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Isolation of 3-amino-4-nitrobenzyl acetate: evidence of an undisclosed impurity in 5-amino-2-nitrobenzoic acid

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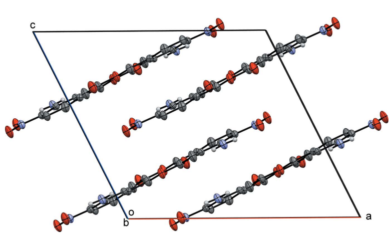
Yellow crystals of the title compound 3-amino-4-nitrobenzyl acetate, $C_9H_{10}N_2O_4$, were isolated from the reaction of acetic anhydride with (5-amino-2-nitrophenyl)methanol, prepared from reduction of commerically available 5-amino-2-nitrobenzoic acid with borane–THF. The molecule is essentially planar (r.m.s. deviation = 0.028 Å). The molecules are linked by intermolecular N—H···O hydrogen-bonding interactions between the carbonyl and amine groups, forming a zigzag chain along the *b*-axis direction lying in a plane parallel to ($\overline{1}02$). The chains are stacked along the *c* axis by π–π interactions [centroid–centroid distances = 3.6240 (3) and 3.5855 (4) Å]. A strong intramolecular N—H···O hydrogen-bonding interaction is observed between the nitro group and the amine group [2.660 (2) Å].



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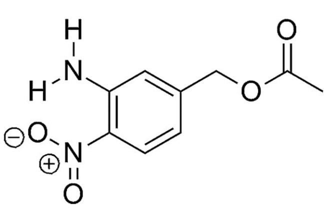
1. Chemical Context

Often commercially available chemicals are sold with minor impurities in the range 1–5%; the user may choose to 'use as received' or further purify. The identities of the impurities are rarely disclosed in fine chemicals. Though these impurities may serve as benign spectators, in some cases they might hinder reactivity and/or produce undesirable by-products that are difficult to separate from the desired product. Therefore, it is important to identify these impurities to allow the users to decide if further purification is warranted. We recently purchased 5-amino-2-nitrobenzoic acid from Acros Organics© (5 g, 97%, AC33074-0050) for our ongoing studies of photo-induced decarboxylation of *ortho*-nitrobenzyl esters (Cabane *et al.*, 2010; Pocker *et al.*, 1978). The isolation of the title compound, 3-amino-4-nitrobenzyl acetate, after the reaction of crude (5-amino-2-nitrophenyl)methanol, prepared from the reduction of 5-amino-2-nitrobenzoic acid, with acetic anhydride suggests 3-amino-4-nitrobenzoic acid is an impurity in the commercially available starting material.



2. Structural Commentary

The asymmetric unit of the title compound (Fig. 1) displays an essentially planar molecule (r.m.s.d. 0.028 Å) with the amine, nitro and acetate groups resting in the plane of the arene. The

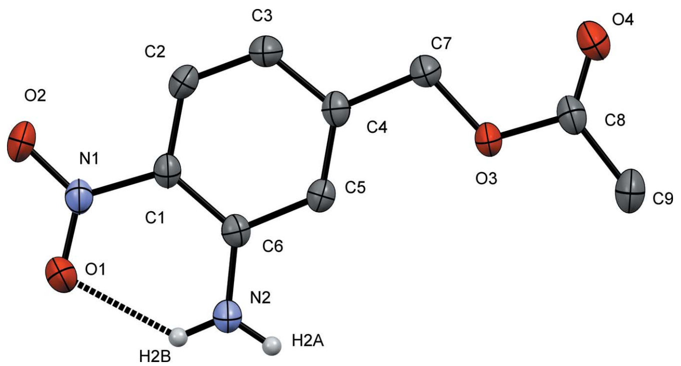


Figure 1
A displacement ellipsoid plot of 3-amino-4-nitrobenzyl acetate (50% probability level). C-bound H atoms have been omitted for clarity.

carbonyl, C═O [1.208 (2) Å], and ester, C—O [1.3477 (19) Å], bond distances are unassuming. The nitro bond distances [O1—N1 1.2500 (16) and O2—N1 1.2401 (17) Å] are similar to those in *N*-(3-chlorophenyl)-3-nitropyridin-2-amine [1.222 (2) and 1.245 (2) Å] (Aznan *et al.*, 2011). Atom O1 of the nitro group is involved in strong intramolecular hydrogen bonding [graph set *S*1, 1(6)] between H2*B* of the amine at a distance of 2.06 (2) Å, forming a rigid, thermodynamically stable six-membered ring (Fig. 1). The elongated O1—N1 bond distance, as compared to the O2—N1 distance, is consistent with resonance-assisted hydrogen bonding between O1 and H2*B* (Beck & Mo, 2006).

