

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

(4-Nitrophenyl)methanol

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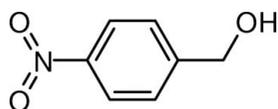
Received 25 May 2012; accepted 31 May 2012

Key indicators: single-crystal X-ray study; $T = 150$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ ; R factor = 0.032; wR factor = 0.099; data-to-parameter ratio = 13.9.

In the crystal of the title compound, $\text{C}_7\text{H}_7\text{NO}_3$, molecules associate into infinite chains *via* $\text{O}-\text{H}\cdots\text{O}(\text{NO}_2)$ hydrogen bonds propagating in the [101] direction. These chains are linked *via* $\text{C}-\text{H}\cdots\text{O}(\text{NO}_2)$ hydrogen bonds to form double-stranded ribbons lying parallel to the *ac* plane. The ribbons stack along the *b* axis by means of $\pi-\pi$ interactions involving the benzene rings and the nitro group. The centroid-centroid distances of the alternating parallel aromatic rings are 3.6514 (7) and 3.8044 (7) .

Related literature

For the crystal structure of a Zn^{II} complex with *O*-coordinated 4-nitrobenzyl alcohol, see: Koller *et al.* (2009). For a survey of typical bond lengths in organic compounds, see: Allen *et al.* (2006).



Experimental

Crystal data

$\text{C}_7\text{H}_7\text{NO}_3$
 $M_r = 153.14$
Triclinic, $P\bar{1}$
 $a = 6.2216$ (5) 
 $b = 7.4096$ (6) 
 $c = 7.7833$ (6) 

$\alpha = 110.867$ (2)°
 $\beta = 93.667$ (2)°
 $\gamma = 90.748$ (3)°
 $V = 334.34$ (5) ³
 $Z = 2$
Mo $K\alpha$ radiation

$\mu = 0.12$ mm⁻¹
 $T = 150$ K

 $0.53 \times 0.31 \times 0.28$ mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 2001)
 $T_{\text{min}} = 0.939$, $T_{\text{max}} = 0.967$

5239 measured reflections
1442 independent reflections
1269 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.016$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.099$
 $S = 1.10$
1442 reflections
104 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.25$ e ⁻³
 $\Delta\rho_{\text{min}} = -0.29$ e ⁻³

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

| $D-\text{H}\cdots A$ | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|---|--------------|--------------------|-------------|----------------------|
| $\text{O1}-\text{H1O}\cdots\text{O2}^{\text{ii}}$ | 0.83 (2) | 2.09 (2) | 2.9095 (12) | 173 (2) |
| $\text{C3}-\text{H3}\cdots\text{O3}^{\text{ii}}$ | 0.95 | 2.54 | 3.3799 (14) | 148 |

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

Data collection: APEX2 (Bruker, 2007); cell refinement: SAINT (Bruker, 2007); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: PLATON (Spek, 2009); software used to prepare material for publication: PLATON.

Financial support from the Ministry of Education of the Czech Republic (project No. MSM0021620857) is gratefully acknowledged.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SU2438).

References

- Allen, F. H., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (2006). *International Tables for Crystallography*, Vol. C, ch. 9.5, pp. 790–811. Dordrecht: Kluwer Academic Publishers.
- Bruker (2001). SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (2007). APEX2 and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.
- Koller, R., Stanek, K., Stolz, D., Aardoom, R., Niedermann, K. & Togni, A. (2009). *Angew. Chem. Int. Ed.* **48**, 4332–4336.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.

supporting information

Acta Cryst. (2012). E68, o2012 [https://doi.org/10.1107/S1600536812024865]

(4-Nitrophenyl)methanol

Ivana Čísařová and Petr Štěpnička

S1. Comment

The title compound, (4-nitrophenyl)methanol [common name: 4-nitrobenzyl alcohol], is a readily available reactive organic building block, commonly used in many organic reactions. As it can separate from the reaction mixture in the form of thin crystals and thus be mistakenly taken for the desired product (D. Drahoňovský, private communication), we decided to determine its molecular structure which surprisingly was unknown. The only structurally characterized compound comprising the title alcohol reported to date is a Zn(II) complex, $[\text{ZnL}_2(4\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{OH})_2(\text{H}_2\text{O})_2](\text{NTf}_2)_2$ [where L = 1-(trifluoromethyl)-1,2-benziodoxol-3(1*H*)-one and Tf = CF_3SO_3], isolated from the reaction mixture after zinc-catalysed trifluoromethylation of alcohols with L and $\text{Zn}(\text{NTf}_2)_2$ (Koller *et al.*, 2009).

