring [dihedral angle = 7.13 (6)°] despite the presence of an intramolecular N—H···O(carbonyl) hydrogen bond. Three-molecule aggregates are formed via O—H···N(pyridyl) hydrogen bonds, and these are connected into supramolecular layers in the bc plane by N—H···O(carbonyl) hydrogen bonds and π–π interactions between pyridine and benzene rings [inter-centroid distance = 3.6332 (9) Å]. Layers are connected along the a axis by weak π–π interactions between benzene rings [3.9577 (10) Å].

Related literature

For co-crystals of 2-aminobenzoic acid with pyridyl derivatives, see: Arman, Kaulgud et al. (2012); Arman, Miller et al. (2012). For the isostructural 4,4′-bipyridyl analogue, see: Arman & Tiekink (2013).
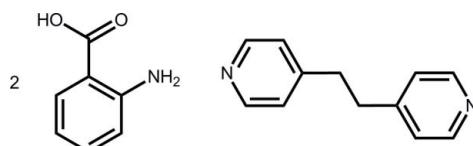
Experimental

Crystal data

C₁₂H₁₂N₂·2C₇H₇NO₂ ·
$C_{12}H_{12}N_2 \cdot 2C_7H_7NO_2$
M_r = 458.51
a = 11.305 (2) Å
b = 11.102 (2) Å
c = 8.8737 (16) Å
β = 94.565 (5)°
V = 1110.2 (4) Å³
Z = 2
Monoclinic, $P2_1/c$
Mo $K\alpha$ radiation
μ = 0.09 mm⁻¹
T = 98 K
0.34 × 0.10 × 0.07 mm

Data collection

Rigaku AFC12/SATURN724 diffractometer
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
T_{min} = 0.864, T_{max} = 1.000
8527 measured reflections
2545 independent reflections
2386 reflections with $I > 2\sigma(I)$
R_{int} = 0.039

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.112
S = 1.08
2545 reflections
163 parameters
3 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.36 e Å⁻³
$\Delta\rho_{min}$ = −0.21 e Å⁻³

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1n···O2	0.86 (1)	2.03 (1)	2.6961 (15)	134 (2)
O1—H1o···N2	0.86 (1)	1.78 (1)	2.6290 (14)	172 (2)
N1—H2n···O2ⁱ	0.85 (1)	2.19 (1)	3.0106 (15)	163 (1)

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

Data collection: CrystalClear (Molecular Structure Corporation & Rigaku, 2005); cell refinement: CrystalClear; data reduction: CrystalClear; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEPII (Johnson, 1976) and DIAMOND (Brandenburg, 2006); software used to prepare material for publication: publCIF (Westrip, 2010).

References

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Sheldrick, G. M. (2008). Acta Cryst. A**64**, 112–122.
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supporting information

2-Aminobenzoic acid–4-[2-(pyridin-4-yl)ethyl]pyridine (2/1)

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S1. Comment

During continuing structural studies of co-crystals involving 2-aminobenzoic acid (anthranilic acid) and variously substituted pyridyl derivatives (Arman, Kaulgud *et al.*, 2012; Arman, Miller *et al.*, 2012), the title co-crystal, (I), was characterized.

The asymmetric unit of (I), Fig. 1, comprises a molecule of 2-aminobenzoic acid in a general position and half a molecule of 4,4′-bipyridylethane, being disposed about a centre of inversion. Despite the presence of an intramolecular N1—H⋯O2 hydrogen bond, Table 1, the carboxylic acid residue is slightly twisted out of the plane of the benzene ring to which it is connected, forming a dihedral angle of 7.13 (6)°. The 4,4′-bipyridylethane molecule is also almost planar with the r.m.s. deviation of the 14 non-hydrogen atoms being 0.066 Å. The structure of (I) is isostructural with the 4,4′-bi-pyridyl derivative (Arman & Tiekink, 2013).

