

Crystal structure of 4-aminobenzoic acid–4-methylpyridine (1/1)

M. Krishna Kumar,^a P. Pandi,^b S. Sudhakar,^a
G. Chakkaravarthi^{c*} and R. Mohan Kumar^{a*}

^aDepartment of Physics, Presidency College, Chennai 600 005, India, ^bDepartment of Physics, Panimalar Engineering College, Chennai 600 123, India, and

^cDepartment of Physics, CPCL Polytechnic College, Chennai 600 068, India.

*Correspondence e-mail: chakkaravarthi_2005@yahoo.com, mohan66@hotmail.com

Received 2 January 2015; accepted 14 January 2015

Edited by W. T. A. Harrison, University of Aberdeen, Scotland

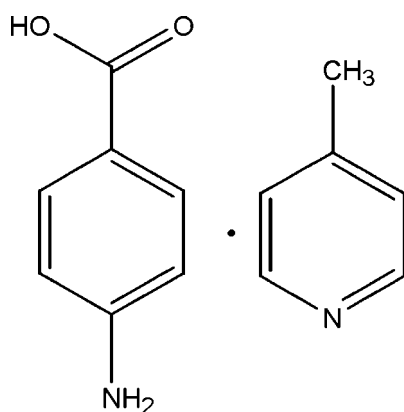
In the title 1:1 adduct, C₆H₇N·C₇H₇NO₂, the carboxylic acid group is twisted at an angle of 4.32 (18)° with respect to the attached benzene ring. In the crystal, the carboxylic acid group is linked to the pyridine ring by an O—H···N hydrogen bond, forming a dimer. The dimers are linked by N—H···O hydrogen bonds, generating (010) sheets.

Keywords: crystal structure; adduct; O—H···N and N—H···O hydrogen bonds; layered structure.

CCDC reference: 1043592

1. Related literature

For background to pyridine derivatives, see: Tomaru *et al.* (1991). Katritzky *et al.* (1996); Akkurt *et al.* (2005). For related structures, see: Smith & Wermuth (2010); Hemamalini & Fun (2010); Kannan *et al.* (2012); Thanigaimani *et al.* (2012); Muralidharan *et al.* (2013).



2. Experimental

2.1. Crystal data

C ₆ H ₇ N·C ₇ H ₇ NO ₂	$V = 620.49 (11) \text{ \AA}^3$
$M_r = 230.26$	$Z = 2$
Monoclinic, Pc	Mo $K\alpha$ radiation
$a = 7.5970 (7) \text{ \AA}$	$\mu = 0.09 \text{ mm}^{-1}$
$b = 11.6665 (12) \text{ \AA}$	$T = 295 \text{ K}$
$c = 7.6754 (8) \text{ \AA}$	$0.28 \times 0.24 \times 0.20 \text{ mm}$
$\beta = 114.200 (3)^\circ$	

2.2. Data collection

Bruker Kappa APEXII CCD diffractometer	10064 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	2144 independent reflections
$T_{\min} = 0.977$, $T_{\max} = 0.983$	1458 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.030$

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.108$	$\Delta\rho_{\text{max}} = 0.12 \text{ e \AA}^{-3}$
$S = 1.03$	$\Delta\rho_{\text{min}} = -0.13 \text{ e \AA}^{-3}$
2144 reflections	
159 parameters	
3 restraints	

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1···N2 ⁱ	0.84 (1)	1.81 (1)	2.644 (3)	177 (4)
N1—H1A···O2 ⁱⁱ	0.86	2.32	3.049 (3)	142
N1—H1B···O2 ⁱⁱⁱ	0.86	2.17	3.031 (3)	174

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

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINTE* (Bruker, 2004); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2015); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97*.

Acknowledgements

The authors wish to acknowledge the SAIF, IIT, Madras, for the data collection.

Supporting information for this paper is available from the IUCr electronic archives (Reference: HB7348).

References

- Akkurt, M., Karaca, S., Jarrahpour, A. A., Zarei, M. & Büyükgüngör, O. (2005). *Acta Cryst.* **E61**, o776–o778.
- Bruker (2004). *APEX2* and *SAINTE*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Hemamalini, M. & Fun, H.-K. (2010). *Acta Cryst.* **E66**, o2151–o2152.
- Kannan, V., Sugumar, P., Brahadeeswaran, S. & Ponnuswamy, M. N. (2012). *Acta Cryst.* **E68**, o3187.
- Katritzky, A. R., Rees, C. W. & Scriven, E. F. V. (1996). In *Comprehensive Heterocyclic Chemistry II*. Oxford: Pergamon Press.