The molecular geometry of the title compound, Fig. 1, is rather unexceptional with bond distances falling in the usual ranges (Allen *et al.*, 2006). The substituents in the *para* positions of the benzene ring bind symmetrically as indicated by the O2/O3—N1—C4 angles of 118.10 (9)° and 119.34 (9)° for the NO₂ group and by the angles C2/C6—C1—C7 of 119.21 (10)° and 121.32 (10)° for the CH₂OH moiety. The nitro group is rotated from the plane of the benzene ring by as little as 0.44 (13)°. On the other hand, the hydroxy group is displaced from the plane of the central ring, being rotated by the pivotal C1—C7 bond. The perpendicular distance of O1 atom from the plane of the benzene ring is 0.356 (1) Å and the torsion angle C6—C1—C7—O1 is 16.73 (16)°. A relatively small but statistically significant difference observed for the individual N—O distances [viz: N1—O2 = 1.2369 (12) Å and N1—O3 = 1.2240 (13) Å] can be accounted for by different intermolecular interactions in which the respective NO₂ oxygen atoms participate.

In the crystal, molecules associate into ribbons via a combination of O—H···O and C—H···O hydrogen bonds (Fig. 2 and Table 1). The shorter O1—H1O···O2 interactions result in the formation of infinite chains from molecules related by translation in the [1 0 1] direction, whereas the soft C3—H3···O3 contacts are formed between inversion-related molecules and thus cross-link the chains with their parallel, inversion-related counterparts into infinite ribbons oriented parallel to the *ac* plane.

Furthermore, the molecules associate into columnar stacks oriented along the crystallographic *b*-axis by means of $\pi\cdots\pi$ interactions (Figs. 3 and 4). The interacting molecules lie across crystallographic inversion centers and are therefore exactly parallel. Mutual offset of the interacting molecules by ca. 1.4 Å (pairs A in Fig. 3) and 1.7 Å (pairs B in Fig. 3) allows for efficient interactions between the π -systems of the benzene rings and also for interactions between the π -systems of the benzene rings and the nitro groups. Distances of the centroids of the benzene rings are 3.6514 (7) Å for molecules located around inversion centres at *b*/2 (pairs A) and 3.8044 (7) Å for molecules related by the inversion centres at *b* = 0 and 1 (pairs B). Distances of the nitrogen atom from atom C1 in pairs A and B are ca. 4.2 Å and ca. 4.4 Å, respectively.

S2. Experimental

Yellowish prismatic crystals suitable for X-ray diffraction analysis were selected directly from a commercial sample of the title compound (Aldrich, 99%). Attempts to recrystallize the compound from hot heptane led only to very thin, plate-like crystal aggregates, which were not suitable for X-ray diffraction analysis.

S3. Refinement

The OH hydrogen atom was located in a difference electron density map and refined freely. The C-bound H atoms were included in calculated positions and refined as riding atoms: C-H = 0.95 and 0.97 Å for aromatic and methylene H atoms, respectively, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