The components of the co-crystal are connected into a three-molecule aggregate *via* O1—H⋯N2 hydrogen bonds, Table 1. These are connected into supramolecular layers in the *bc* plane by N1—H⋯O2 hydrogen bonds, Fig. 2. Additional stability to the layers is afforded by π—π interactions between the pyridyl and benzene rings [inter-centroid distance = 3.6332 (9) Å, angle of inclination = 1.71 (6)° for symmetry operation *x*, *y*, 1 + *z*], Fig. 2. Weaker π—π interactions between centrosymmetrically related benzene rings [3.9577 (10) Å for symmetry operation: -*x*, -*y*, -*z*] provide the links between the layers, Fig. 3.

S2. Experimental

Crystals of (I) were obtained by the co-crystallization of 4,4′-bipyridylethane (Sigma Aldrich, 0.11 mmol) and anthranilic acid (Sigma-Aldrich, 0.22 mmol) in acetone solution. Crystals were obtained by slow evaporation. Melting point: 381–385 K. IR spectra(cm^{-1}): 750(sh)(*m*), 830(*s*)(sh), 1016(w), 1063(w), 1153(*m*), 1238(*m*), 1295(*s*), 1413(*m*), 1607(*m*), 1661(*m*), 2922(br), 3342(*m*), 3449(*m*).

S3. Refinement

C-bound H-atoms were placed in calculated positions (C—H = 0.95-0.99 Å) and were included in the refinement in the riding model approximation with U_{iso}(H) set to 1.2U_{eq}(C). The O-bound and N-bound H-atoms were located in a difference Fourier map and were refined with a distance restraints of O—H = 0.84±0.01 Å and N—H = 0.88±0.01 Å, and with U_{iso}(H) = 1.2U_{eq}(N) and 1.5U_{eq}(O).
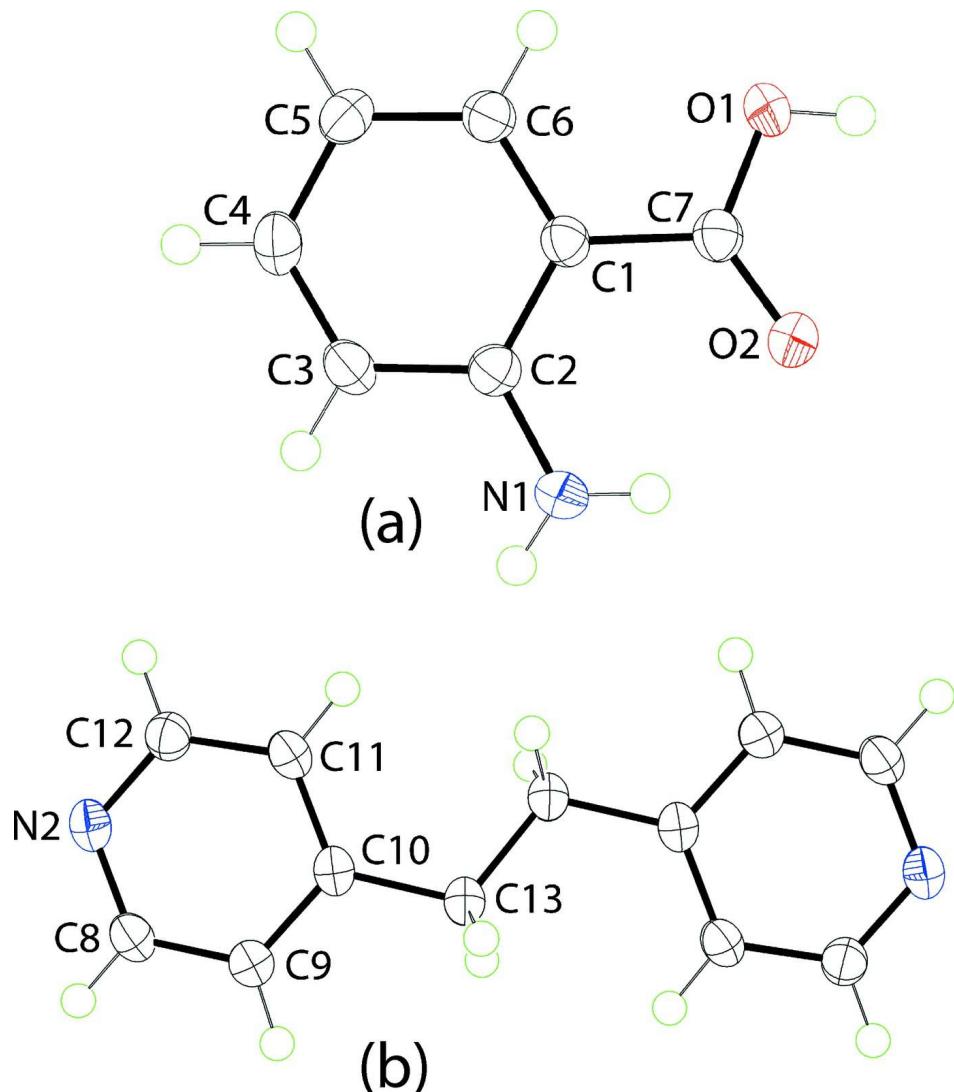
Figure 1