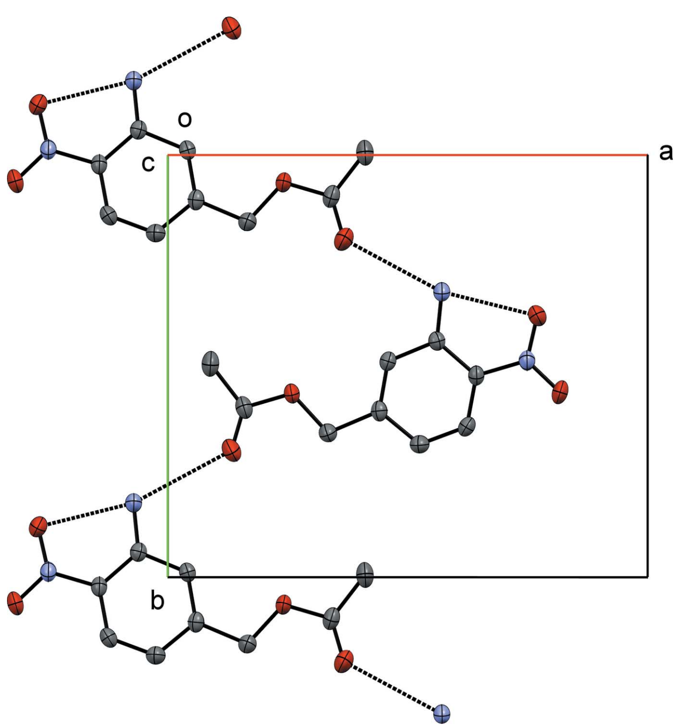


Figure 2
A single of layer of the unit cell of 3-amino-4-nitrobenzoic acid through the *ab* plane (observed down the *c* axis), highlighting the hydrogen-bonding motif.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*A*···O4^{i}	0.83 (2)	2.18 (2)	3.005 (2)	171.5 (17)
N2—H2*B*···O1	0.84 (2)	2.06 (2)	2.6600 (19)	128.0 (16)
N2—H2*B*···O1^{ii}	0.84 (2)	2.44 (2)	3.1443 (19)	142.7 (16)

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

3. Supramolecular Features

The crystal structure of 3-amino-4-nitrobenzyl acetate has interesting supramolecular features. The molecules are arranged in layers held together by intermolecular N2—H2*A*···O4 [3.005 (2) Å] hydrogen bonding [graph set *C*1,1(9)] interactions between the carbonyl and amine groups forming a zigzag chain along the *b*-axis direction (Fig. 2 and Table 1) lying in a plane parallel to ($\bar{1}$02). A view of a single layer along the *ab* plane, observed down the *c* axis (Fig. 2) provides a representative illustration of the hydrogen-bonding interactions of 3-amino-4-nitrobenzyl acetate. Observing the unit cell along the *b*-axis (Fig. 3) shows four layers along the *c* axis separated at a distance of 3.3163 (10) Å with the arene groups stacked one above the other. The chains stack along the *c* axis by *π*–*π* interactions [centroid–centroid distances = 3.6240 (3) Å (symmetry code 1 − *x*, 1 − *y*, 1 − *z*) and 3.5855 (4) Å (symmetry code 1 − *x*, *y*, $\frac{3}{2}$ − *z*)].

4. Database Survey

For a related benzyl acetate structure, see Kasuga *et al.* (2015). For alkyl- and aryl-3-amino-4-nitro-benzoates and benzoic acids displaying similar intramolecular hydrogen bonding between the amino and nitro groups, see: Narendra Babu *et al.* (2009); Abdul Rahim *et al.* (2010); Yoon *et al.* (2011); Yoon *et al.* (2012).

