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N'-(2,4-Dinitrophenyl)acetohydrazide

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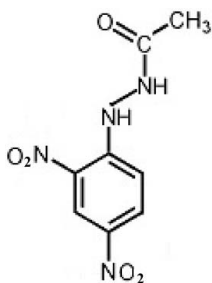
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 Key indicators: single-crystal X-ray study; $T = 150$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.031; wR factor = 0.079; data-to-parameter ratio = 11.1.

In the title compound, $\text{C}_8\text{H}_8\text{N}_4\text{O}_5$, the nitro groups *ortho* and *para* to the hydrazone group are twisted by 10.0 (2) and 3.6 (2)°, respectively, relative to the aromatic ring. The structure exhibits an intramolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bond between the hydrazone and *ortho*-nitro groups. There is a strong intermolecular $\text{C}=\text{O}\cdots\text{H}-\text{N}$ hydrogen bond, giving rise to chains, and weaker $\text{ONO}\cdots\text{NO}_2$ [2.944 (2) Å] and $\text{C}-\text{H}\cdots\text{O}-\text{N}$ interactions linking the molecules into a three-dimensional network.

Related literature

For related literature, see: Domiano *et al.* (1984); Guo (2007); Li *et al.* (1988); Rudnicka & Osmialowska (1979); Sakamoto *et al.* (1993); Siddiqui *et al.* (2007); Zia-ur-Rehman *et al.* (2005, 2006).



Experimental

Crystal data

 $\text{C}_8\text{H}_8\text{N}_4\text{O}_5$
 $M_r = 240.18$

 Orthorhombic, $P2_12_12_1$
 $a = 4.8585$ (4) Å

 $b = 10.7703$ (8) Å

 $c = 19.1059$ (14) Å

 $V = 999.76$ (13) Å³
 $Z = 4$

 Mo $K\alpha$ radiation

 $\mu = 0.14$ mm⁻¹
 $T = 150$ (2) K

 $0.57 \times 0.09 \times 0.06$ mm

Data collection

 Bruker APEXII CCD diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 2007)
 $T_{\text{min}} = 0.927$, $T_{\text{max}} = 0.992$

 11843 measured reflections
 1794 independent reflections
 1616 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.031$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.030$
 $wR(F^2) = 0.078$
 $S = 1.03$

1794 reflections

161 parameters

H atoms treated by a mixture of independent and constrained refinement

 $\Delta\rho_{\text{max}} = 0.27$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.17$ e Å⁻³
Table 1

Hydrogen-bond geometry (Å, °).

| $D-\text{H}\cdots A$ | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|--|--------------|--------------------|-------------|----------------------|
| $\text{N3}-\text{H3}\cdots\text{O2}$ | 0.83 (2) | 2.001 (18) | 2.5942 (16) | 127.9 (16) |
| $\text{N4}-\text{H4}\cdots\text{O5}^{\text{i}}$ | 0.85 (2) | 1.95 (2) | 2.7748 (16) | 164.0 (17) |
| $\text{C5}-\text{H5}\cdots\text{O4}^{\text{ii}}$ | 0.95 | 2.44 | 3.249 (2) | 143 |
| $\text{C8}-\text{H8A}\cdots\text{O2}^{\text{iii}}$ | 0.98 | 2.58 | 3.269 (2) | 128 |
| $\text{C8}-\text{H8C}\cdots\text{O3}^{\text{iv}}$ | 0.98 | 2.57 | 3.527 (2) | 165 |

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

Data collection: APEX2 (Bruker, 2006); cell refinement: SAINT (Bruker, 2006); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL and local programs.

The authors are grateful to the Pakistan Council of Scientific & Industrial Research Laboratories Complex, Lahore, for providing the necessary facilities.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2733).