- Muralidharan, S., Elavarasu, N., Srinivasan, T., Gopalakrishnan, R. & Velmurugan, D. (2013). *Acta Cryst.* **E69**, o910.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.
- Smith, G. & Wermuth, U. D. (2010). *Acta Cryst.* **E66**, o1254.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Thanigaimani, K., Farhadikoutenaie, A., Khalib, N. C., Arshad, S. & Razak, I. A. (2012). *Acta Cryst.* **E68**, o3196–o3197.
- Tomaru, S., Matsumoto, S., Kurihara, T., Suzuki, H., Ooba, N. & Kaino, T. (1991). *Appl. Phys. Lett.* **58**, 2583–2585.

supporting information

Acta Cryst. (2015). E71, o125–o126 [doi:10.1107/S2056989015000791]

Crystal structure of 4-aminobenzoic acid–4-methylpyridine (1/1)

M. Krishna Kumar, P. Pandi, S. Sudhahar, G. Chakkaravarthi and R. Mohan Kumar

S1. Chemical context

Aminopyridine and its derivatives play an important role in heterocyclic chemistry (Katritzky *et al.*, 1996). Some pyridine derivatives possess nonlinear optical (NLO) properties (Tomaru *et al.*, 1991) and possess antibacterial and anti-fungal activities (Akkurt *et al.*, 2005). we herewith, report the synthesis and the crystal structure of (I) (Fig. 1).

S2. Structural commentary

The molecular structure of the title compound (I) is shown in (Fig. 1). It consists of two independent molecules in the asymmetric unit. In the 4-aminobenzoic acid molecule, the carboxyl group is twisted at an angle of 4.32 (18)° with respect to the aromatic ring. In the 4-methylpyridine molecule, the pyridine ring (C8—C12/N2) is almost planar [maximum deviation 0.002 (3) Å]. The dihedral angle between the benzene ring (C1—C6) and pyridine ring (C8—C12/N2) is 57.11 (14)°.

S3. Supramolecular features

In the crystal structure, 4-aminobenzoate and 4-methylpyridine molecules are linked by weak intermolecular O—H···N hydrogen bonds and forms infinite one-dimensional chain along [0 0 1]. The adjacent 4-aminobenzoate molecules are connected by weak intermolecular N—H···O hydrogen bonds, forming R²₂(12) ring motif in a two-dimensional network in the (010) plane (Table 2 & Fig. 2).

S4. Database survey

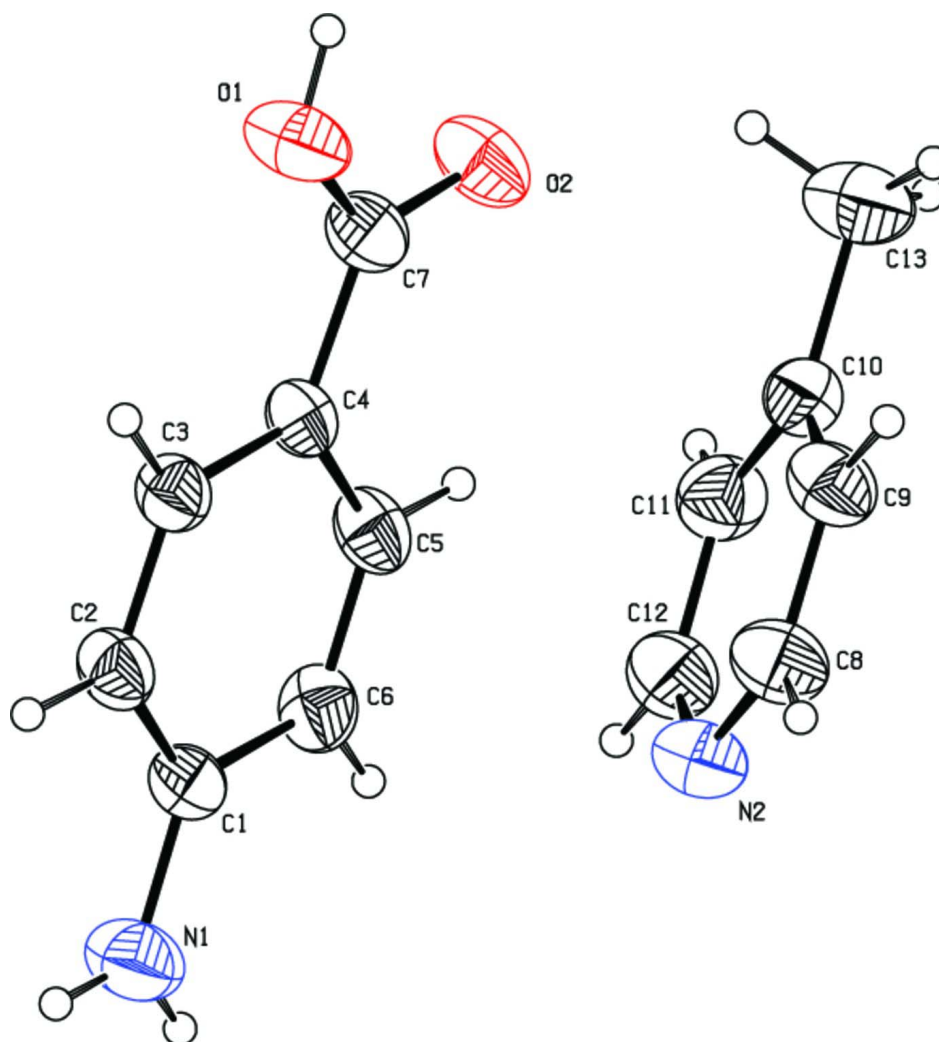
Several similar structures containing methylpyridinium and nitrobenzoate molecules have been reported earlier: i.e., 2-Amino-5-methylpyridinium 2-aminobenzoate (Thanigaimani *et al.*, 2012); 2-Amino-5-chloropyridinium 4-aminobenzoate (Kannan *et al.*, 2012); 2-Amino-4-methylpyridinium 2-nitrobenzoate (Muralidharan *et al.*, 2013); 4-Methylpyridinium 2-carboxy-4,5-dichlorobenzoate monohydrate [Smith & Wermuth, (2010)]; 2-Amino-4-methylpyridinium 2-hydroxybenzoate [Hemamalini & Fun (2010)].