Molecular structures of the components of (I), showing atom-labelling scheme and displacement ellipsoids at the 70% probability level: (*a*) 2-aminobenzoic acid and (*b*) 4,4′-bipyridylethane (unlabelled atoms are related by the symmetry operation: 1 - *x*, -*y*, 2 - *z*).
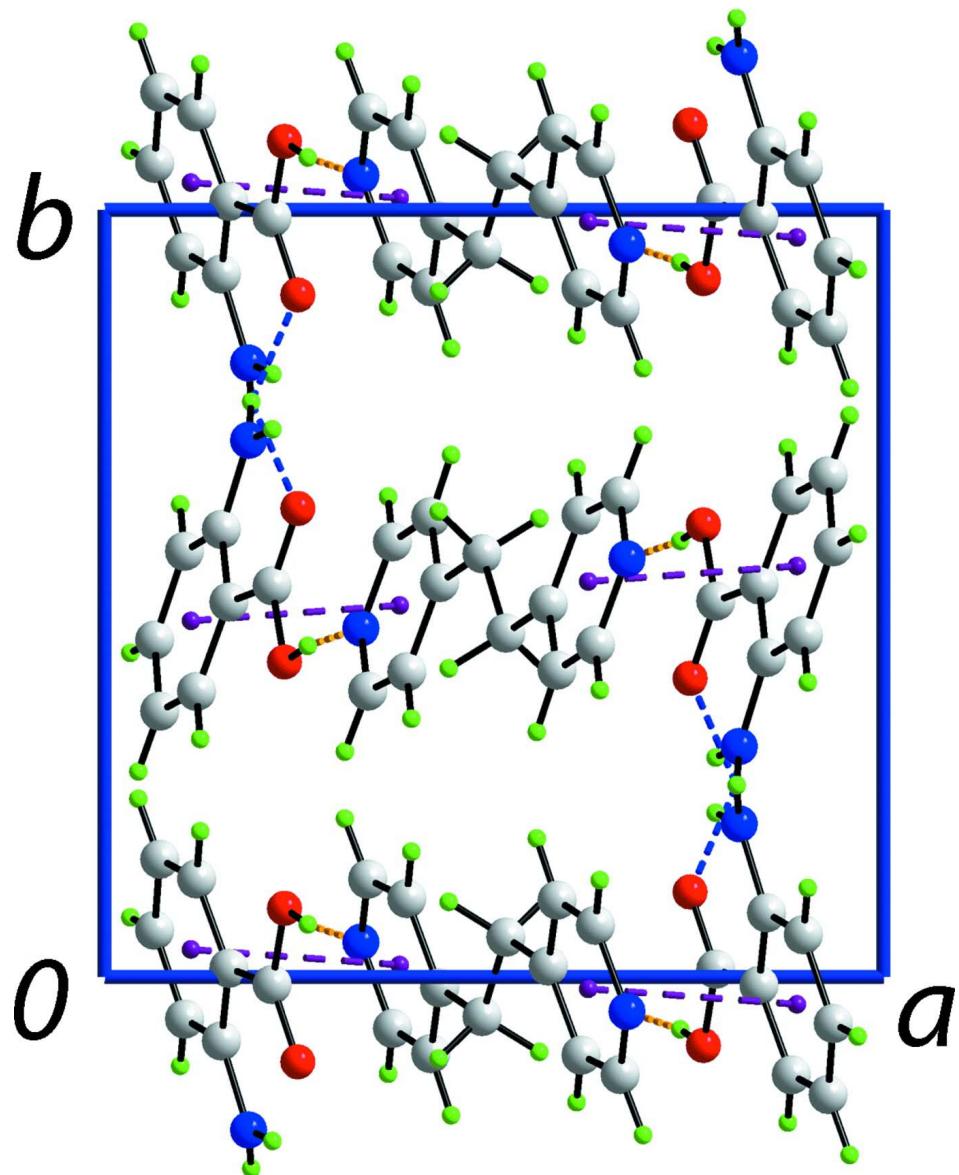
Figure 2