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supporting information

Acta Cryst. (2008). E64, o1441 [doi:10.1107/S1600536808019685]

***N'*-(2,4-Dinitrophenyl)acetohydrazide**

Muhammad Zia-ur-Rehman, Mark R. J. Elsegood, Shahid Mahmud and Hamid Latif Siddiqui

S1. Comment

The chemistry of hydrazones has been intensely investigated in recent years due to their excellent coordinating capability (Domiano *et al.*, 1984) and pharmacological activities (Li *et al.*, 1988). These compounds are also being used as precursors for the efficient synthesis of various condensed heterocycles in organic chemistry (Rudnicka & Osmialowska, 1979) and as highly selective metal scavengers (Sakamoto *et al.*, 1993) in analytical chemistry. In continuation of our ongoing work on the synthesis of various heterocyclic compounds (Zia-ur-Rehman *et al.*, 2005, 2006; Siddiqui *et al.*, 2007), the title compound, (I), was synthesized by reacting 2,4-dinitrophenylhydrazine with acetic anhydride.

Most of the bond lengths and angles in (I) are similar to those in related molecules (Guo, 2007). The nitro groups *ortho* and *para* to the hydrazone group are twisted out of this plane by 10.0 (2) and 3.6 (2)°, respectively. The larger twist of the *ortho*-nitro group arises due to the desire to form an intramolecular hydrogen bond which results in a six-membered ring (Fig. 1 and Table 1). Each molecule also forms an intermolecular N—H···O=C hydrogen bond giving rise to stacks of molecules parallel to *a* (Fig. 2). The hydrogen-bonded chains of (I) are further linked together into a three-dimensional network (Fig. 3) *via* weaker C—H···O—N interactions involving the nitro groups and methyl and aryl H atoms (range 2.4–2.6 Å) along with some weak ONO···NO₂ interactions [O1···N1ⁱ = 2.944 (2) Å; symmetry code: (i) -0.5+x, 1.5-y, 2-z].

S2. Experimental

A mixture of 2,4-dinitrophenylhydrazine (1.981 g; 10.0 mmoles) and acetic anhydride (5.0 ml) was stirred for a period of six hours at room temperature. Then, this mixture was poured into ice cooled water and neutralized with 10% sodium bicarbonate solution. The precipitated solids were collected by filtration, washed and dried. Crystals suitable for X-ray crystallography were grown by slow evaporation of solution of the title compound in a mixture of ethanol and water (90:10); m.p. 471 K; yield: 82%.

S3. Refinement

1255 Friedel pairs were merged. H atoms bound to C were placed in geometric positions (C—H distance = 0.95 Å for aryl-H; 0.98 Å for methyl-H) using a riding model. H atoms on N had coordinates freely refined. U_{iso} values were set to $1.2U_{\text{eq}}$ of the carrier atom ($1.5U_{\text{eq}}$ for methyl-H).