S5. Synthesis and crystallization

Equimolar quantity of 4-methylpyridine and 4-aminobenzoic acid were dissolved in methanol-water mixed solvent and colourless blocks of the title adduct were grown by slow evaporation of the solvents.

S6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The hydrogen atoms attached to C atoms and N atom were fixed geometrically and treated as riding with C—H = 0.93 Å (aromatic) or 0.96 Å (methyl) and N—H = 0.86 Å with U_{iso}(H) = 1.2 U_{eq}(C or N) or 1.5 U_{eq}(C) The hydroxyl H atom was located in a difference Fourier map, and refined with U_{iso}(H) = 1.2 U_{eq}(O) and distance restraint O—H = 0.82 Å.

**Figure 1**

The molecular structure of (I), with 30% probability displacement ellipsoids for non-H atoms.

4-Aminobenzoic acid-4-methylpyridine (1/1)

Crystal data

$C_6H_7N \cdot C_7H_7NO_2$

$M_r = 230.26$

Monoclinic, Pc

Hall symbol: $P -2yc$

$a = 7.5970$ (7) Å

$b = 11.6665$ (12) Å

$c = 7.6754$ (8) Å

$\beta = 114.200$ (3)°

$V = 620.49$ (11) Å³

$Z = 2$

$F(000) = 244$

$D_x = 1.232$ Mg m⁻³

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

Cell parameters from 2749 reflections

$\theta = 3.4$ – 21.8 °

$\mu = 0.09$ mm⁻¹

$T = 295$ K

Block, colourless

$0.28 \times 0.24 \times 0.20$ mm

Data collection

Bruker Kappa APEXII CCD
diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
 ω and φ scan
Absorption correction: multi-scan
(*SADABS*; Sheldrick, 1996)
 $T_{\min} = 0.977$, $T_{\max} = 0.983$

10064 measured reflections
2144 independent reflections
1458 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.030$
 $\theta_{\max} = 26.7^\circ$, $\theta_{\min} = 3.4^\circ$
 $h = -9 \rightarrow 8$
 $k = -14 \rightarrow 14$
 $l = -9 \rightarrow 9$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.108$
 $S = 1.03$
2144 reflections
159 parameters
3 restraints
Primary atom site location: structure-invariant
direct methods
Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites
H atoms treated by a mixture of independent
and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0554P)^2 + 0.0229P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.12 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.13 \text{ e } \text{\AA}^{-3}$
Extinction correction: *SHELXL97* (Sheldrick,
2008), $F_c^* = kFc[1 + 0.001x \text{Fc}^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.013 (4)

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.