5. Synthesis and Crystallization

(5-Amino-2-nitrophenyl)methanol: (5-amino-2-nitrophenyl)-methanol was prepared by a modified literature protocol

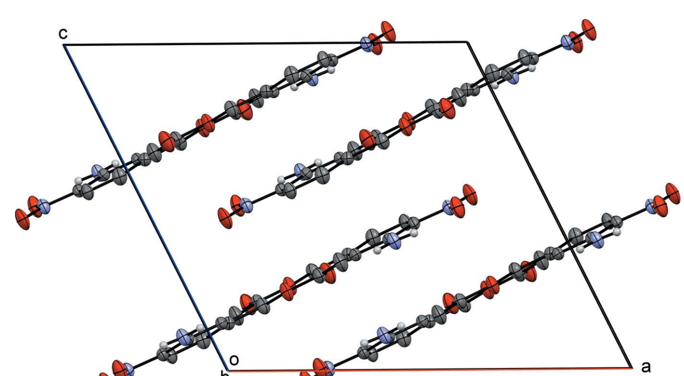


Figure 3
A displacement ellipsoid plot of the unit cell of 3-amino-4-nitrobenzoic acid observed down the *b* axis.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_9H_{10}N_2O_4$
M_r	210.19
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	173
a, *b*, *c* (Å)	14.4803 (15), 11.4054 (11), 13.0936 (13)
β (°)	116.341 (8)
V (Å^3)	1937.9 (4)
Z	8
Radiation type	Mo *K*α
μ (mm^{-1})	0.12
Crystal size (mm)	0.25 × 0.25 × 0.10
Data collection	
Diffractometer	Rigaku Mercury375R
Absorption correction	Multi-scan (*REQAB*; Rigaku, 1998)
T_{min}, T_{max}	0.840, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8409, 1759, 1348
R_{int}	0.045
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.601
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.037, 0.098, 1.06
No. of reflections	1759
No. of parameters	176
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.21, −0.17

Computer programs: *CrystalClear-SM Expert* (Rigaku, 2014), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2013* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

(Yoon *et al.* 1973). To a solution of 5-amino-2-nitrobenzoic acid (97%, 1.5 g, 8.2 mmol) dissolved in tetrahydrofuran (10 mL), borane–THF (27.6 mL, 1.0 *M* in THF, 27.6 mmol) was added dropwise by dropping funnel over 30 minutes. The reaction was stirred overnight at room temperature. The reaction was quenched with aqueous potassium hydroxide (2.45 *M*) until pH 11 was reached and continued to be stirred for 6 h, resulting in a greenish-brown solution. The solution was treated with a saturated solution of potassium carbonate followed by treatment with hydrochloric acid until pH 1 was reached. The reaction mixture was extracted with diethyl ether three times; organic portions were collected and dried with anhydrous sodium sulfate overnight. The solution was filtered under vacuum, the filtrate was collected and all solvent removed under rotary evaporation to give a green powder (0.68 g, 49%). ^{1}H NMR, (300 MHz, acetone-d_6) δ: 4.61 (*t*, 1H, –OH, $^3J_{HH}$ = 5.3 Hz), 4.95 (*d*, 2H, CH_2, $^3J_{HH}$ = 5.3 Hz) , 6.03 (*bs*, 2H, NH_2), 6.63 (*d*d, 1H, Ar-H, $^3J_{HH}$ = 8.8 Hz, $^3J_{HH}$ = 2.3 Hz), 7.07 (*m*, 1H, Ar-H), 8.02 (*dd*, 1H, $^3J_{HH}$ = 9.4 Hz, $^3J_{HH}$ = 3.0 Hz) (Aujard *et al.* 2006). Note: minor impurities were observed in the base line in the aromatic region.