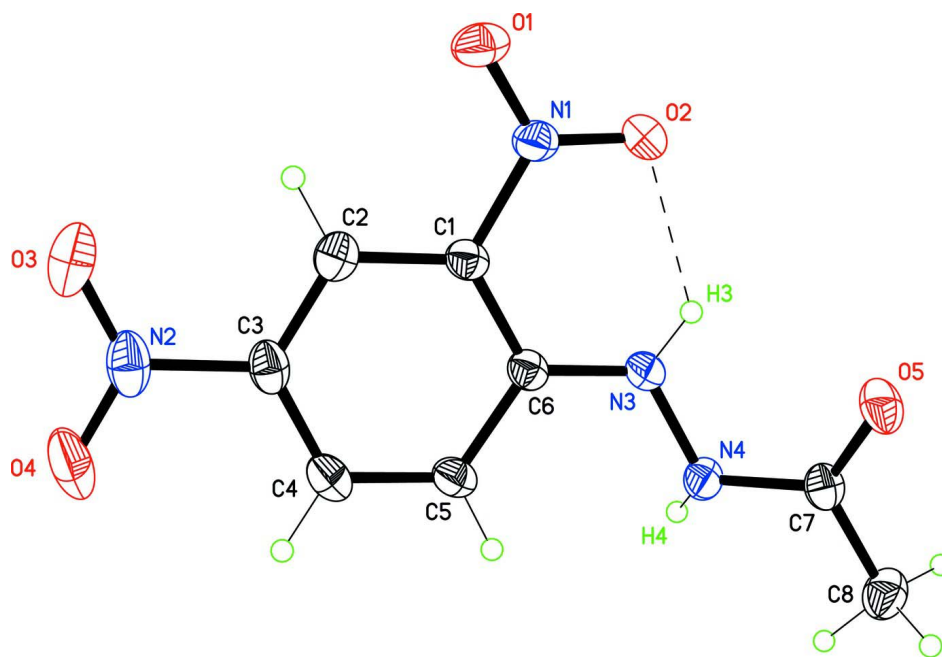
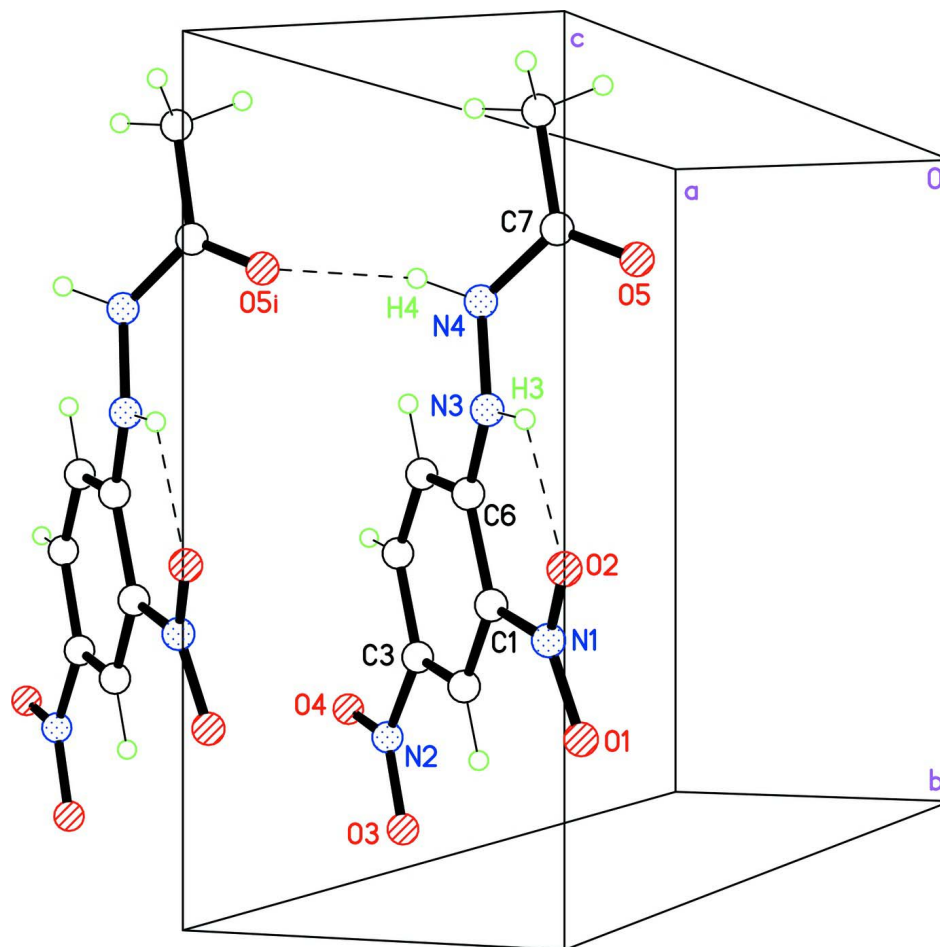


Figure 1

The asymmetric unit of the title compound showing the intramolecular hydrogen bond. Displacement ellipsoids are drawn at the 50% probability level.