Side-on view of the supramolecular layer in the *bc* plane in (I). The three-molecule aggregates are sustained by O—H···N hydrogen bonds shown as orange dashed lines. These are connected into layers by N—H···O and π—π interactions, shown as blue and purple dashed lines, respectively.
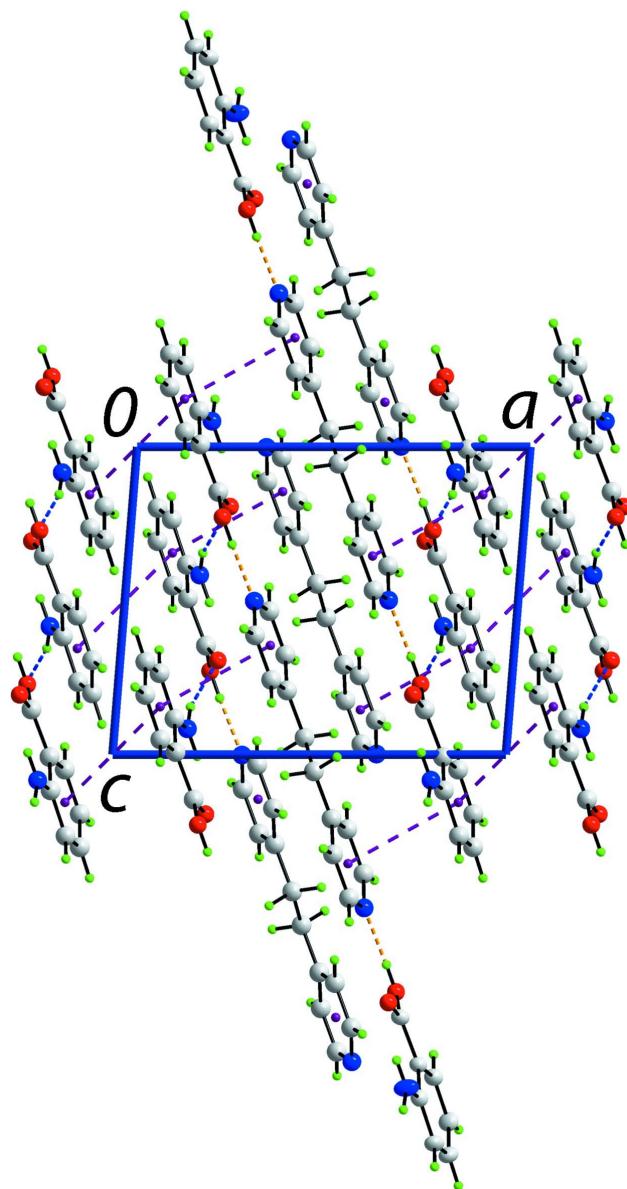
Figure 3