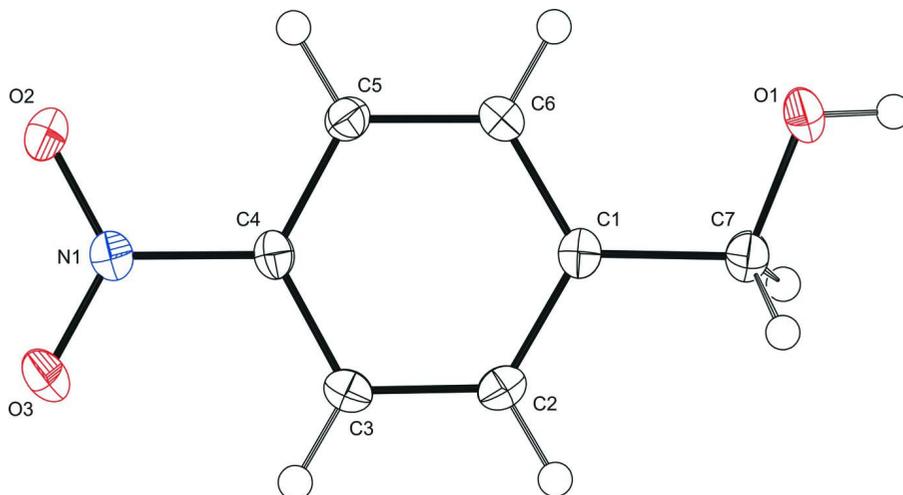


Figure 1

A view of the molecular structure of the title compound, showing the atom-labeling scheme. The displacement ellipsoids are drawn at the 50% probability level.

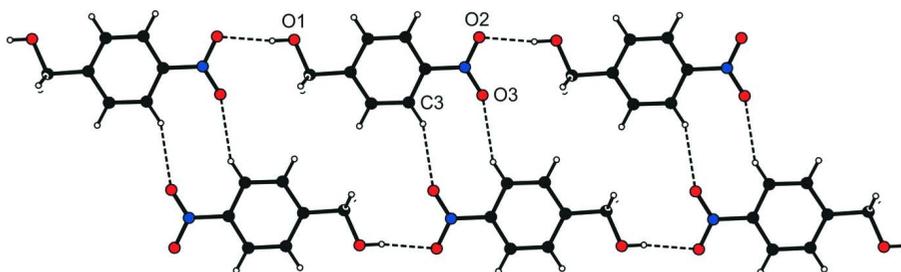


Figure 2

A section of H-bonded ribbons in the structure of the title compound. Hydrogen bonds are indicated with dashed lines.