**Figure 2**

Perspective view of molecules linked *via* intermolecular N—H...O=C hydrogen bonds parallel to *a*.

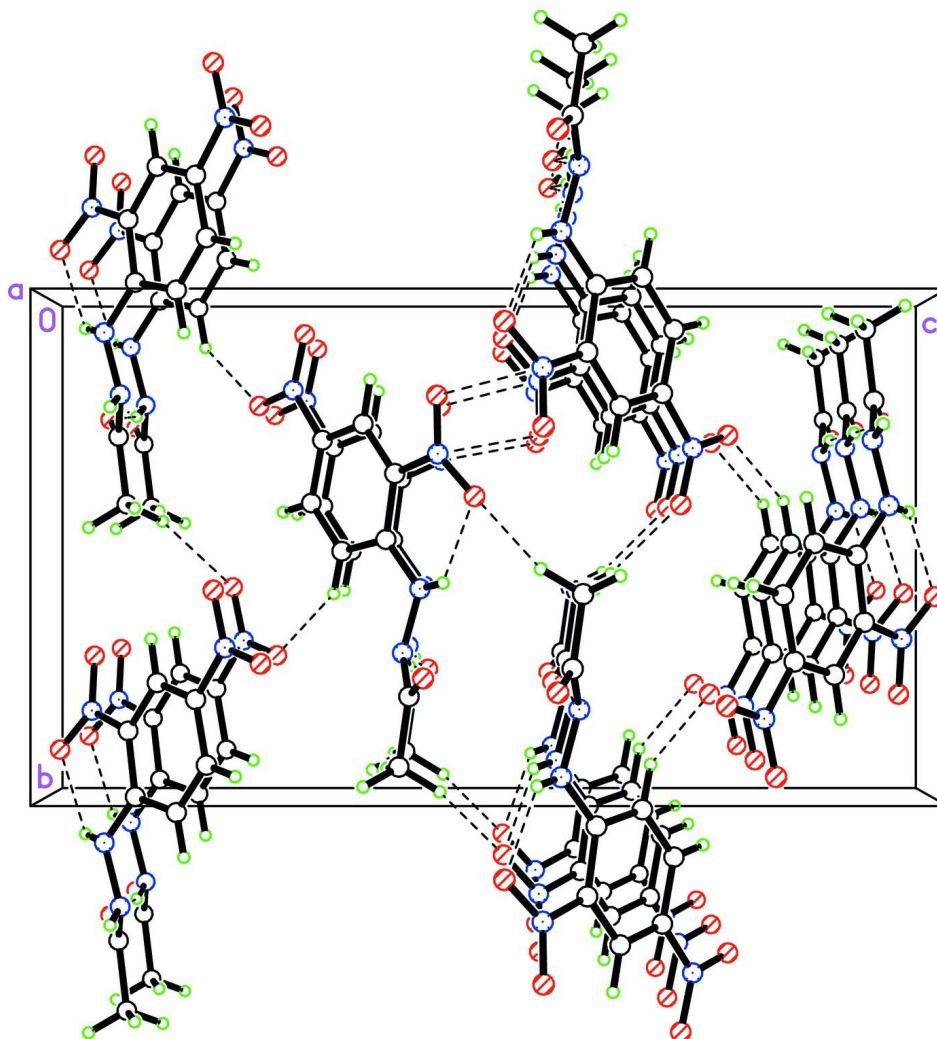


Figure 3

Perspective view of the three-dimensional crystal packing showing hydrogen-bonds and other intermolecular interactions (dashed lines). H atoms not involved in hydrogen bonding have been omitted for clarity.