Unit-cell contents of (I) viewed in projection down the *b* axis. The O—H⋯N, N—H⋯O and π—π interactions are shown as orange, blue and purple dashed lines, respectively.

2-Aminobenzoic acid–4-[2-(pyridin-4-yl)ethyl]pyridine (2/1)

Crystal data
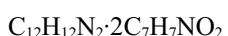
$C_{12}H_{12}N_2 \cdot 2C_7H_7NO_2$	$V = 1110.2\ (4)$ Å^3
$M_r = 458.51$	$Z = 2$
Monoclinic, $P2_1/c$	$F(000) = 484$
Hall symbol: -P 2ybc	$D_x = 1.372$ Mg m^{-3}
$a = 11.305\ (2)$ Å	Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å
$b = 11.102\ (2)$ Å	Cell parameters from 3826 reflections
$c = 8.8737\ (16)$ Å	$\theta = 2.6–40.2°$
$\beta = 94.565\ (5)°$	$\mu = 0.09$ mm^{-1}

T = 98 K

Needle, gold

$0.34 \times 0.10 \times 0.07$ mm

Data collection

Rigaku AFC12K/SATURN724 diffractometer	8527 measured reflections
Radiation source: fine-focus sealed tube	2545 independent reflections
Graphite monochromator	2386 reflections with $I > 2\sigma(I)$
ω scans	R_{int} = 0.039
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)	θ_{max} = 27.5°, θ_{min} = 2.6°
	$h = -14\rightarrow14$
	$k = -14\rightarrow14$
T_{min} = 0.864, T_{max} = 1.000	$l = -9\rightarrow11$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)]$ = 0.045	Hydrogen site location: inferred from neighbouring sites
$wR(F^2)$ = 0.112	
S = 1.08	H atoms treated by a mixture of independent and constrained refinement
2545 reflections	
163 parameters	$w = 1/[\sigma^2(F_o^2) + (0.0469P)^2 + 0.5018P]$ where $P = (F_o^2 + 2F_c^2)/3$
3 restraints	
Primary atom site location: structure-invariant direct methods	$(\Delta/\sigma)_{max} < 0.001$
	$\Delta\rho_{max}$ = 0.36 e Å⁻³
	$\Delta\rho_{min}$ = −0.21 e Å⁻³

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

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

	x	y	z	U_{iso}*/U_{eq}
O1	0.23122 (9)	0.08940 (8)	0.22847 (10)	0.0230 (2)
H1O	0.2610 (14)	0.0684 (16)	0.3166 (13)	0.035*
O2	0.24830 (8)	−0.11075 (8)	0.19402 (10)	0.0221 (2)
N1	0.18511 (11)	−0.19962 (10)	−0.08352 (12)	0.0232 (3)
H1N	0.2156 (13)	−0.2139 (15)	0.0061 (12)	0.028*
H2N	0.1885 (14)	−0.2498 (12)	−0.1548 (14)	0.028*
C1	0.15987 (10)	0.01116 (10)	−0.00795 (13)	0.0161 (2)
C2	0.15020 (10)	−0.08349 (11)	−0.11662 (13)	0.0172 (2)
C3	0.10295 (11)	−0.05498 (11)	−0.26429 (13)	0.0193 (3)
H3	0.0973	−0.1160	−0.3396	0.023*
C4	0.06456 (11)	0.06078 (12)	−0.30126 (13)	0.0208 (3)
H4	0.0332	0.0776	−0.4016	0.025*
C5	0.07110 (11)	0.15347 (11)	−0.19362 (14)	0.0204 (3)