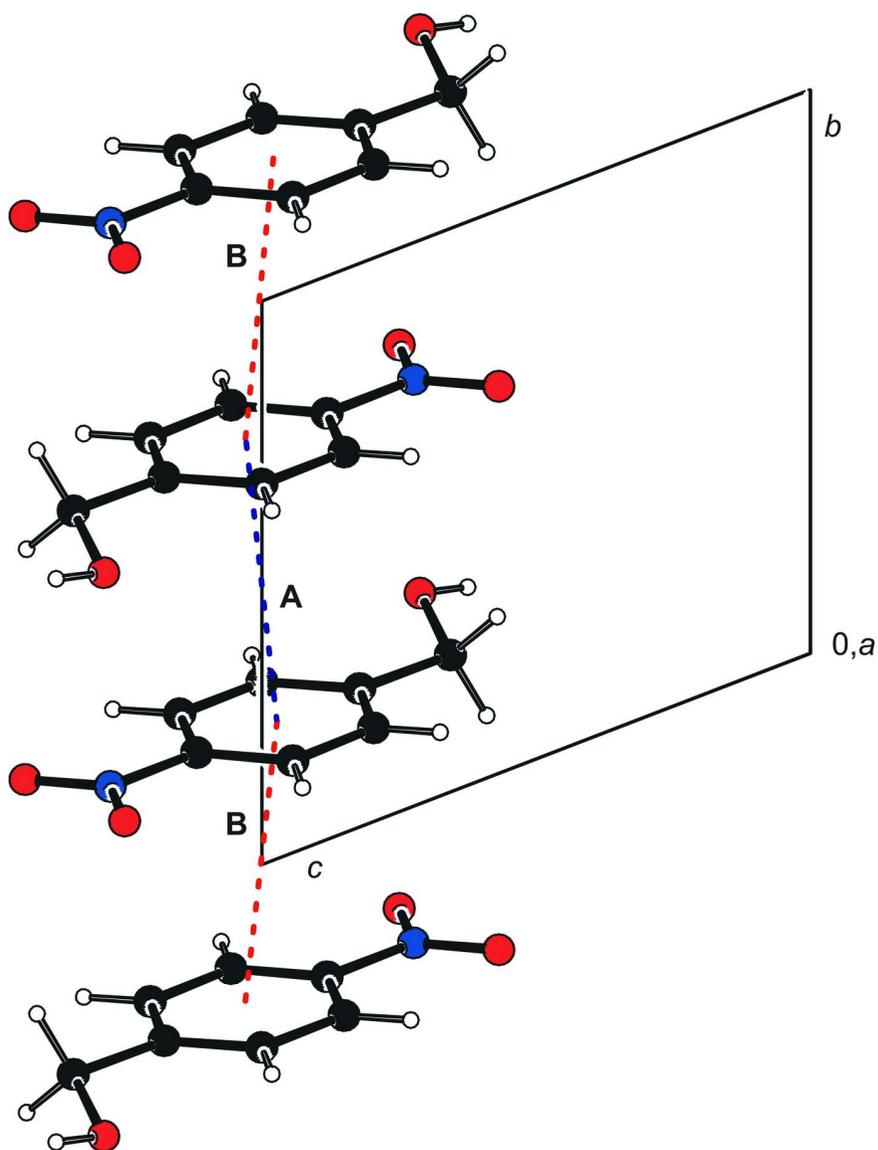


Figure 3

A view along the a axis of the π - π stacking interactions of individual molecules in the structure of the title compound.

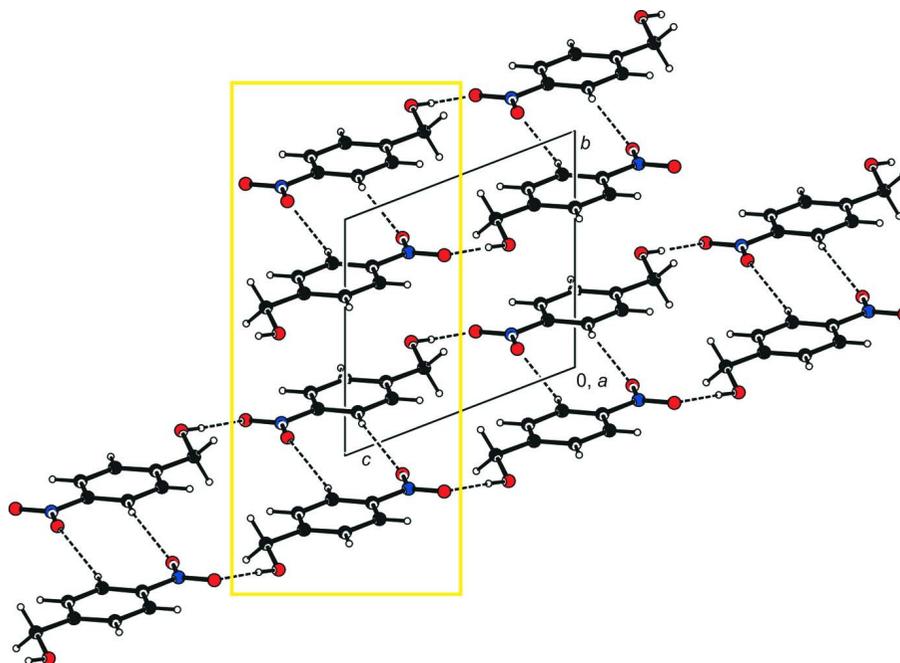


Figure 4

A view along the *a* axis of the crystal packing of the title compound, highlighting the interplay of hydrogen bonding (see Table 1) and $\pi\cdots\pi$ interactions [The yellow box limits the section presented in Fig. 3].