3-Amino-4-nitrobenzyl acetate: (5-amino-2-nitrophenyl)-methanol (10 mg, 0.0595 mmol) and triethylamine (17 µL, 0.119 mmol) were dissolved in acetonitrile-d_6 (0.7 mL) and added to an NMR tube. Acetic anhydride (11.2 µL, 0.119 mmol) was added to the tube *via* a syringe. The tube was held at room temperature overnight. On completion of the reaction the solvent was removed *in vacuo* and the residue was reconstituted in a minimum amount of methylene chloride. The sample was loaded on a column of silica and eluted with an ethyl acetate/hexane solution (70/30 *v*/*v* %). The separated solutions were allowed to slowly evaporate at room temperature. The parent compound (5-amino-2-nitrobenzyl acetate) elutes first and is isolated as a yellow powder. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.10 (*s*, 3H, C*H*$_3$), 4.35 (*bs*, 2H, N*H*$_2$), 5.50 (*s*, 2H, C*H*$_2$), 6.55 (*dd*, 1H, Ar-H, $^3J_{HH}$ = 8.9 Hz, $^5J_{HH}$ = 2.5 Hz), 6.68 (*m*, 1H, Ar-H), 8.09 (*dd*, 1H, Ar-H, $^3J_{HH}$ = 8.9 Hz, $^5J_{HH}$ = 2.5 Hz) (Serafinowski *et al.* 2008). Yellow crystals of the title compound were isolated (less than 1 mg) in later eluate. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.19 (*s*, 3H, C*H*$_3$), 5.53 (*s*, 2H, C*H*$_2$), 7.44 (*bs*, 2H, N*H*$_2$), 7.65 (*dd*, 1H, Ar-H, $^3J_{HH}$ = 8.9 Hz, $^5J_{HH}$ = 2.5 Hz), 7.75 (m, 1H, Ar-H), 8.15 (*d*, 1H, Ar-H, $^3J_{HH}$ = 8.9 Hz).

5.1. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Hydrogen atoms were refined freely.

Acknowledgements

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Computing details

Data collection: *CrystalClear-SM Expert* (Rigaku, 2014); cell refinement: *CrystalClear-SM Expert* (Rigaku, 2014); data reduction: *CrystalClear-SM Expert* (Rigaku, 2014); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2015b); molecular graphics: OLEX2 (Dolomanov *et al.*, 2009); software used to prepare material for publication: OLEX2 (Dolomanov *et al.*, 2009).

3-Amino-4-nitrobenzyl acetate

Crystal data

$C_9H_{10}N_2O_4$
M_r = 210.19
Monoclinic, $C2/c$
a = 14.4803 (15) Å
b = 11.4054 (11) Å
c = 13.0936 (13) Å
β = 116.341 (8)°
V = 1937.9 (4) Å^3
Z = 8
$F(000)$ = 880
D_x = 1.441 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71075 Å
Cell parameters from 513 reflections
θ = 1.6–25.4°
μ = 0.12 mm^{-1}
T = 173 K
Prism, yellow
0.25 × 0.25 × 0.10 mm

Data collection

Rigaku Mercury375R (2x2 bin mode) diffractometer
Radiation source: Sealed Tube
Graphite Monochromator monochromator
Detector resolution: 13.6612 pixels mm^{-1}
profile data from ω scans
Absorption correction: multi-scan (*REQAB*; Rigaku, 1998)
T_{min} = 0.840, T_{max} = 1.000
8409 measured reflections
1759 independent reflections
1348 reflections with $I > 2\sigma(I)$
R_{int} = 0.045
θ_{max} = 25.3°, θ_{min} = 2.4°
$h = -17 \rightarrow 17$
$k = -13 \rightarrow 13$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.098
S = 1.06
1759 reflections
176 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: difference Fourier map
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0578P)^2 + 0.2118P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}