H5	0.0436	0.2322	−0.2196	0.024*
C6	0.11832 (10)	0.12773 (11)	−0.04894 (13)	0.0181 (3)
H6	0.1230	0.1899	0.0249	0.022*
C7	0.21531 (10)	−0.01002 (11)	0.14633 (13)	0.0172 (2)
N2	0.32920 (9)	0.04519 (10)	0.50153 (11)	0.0194 (2)
C8	0.36977 (11)	−0.06728 (11)	0.53384 (13)	0.0199 (3)
H8	0.3642	−0.1262	0.4559	0.024*
C9	0.41896 (11)	−0.10008 (11)	0.67537 (13)	0.0195 (3)
H9	0.4450	−0.1805	0.6939	0.023*
C10	0.43024 (10)	−0.01417 (11)	0.79159 (13)	0.0175 (3)
C11	0.38823 (11)	0.10211 (11)	0.75721 (13)	0.0189 (3)
H11	0.3940	0.1633	0.8323	0.023*
C12	0.33799 (11)	0.12738 (11)	0.61248 (13)	0.0197 (3)
H12	0.3087	0.2063	0.5914	0.024*
C13	0.48476 (11)	−0.05171 (11)	0.94524 (13)	0.0192 (3)
H13A	0.5581	−0.0978	0.9316	0.023*
H13B	0.4289	−0.1066	0.9916	0.023*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0346 (5)	0.0189 (5)	0.0145 (4)	0.0008 (4)	−0.0047 (4)	−0.0020 (3)
O2	0.0306 (5)	0.0181 (4)	0.0170 (4)	0.0008 (3)	−0.0013 (3)	0.0020 (3)
N1	0.0359 (6)	0.0157 (5)	0.0175 (5)	0.0027 (4)	−0.0014 (4)	−0.0031 (4)
C1	0.0178 (5)	0.0164 (6)	0.0141 (5)	−0.0013 (4)	0.0019 (4)	−0.0001 (4)
C2	0.0176 (5)	0.0167 (6)	0.0174 (5)	−0.0014 (4)	0.0023 (4)	0.0005 (4)
C3	0.0227 (6)	0.0200 (6)	0.0151 (5)	−0.0039 (5)	0.0009 (4)	−0.0026 (4)
C4	0.0219 (6)	0.0244 (6)	0.0156 (5)	−0.0023 (5)	−0.0015 (4)	0.0027 (4)
C5	0.0222 (6)	0.0176 (6)	0.0211 (6)	0.0022 (5)	0.0002 (4)	0.0031 (5)
C6	0.0205 (5)	0.0168 (6)	0.0171 (5)	−0.0005 (4)	0.0022 (4)	−0.0005 (4)
C7	0.0194 (5)	0.0176 (6)	0.0148 (5)	−0.0006 (4)	0.0027 (4)	0.0005 (4)
N2	0.0201 (5)	0.0232 (5)	0.0146 (5)	−0.0025 (4)	−0.0002 (4)	−0.0002 (4)
C8	0.0223 (6)	0.0206 (6)	0.0166 (5)	−0.0023 (5)	0.0009 (4)	−0.0032 (4)
C9	0.0208 (6)	0.0191 (6)	0.0184 (6)	0.0005 (4)	−0.0002 (4)	−0.0012 (4)
C10	0.0170 (5)	0.0209 (6)	0.0144 (5)	−0.0017 (4)	0.0003 (4)	0.0000 (4)
C11	0.0201 (6)	0.0198 (6)	0.0166 (5)	−0.0025 (4)	0.0002 (4)	−0.0028 (4)
C12	0.0212 (6)	0.0194 (6)	0.0184 (6)	−0.0013 (4)	0.0002 (4)	0.0009 (4)
C13	0.0213 (6)	0.0201 (6)	0.0156 (5)	0.0001 (5)	−0.0017 (4)	0.0002 (5)

Geometric parameters (Å, º)

O1—C7	1.3271 (14)	C6—H6	0.9500
O1—H1O	0.859 (9)	N2—C12	1.3402 (16)
O2—C7	1.2425 (15)	N2—C8	1.3530 (16)
N1—C2	1.3732 (16)	C8—C9	1.3813 (17)
N1—H1N	0.856 (9)	C8—H8	0.9500
N1—H2N	0.845 (9)	C9—C10	1.4031 (16)
C1—C6	1.4144 (16)	C9—H9	0.9500