(4-nitrophenyl)methanol

Crystal data

$C_7H_7NO_3$

$M_r = 153.14$

Triclinic, $P\bar{1}$

Hall symbol: $-P\ 1$

$a = 6.2216$ (5) Å

$b = 7.4096$ (6) Å

$c = 7.7833$ (6) Å

$\alpha = 110.867$ (2)°

$\beta = 93.667$ (2)°

$\gamma = 90.748$ (3)°

$V = 334.34$ (5) Å³

$Z = 2$

$F(000) = 160$

$D_x = 1.521$ Mg m⁻³

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

Cell parameters from 3056 reflections

$\theta = 2.9\text{--}27.0^\circ$

$\mu = 0.12$ mm⁻¹

$T = 150$ K

Prism, colorless

$0.53 \times 0.31 \times 0.28$ mm

Data collection

Bruker APEXII CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2001)

$T_{\min} = 0.939$, $T_{\max} = 0.967$

5239 measured reflections

1442 independent reflections

1269 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.016$

$\theta_{\max} = 27.0^\circ$, $\theta_{\min} = 2.8^\circ$

$h = -7 \rightarrow 7$

$k = -9 \rightarrow 9$

$l = -9 \rightarrow 9$

Refinement

| | |
|--|--|
| Refinement on F^2 | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.032$ | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2) = 0.099$ | $w = 1/[\sigma^2(F_o^2) + (0.0549P)^2 + 0.0737P]$ |
| $S = 1.10$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| 1442 reflections | $(\Delta/\sigma)_{\max} < 0.001$ |
| 104 parameters | $\Delta\rho_{\max} = 0.25 \text{ e } \text{\AA}^{-3}$ |
| 0 restraints | $\Delta\rho_{\min} = -0.29 \text{ e } \text{\AA}^{-3}$ |
| Primary atom site location: structure-invariant direct methods | |

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.

Refinement. Refinement of F^2 against all diffractions. 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 $F^2 > \sigma(F^2)$ 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)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|--------------|--------------|----------------------------------|
| O1 | 0.55157 (14) | 0.37365 (14) | 0.71166 (12) | 0.0289 (2) |
| H1O | 0.459 (3) | 0.352 (3) | 0.625 (3) | 0.059 (6)* |
| O2 | 1.19725 (14) | 0.31301 (14) | 1.43192 (11) | 0.0291 (2) |
| O3 | 1.44094 (13) | 0.17141 (12) | 1.25026 (12) | 0.0260 (2) |
| N1 | 1.26402 (15) | 0.24252 (13) | 1.27641 (13) | 0.0185 (2) |
| C1 | 0.86002 (18) | 0.24567 (15) | 0.82183 (15) | 0.0164 (2) |
| C2 | 1.06259 (18) | 0.16628 (15) | 0.79623 (15) | 0.0187 (3) |
| H2 | 1.1093 | 0.1130 | 0.6751 | 0.022* |
| C3 | 1.19706 (17) | 0.16352 (15) | 0.94381 (15) | 0.0177 (3) |
| H3 | 1.3348 | 0.1088 | 0.9260 | 0.021* |
| C4 | 1.12356 (17) | 0.24351 (14) | 1.11879 (14) | 0.0158 (2) |
| C5 | 0.92362 (18) | 0.32390 (15) | 1.14985 (15) | 0.0173 (2) |
| H5 | 0.8781 | 0.3776 | 1.2714 | 0.021* |
| C6 | 0.79120 (17) | 0.32436 (15) | 0.99981 (15) | 0.0172 (2) |
| H6 | 0.6531 | 0.3784 | 1.0182 | 0.021* |
| C7 | 0.71876 (19) | 0.24303 (16) | 0.65630 (15) | 0.0215 (3) |
| H7A | 0.8064 | 0.2792 | 0.5710 | 0.026* |
| H7B | 0.6562 | 0.1109 | 0.5901 | 0.026* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|----|------------|------------|------------|------------|-------------|------------|
| O1 | 0.0235 (5) | 0.0379 (5) | 0.0213 (4) | 0.0103 (4) | -0.0055 (3) | 0.0068 (4) |
| O2 | 0.0257 (5) | 0.0455 (6) | 0.0151 (4) | 0.0062 (4) | 0.0000 (3) | 0.0098 (4) |