Special details

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

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O3	0.74138 (8)	0.43515 (9)	0.74195 (10)	0.0324 (3)
O1	0.23008 (8)	0.61948 (10)	0.50492 (11)	0.0418 (3)
O2	0.18245 (8)	0.43814 (10)	0.46692 (11)	0.0436 (3)
O4	0.86707 (9)	0.30050 (11)	0.79735 (12)	0.0456 (4)
N1	0.25141 (9)	0.51321 (11)	0.50551 (11)	0.0288 (3)
N2	0.42892 (12)	0.67596 (12)	0.60612 (12)	0.0300 (3)
H2A	0.4821 (16)	0.7166 (16)	0.6337 (16)	0.036 (5)*
H2B	0.3700 (16)	0.7046 (15)	0.5821 (16)	0.039 (5)*
C6	0.43920 (11)	0.55950 (12)	0.60073 (12)	0.0228 (3)
C1	0.35704 (10)	0.47782 (13)	0.55271 (12)	0.0245 (3)
C4	0.55919 (11)	0.39372 (13)	0.64720 (12)	0.0252 (3)
C5	0.54112 (10)	0.51152 (13)	0.64747 (11)	0.0228 (3)
H5	0.5978 (13)	0.5675 (14)	0.6814 (13)	0.024 (4)*
C2	0.37680 (12)	0.35678 (14)	0.54982 (13)	0.0295 (4)
H2	0.3212 (13)	0.3041 (14)	0.5154 (15)	0.031 (4)*
C3	0.47512 (12)	0.31496 (14)	0.59587 (14)	0.0312 (4)
H3	0.4895 (13)	0.2318 (16)	0.5930 (15)	0.033 (4)*
C7	0.66619 (11)	0.34199 (14)	0.69873 (14)	0.0296 (4)
H7A	0.6780 (14)	0.2874 (16)	0.7620 (16)	0.040 (5)*
H7B	0.6772 (12)	0.2957 (14)	0.6407 (15)	0.032 (4)*
C8	0.84105 (11)	0.40198 (15)	0.79024 (13)	0.0307 (4)
C9	0.91100 (13)	0.50537 (18)	0.83137 (18)	0.0419 (5)
H9A	0.8961 (16)	0.5562 (19)	0.7680 (19)	0.055 (6)*
H9B	0.9809 (17)	0.4806 (16)	0.8703 (17)	0.046 (5)*
H9C	0.8934 (17)	0.554 (2)	0.881 (2)	0.067 (7)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O3	0.0175 (5)	0.0288 (6)	0.0445 (7)	0.0021 (4)	0.0080 (5)	−0.0018 (5)
O1	0.0242 (6)	0.0319 (7)	0.0621 (8)	0.0054 (5)	0.0128 (6)	0.0060 (5)
O2	0.0194 (6)	0.0411 (7)	0.0601 (8)	−0.0073 (5)	0.0085 (6)	−0.0033 (6)
O4	0.0271 (6)	0.0400 (8)	0.0605 (8)	0.0089 (5)	0.0111 (6)	−0.0009 (6)
N1	0.0188 (6)	0.0314 (8)	0.0327 (7)	0.0002 (5)	0.0083 (5)	0.0031 (6)
N2	0.0199 (7)	0.0271 (8)	0.0379 (8)	0.0002 (6)	0.0082 (6)	−0.0025 (6)
C6	0.0214 (7)	0.0266 (8)	0.0210 (7)	0.0013 (6)	0.0098 (6)	0.0011 (6)
C1	0.0180 (7)	0.0307 (8)	0.0234 (7)	0.0004 (6)	0.0078 (6)	0.0027 (6)
C4	0.0210 (7)	0.0312 (8)	0.0239 (7)	0.0010 (6)	0.0104 (6)	0.0002 (6)
C5	0.0198 (8)	0.0271 (8)	0.0212 (7)	−0.0025 (6)	0.0086 (6)	−0.0011 (6)

C2	0.0218 (8)	0.0283 (9)	0.0358 (9)	−0.0063 (7)	0.0105 (7)	−0.0029 (7)
C3	0.0279 (8)	0.0238 (9)	0.0406 (9)	−0.0004 (6)	0.0142 (7)	−0.0017 (7)
C7	0.0237 (8)	0.0262 (8)	0.0363 (9)	0.0007 (6)	0.0110 (7)	−0.0024 (7)
C8	0.0211 (8)	0.0379 (10)	0.0305 (8)	0.0056 (7)	0.0091 (7)	0.0011 (7)
C9	0.0214 (9)	0.0483 (12)	0.0489 (11)	−0.0017 (8)	0.0091 (8)	−0.0015 (9)

Geometric parameters (Å, º)