C1—C2	1.4246 (16)	C10—C11	1.4007 (17)
C1—C7	1.4783 (16)	C10—C13	1.5096 (16)
C2—C3	1.4111 (16)	C11—C12	1.3910 (16)
C3—C4	1.3875 (18)	C11—H11	0.9500
C3—H3	0.9500	C12—H12	0.9500
C4—C5	1.4020 (17)	C13—C13^i	1.526 (2)
C4—H4	0.9500	C13—H13A	0.9900
C5—C6	1.3805 (16)	C13—H13B	0.9900
C5—H5	0.9500		
C7—O1—H1O	107.5 (12)	O1—C7—C1	113.90 (10)
C2—N1—H1N	117.4 (11)	C12—N2—C8	117.95 (10)
C2—N1—H2N	119.2 (11)	N2—C8—C9	122.76 (11)
H1N—N1—H2N	122.3 (16)	N2—C8—H8	118.6
C6—C1—C2	119.66 (11)	C9—C8—H8	118.6
C6—C1—C7	119.43 (10)	C8—C9—C10	119.70 (11)
C2—C1—C7	120.90 (11)	C8—C9—H9	120.1
N1—C2—C3	119.37 (11)	C10—C9—H9	120.1
N1—C2—C1	122.85 (11)	C11—C10—C9	117.20 (11)
C3—C2—C1	117.78 (11)	C11—C10—C13	123.93 (11)
C4—C3—C2	121.03 (11)	C9—C10—C13	118.87 (11)
C4—C3—H3	119.5	C12—C11—C10	119.56 (11)
C2—C3—H3	119.5	C12—C11—H11	120.2
C3—C4—C5	121.35 (11)	C10—C11—H11	120.2
C3—C4—H4	119.3	N2—C12—C11	122.81 (12)
C5—C4—H4	119.3	N2—C12—H12	118.6
C6—C5—C4	118.50 (11)	C11—C12—H12	118.6
C6—C5—H5	120.7	C10—C13—C13^i	115.01 (13)
C4—C5—H5	120.7	C10—C13—H13A	108.5
C5—C6—C1	121.63 (11)	C13^i—C13—H13A	108.5
C5—C6—H6	119.2	C10—C13—H13B	108.5
C1—C6—H6	119.2	C13^i—C13—H13B	108.5
O2—C7—O1	122.52 (11)	H13A—C13—H13B	107.5
O2—C7—C1	123.52 (11)		
C6—C1—C2—N1	−177.85 (11)	C6—C1—C7—O1	−6.50 (16)
C7—C1—C2—N1	3.56 (18)	C2—C1—C7—O1	172.09 (10)
C6—C1—C2—C3	2.41 (17)	C12—N2—C8—C9	0.20 (18)
C7—C1—C2—C3	−176.18 (10)	N2—C8—C9—C10	−1.20 (18)
N1—C2—C3—C4	178.72 (11)	C8—C9—C10—C11	1.02 (17)
C1—C2—C3—C4	−1.53 (17)	C8—C9—C10—C13	−179.72 (11)
C2—C3—C4—C5	−0.08 (18)	C9—C10—C11—C12	0.05 (17)
C3—C4—C5—C6	0.82 (18)	C13—C10—C11—C12	−179.16 (11)
C4—C5—C6—C1	0.11 (18)	C8—N2—C12—C11	0.95 (18)
C2—C1—C6—C5	−1.75 (18)	C10—C11—C12—N2	−1.08 (19)
C7—C1—C6—C5	176.86 (11)	C11—C10—C13—C13^i	−12.1 (2)

| C6—C1—C7—O2 | 176.01 (11) | C9—C10—C13—C13[i] | 168.71 (12) |
| C2—C1—C7—O2 | −5.40 (18) | | |

Symmetry code: (i) −*x*+1, −*y*, −*z*+2.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1n···O2	0.86 (1)	2.03 (1)	2.6961 (15)	134 (2)
O1—H1o···N2	0.86 (1)	1.78 (1)	2.6290 (14)	172 (2)
N1—H2n···O2[ii]	0.85 (1)	2.19 (1)	3.0106 (15)	163 (1)

Symmetry code: (ii) *x*, −*y*−1/2, *z*−1/2.