| | | | | | | |
|----|------------|------------|------------|-------------|-------------|------------|
| O3 | 0.0197 (4) | 0.0303 (5) | 0.0278 (5) | 0.0086 (3) | -0.0016 (3) | 0.0103 (4) |
| N1 | 0.0176 (5) | 0.0194 (5) | 0.0191 (5) | 0.0006 (3) | -0.0008 (4) | 0.0081 (4) |
| C1 | 0.0184 (5) | 0.0137 (5) | 0.0171 (5) | -0.0021 (4) | -0.0014 (4) | 0.0060 (4) |
| C2 | 0.0217 (6) | 0.0175 (5) | 0.0155 (5) | 0.0010 (4) | 0.0034 (4) | 0.0041 (4) |
| C3 | 0.0160 (5) | 0.0162 (5) | 0.0209 (6) | 0.0024 (4) | 0.0028 (4) | 0.0062 (4) |
| C4 | 0.0161 (5) | 0.0145 (5) | 0.0172 (5) | -0.0011 (4) | -0.0020 (4) | 0.0066 (4) |
| C5 | 0.0180 (5) | 0.0185 (5) | 0.0154 (5) | 0.0007 (4) | 0.0022 (4) | 0.0058 (4) |
| C6 | 0.0146 (5) | 0.0171 (5) | 0.0201 (5) | 0.0015 (4) | 0.0010 (4) | 0.0071 (4) |
| C7 | 0.0225 (6) | 0.0235 (6) | 0.0173 (5) | 0.0031 (4) | -0.0015 (4) | 0.0063 (4) |

Geometric parameters (Å, °)

| | | | |
|-----------|-------------|------------|-------------|
| O1—C7 | 1.4110 (13) | C2—H2 | 0.9500 |
| O1—H1O | 0.82 (2) | C3—C4 | 1.3881 (15) |
| O2—N1 | 1.2369 (12) | C3—H3 | 0.9500 |
| O3—N1 | 1.2239 (12) | C4—C5 | 1.3842 (15) |
| N1—C4 | 1.4623 (13) | C5—C6 | 1.3865 (15) |
| C1—C2 | 1.3936 (15) | C5—H5 | 0.9500 |
| C1—C6 | 1.3961 (15) | C6—H6 | 0.9500 |
| C1—C7 | 1.5065 (14) | C7—H7A | 0.9900 |
| C2—C3 | 1.3835 (15) | C7—H7B | 0.9900 |
| C7—O1—H1O | 109.2 (14) | C5—C4—N1 | 118.87 (10) |
| O3—N1—O2 | 122.56 (9) | C3—C4—N1 | 118.37 (10) |
| O3—N1—C4 | 119.34 (9) | C4—C5—C6 | 118.59 (10) |
| O2—N1—C4 | 118.10 (9) | C4—C5—H5 | 120.7 |
| C2—C1—C6 | 119.46 (10) | C6—C5—H5 | 120.7 |
| C2—C1—C7 | 119.21 (10) | C5—C6—C1 | 120.24 (10) |
| C6—C1—C7 | 121.32 (10) | C5—C6—H6 | 119.9 |
| C3—C2—C1 | 121.30 (10) | C1—C6—H6 | 119.9 |
| C3—C2—H2 | 119.3 | O1—C7—C1 | 110.28 (9) |
| C1—C2—H2 | 119.3 | O1—C7—H7A | 109.6 |
| C2—C3—C4 | 117.65 (10) | C1—C7—H7A | 109.6 |
| C2—C3—H3 | 121.2 | O1—C7—H7B | 109.6 |
| C4—C3—H3 | 121.2 | C1—C7—H7B | 109.6 |
| C5—C4—C3 | 122.76 (10) | H7A—C7—H7B | 108.1 |

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—H1O \cdots O2 ⁱ | 0.83 (2) | 2.09 (2) | 2.9095 (12) | 173 (2) |
| C3—H3 \cdots O3 ⁱⁱ | 0.95 | 2.54 | 3.3799 (14) | 148 |

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