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.3693 (4)	0.1034 (2)	0.7149 (4)	0.0567 (6)
C2	0.4434 (4)	0.2029 (2)	0.6722 (4)	0.0591 (7)
H2	0.3671	0.2471	0.5675	0.071*
C3	0.6273 (4)	0.2362 (2)	0.7829 (3)	0.0558 (6)
H3	0.6737	0.3037	0.7529	0.067*
C4	0.7475 (4)	0.1730 (2)	0.9383 (4)	0.0508 (6)
C5	0.6737 (4)	0.0738 (2)	0.9798 (4)	0.0594 (7)
H5	0.7516	0.0294	1.0835	0.071*
C6	0.4892 (4)	0.0392 (2)	0.8724 (4)	0.0629 (7)
H6	0.4429	-0.0278	0.9043	0.076*
C7	0.9416 (4)	0.2104 (2)	1.0596 (4)	0.0587 (7)
C8	0.4371 (5)	0.4546 (2)	1.3188 (5)	0.0729 (8)
H8	0.3567	0.5148	1.3183	0.087*
C9	0.6306 (4)	0.4655 (2)	1.4263 (4)	0.0693 (8)
H9	0.6791	0.5319	1.4967	0.083*

C10	0.7534 (4)	0.3784 (2)	1.4304 (4)	0.0639 (7)
C11	0.6716 (4)	0.2836 (2)	1.3242 (4)	0.0718 (8)
H11	0.7487	0.2220	1.3229	0.086*
C12	0.4767 (5)	0.2790 (3)	1.2196 (4)	0.0766 (9)
H12	0.4249	0.2135	1.1479	0.092*
C13	0.9658 (5)	0.3866 (3)	1.5468 (6)	0.0954 (11)
H13A	1.0310	0.3941	1.4635	0.143*
H13B	1.0099	0.3186	1.6229	0.143*
H13C	0.9930	0.4524	1.6289	0.143*
N1	0.1840 (4)	0.0710 (2)	0.6087 (4)	0.0827 (8)
H1A	0.1113	0.1124	0.5137	0.099*
H1B	0.1395	0.0092	0.6364	0.099*
N2	0.3582 (3)	0.3627 (2)	1.2152 (4)	0.0722 (6)
O1	0.9921 (3)	0.30989 (17)	1.0123 (3)	0.0808 (6)
H1	1.109 (2)	0.324 (3)	1.076 (5)	0.121*
O2	1.0516 (3)	0.15755 (17)	1.1996 (3)	0.0778 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0545 (16)	0.0584 (15)	0.0526 (15)	-0.0071 (14)	0.0173 (13)	-0.0070 (14)
C2	0.0599 (17)	0.0581 (15)	0.0489 (15)	0.0009 (12)	0.0118 (13)	0.0088 (12)
C3	0.0582 (16)	0.0536 (13)	0.0509 (15)	-0.0050 (13)	0.0175 (13)	0.0058 (12)
C4	0.0529 (14)	0.0490 (12)	0.0442 (13)	0.0040 (12)	0.0135 (12)	0.0026 (12)
C5	0.0671 (18)	0.0516 (14)	0.0484 (16)	0.0021 (13)	0.0124 (14)	0.0046 (12)
C6	0.077 (2)	0.0518 (14)	0.0590 (17)	-0.0076 (14)	0.0273 (15)	0.0048 (13)
C7	0.0563 (17)	0.0532 (13)	0.0583 (17)	0.0045 (13)	0.0150 (14)	0.0003 (14)
C8	0.0630 (18)	0.0626 (16)	0.081 (2)	0.0031 (15)	0.0172 (16)	0.0007 (16)
C9	0.068 (2)	0.0617 (17)	0.0665 (19)	-0.0085 (14)	0.0150 (16)	-0.0042 (13)
C10	0.0579 (18)	0.0740 (17)	0.0585 (17)	-0.0045 (16)	0.0225 (14)	0.0063 (15)
C11	0.0680 (19)	0.0723 (18)	0.078 (2)	0.0015 (15)	0.0325 (18)	-0.0048 (16)
C12	0.077 (2)	0.0747 (19)	0.074 (2)	-0.0158 (17)	0.0260 (17)	-0.0171 (16)
C13	0.0604 (19)	0.105 (2)	0.104 (3)	-0.0070 (17)	0.0163 (18)	0.002 (2)
N1	0.0655 (16)	0.0852 (18)	0.0809 (18)	-0.0163 (13)	0.0132 (14)	0.0063 (15)
N2	0.0567 (14)	0.0719 (15)	0.0766 (16)	-0.0059 (13)	0.0157 (12)	-0.0023 (13)
O1	0.0588 (11)	0.0691 (12)	0.0883 (16)	-0.0105 (10)	0.0035 (11)	0.0130 (11)
O2	0.0678 (13)	0.0726 (12)	0.0665 (12)	0.0068 (10)	0.0006 (10)	0.0090 (10)