O3—C7	1.4449 (19)	C4—C3	1.419 (2)
O3—C8	1.3477 (19)	C4—C7	1.509 (2)
O1—N1	1.2500 (16)	C5—H5	0.978 (17)
O2—N1	1.2401 (17)	C2—H2	0.944 (17)
O4—C8	1.208 (2)	C2—C3	1.362 (2)
N1—C1	1.4303 (19)	C3—H3	0.975 (18)
N2—H2A	0.83 (2)	C7—H7A	0.988 (19)
N2—H2B	0.83 (2)	C7—H7B	0.994 (17)
N2—C6	1.342 (2)	C8—C9	1.491 (3)
C6—C1	1.419 (2)	C9—H9A	0.96 (2)
C6—C5	1.4320 (19)	C9—H9B	0.95 (2)
C1—C2	1.414 (2)	C9—H9C	0.97 (2)
C4—C5	1.369 (2)		
C8—O3—C7	116.19 (12)	C3—C2—C1	120.94 (14)
O1—N1—C1	119.36 (12)	C3—C2—H2	119.5 (10)
O2—N1—O1	121.00 (12)	C4—C3—H3	118.7 (10)
O2—N1—C1	119.64 (13)	C2—C3—C4	119.75 (15)
H2A—N2—H2B	122.7 (17)	C2—C3—H3	121.5 (10)
C6—N2—H2A	118.1 (12)	O3—C7—C4	109.47 (13)
C6—N2—H2B	119.1 (12)	O3—C7—H7A	108.3 (11)
N2—C6—C1	125.60 (13)	O3—C7—H7B	109.9 (9)
N2—C6—C5	118.24 (13)	C4—C7—H7A	112.5 (10)
C1—C6—C5	116.16 (13)	C4—C7—H7B	110.3 (10)
C6—C1—N1	122.12 (13)	H7A—C7—H7B	106.2 (14)
C2—C1—N1	117.02 (13)	O3—C8—C9	111.22 (14)
C2—C1—C6	120.86 (13)	O4—C8—O3	122.52 (15)
C5—C4—C3	119.84 (14)	O4—C8—C9	126.26 (15)
C5—C4—C7	122.83 (14)	C8—C9—H9A	108.1 (13)
C3—C4—C7	117.33 (14)	C8—C9—H9B	110.5 (11)
C6—C5—H5	116.3 (9)	C8—C9—H9C	110.8 (13)
C4—C5—C6	122.40 (13)	H9A—C9—H9B	115.0 (17)
C4—C5—H5	121.3 (9)	H9A—C9—H9C	102.2 (18)
C1—C2—H2	119.6 (10)	H9B—C9—H9C	110.0 (17)
O1—N1—C1—C6	0.9 (2)	C5—C6—C1—N1	178.48 (13)
O1—N1—C1—C2	−179.17 (13)	C5—C6—C1—C2	−1.44 (19)
O2—N1—C1—C6	−178.35 (13)	C5—C4—C3—C2	−1.7 (2)
O2—N1—C1—C2	1.6 (2)	C5—C4—C7—O3	−2.0 (2)
N1—C1—C2—C3	−178.07 (14)	C3—C4—C5—C6	2.1 (2)

N2—C6—C1—N1	−1.2 (2)	C3—C4—C7—O3	177.40 (13)
N2—C6—C1—C2	178.91 (14)	C7—O3—C8—O4	0.1 (2)
N2—C6—C5—C4	179.13 (13)	C7—O3—C8—C9	179.98 (14)
C6—C1—C2—C3	1.9 (2)	C7—C4—C5—C6	−178.49 (13)
C1—C6—C5—C4	−0.5 (2)	C7—C4—C3—C2	178.86 (15)
C1—C2—C3—C4	−0.2 (2)	C8—O3—C7—C4	−179.68 (12)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*A*···O4^{i}	0.83 (2)	2.18 (2)	3.005 (2)	171.5 (17)
N2—H2*B*···O1	0.84 (2)	2.06 (2)	2.6600 (19)	128.0 (16)
N2—H2*B*···O1^{ii}	0.84 (2)	2.44 (2)	3.1443 (19)	142.7 (16)

Symmetry codes: (i) −*x*+3/2, *y*+1/2, −*z*+3/2; (ii) −*x*+1/2, −*y*+3/2, −*z*+1.