Geometric parameters (Å, °)

C1—N1	1.359 (4)	C8—H8	0.9300
C1—C2	1.387 (3)	C9—C10	1.371 (4)
C1—C6	1.397 (4)	C9—H9	0.9300
C2—C3	1.361 (4)	C10—C11	1.363 (4)
C2—H2	0.9300	C10—C13	1.493 (5)
C3—C4	1.380 (3)	C11—C12	1.366 (4)
C3—H3	0.9300	C11—H11	0.9300
C4—C5	1.379 (3)	C12—N2	1.319 (4)

C4—C7	1.452 (3)	C12—H12	0.9300
C5—C6	1.364 (4)	C13—H13A	0.9600
C5—H5	0.9300	C13—H13B	0.9600
C6—H6	0.9300	C13—H13C	0.9600
C7—O2	1.224 (3)	N1—H1A	0.8600
C7—O1	1.319 (3)	N1—H1B	0.8600
C8—N2	1.323 (3)	O1—H1	0.836 (10)
C8—C9	1.365 (4)		
N1—C1—C2	120.8 (2)	C8—C9—C10	119.9 (3)
N1—C1—C6	121.2 (2)	C8—C9—H9	120.0
C2—C1—C6	118.0 (2)	C10—C9—H9	120.0
C3—C2—C1	120.2 (2)	C11—C10—C9	116.6 (3)
C3—C2—H2	119.9	C11—C10—C13	121.7 (3)
C1—C2—H2	119.9	C9—C10—C13	121.7 (3)
C2—C3—C4	122.2 (2)	C10—C11—C12	120.2 (3)
C2—C3—H3	118.9	C10—C11—H11	119.9
C4—C3—H3	118.9	C12—C11—H11	119.9
C5—C4—C3	117.4 (2)	N2—C12—C11	123.4 (3)
C5—C4—C7	120.4 (2)	N2—C12—H12	118.3
C3—C4—C7	122.1 (2)	C11—C12—H12	118.3
C6—C5—C4	121.5 (2)	C10—C13—H13A	109.5
C6—C5—H5	119.2	C10—C13—H13B	109.5
C4—C5—H5	119.2	H13A—C13—H13B	109.5
C5—C6—C1	120.6 (2)	C10—C13—H13C	109.5
C5—C6—H6	119.7	H13A—C13—H13C	109.5
C1—C6—H6	119.7	H13B—C13—H13C	109.5
O2—C7—O1	120.9 (3)	C1—N1—H1A	120.0
O2—C7—C4	124.1 (2)	C1—N1—H1B	120.0
O1—C7—C4	115.0 (2)	H1A—N1—H1B	120.0
N2—C8—C9	123.3 (3)	C12—N2—C8	116.6 (3)
N2—C8—H8	118.4	C7—O1—H1	112 (3)
C9—C8—H8	118.4		
N1—C1—C2—C3	178.1 (3)	C3—C4—C7—O2	179.2 (3)
C6—C1—C2—C3	-0.5 (4)	C5—C4—C7—O1	-176.1 (2)
C1—C2—C3—C4	0.9 (4)	C3—C4—C7—O1	1.3 (3)
C2—C3—C4—C5	-0.5 (4)	N2—C8—C9—C10	0.0 (5)
C2—C3—C4—C7	-178.1 (2)	C8—C9—C10—C11	-0.2 (4)
C3—C4—C5—C6	-0.2 (4)	C8—C9—C10—C13	-179.7 (3)
C7—C4—C5—C6	177.4 (2)	C9—C10—C11—C12	0.4 (4)
C4—C5—C6—C1	0.5 (4)	C13—C10—C11—C12	179.9 (3)
N1—C1—C6—C5	-178.8 (3)	C10—C11—C12—N2	-0.4 (5)
C2—C1—C6—C5	-0.2 (4)	C11—C12—N2—C8	0.1 (5)
C5—C4—C7—O2	1.7 (4)	C9—C8—N2—C12	0.1 (5)

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>
O1—H1 \cdots N2 ⁱ	0.84 (1)	1.81 (1)	2.644 (3)	177 (4)
N1—H1A \cdots O2 ⁱⁱ	0.86	2.32	3.049 (3)	142
N1—H1B \cdots O2 ⁱⁱⁱ	0.86	2.17	3.031 (3)	174

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