***N'*-(2,4-Dinitrophenyl)acetohydrazide**

Crystal data

$C_8H_8N_4O_5$

$M_r = 240.18$

Orthorhombic, $P2_12_12_1$

Hall symbol: P 2ac 2ab

$a = 4.8585$ (4) Å

$b = 10.7703$ (8) Å

$c = 19.1059$ (14) Å

$V = 999.76$ (13) Å³

$Z = 4$

$F(000) = 496$

$D_x = 1.596$ Mg m⁻³

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

Cell parameters from 3491 reflections

$\theta = 2.9$ – 27.8°

$\mu = 0.14$ mm⁻¹

$T = 150$ K

Lath, orange

$0.57 \times 0.09 \times 0.06$ mm

Data collection

Bruker APEXII CCD
diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
 ω rotation with narrow frames scans
Absorption correction: multi-scan
(*SADABS*; Sheldrick, 2007)
 $T_{\min} = 0.927$, $T_{\max} = 0.992$

11843 measured reflections
1794 independent reflections
1616 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.031$
 $\theta_{\max} = 30.6^\circ$, $\theta_{\min} = 2.1^\circ$
 $h = -6 \rightarrow 6$
 $k = -15 \rightarrow 15$
 $l = -27 \rightarrow 27$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.030$
 $wR(F^2) = 0.078$
 $S = 1.03$
1794 reflections
161 parameters
0 restraints
Primary atom site location: structure-invariant
direct methods

Secondary atom site location: all non-H atoms
found by direct methods
Hydrogen site location: geom except NH coords
freely refined
H atoms treated by a mixture of independent
and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0462P)^2 + 0.078P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.27 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.17 \text{ e } \text{\AA}^{-3}$

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.

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 $F^2 > \sigma(F^2)$ 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. 1255 Friedel pairs. Friedels merged.

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 | 0.3396 (3) | 0.64098 (13) | 0.89834 (7) | 0.0206 (3) |
| N1 | 0.1186 (2) | 0.67553 (11) | 0.94555 (6) | 0.0239 (2) |
| O1 | 0.0352 (2) | 0.78314 (10) | 0.94499 (6) | 0.0298 (2) |
| O2 | 0.0219 (2) | 0.59512 (11) | 0.98457 (6) | 0.0349 (3) |
| C2 | 0.4679 (3) | 0.73783 (13) | 0.86286 (7) | 0.0234 (3) |
| H2 | 0.4153 | 0.8215 | 0.8710 | 0.028* |
| C3 | 0.6722 (3) | 0.70968 (14) | 0.81593 (7) | 0.0245 (3) |
| N2 | 0.8161 (3) | 0.81093 (13) | 0.78132 (7) | 0.0323 (3) |
| O3 | 0.7483 (3) | 0.91873 (12) | 0.79517 (7) | 0.0428 (3) |
| O4 | 1.0012 (3) | 0.78354 (13) | 0.73998 (7) | 0.0462 (3) |
| C4 | 0.7508 (3) | 0.58725 (15) | 0.80240 (7) | 0.0253 (3) |
| H4A | 0.8903 | 0.5700 | 0.7689 | 0.030* |
| C5 | 0.6255 (3) | 0.49242 (13) | 0.83774 (7) | 0.0231 (3) |
| H5 | 0.6791 | 0.4093 | 0.8283 | 0.028* |
| C6 | 0.4174 (3) | 0.51517 (13) | 0.88817 (7) | 0.0200 (3) |

| | | | | |
|-----|-------------|--------------|-------------|------------|
| N3 | 0.3089 (3) | 0.42103 (11) | 0.92557 (7) | 0.0243 (3) |
| H3 | 0.172 (4) | 0.4329 (16) | 0.9508 (10) | 0.029* |
| N4 | 0.3548 (3) | 0.29805 (11) | 0.90659 (7) | 0.0222 (2) |
| H4 | 0.518 (4) | 0.2710 (16) | 0.9126 (10) | 0.027* |
| C7 | 0.1401 (3) | 0.21961 (13) | 0.91490 (7) | 0.0222 (3) |
| O5 | -0.0894 (2) | 0.25786 (10) | 0.93114 (6) | 0.0291 (2) |
| C8 | 0.2055 (4) | 0.08501 (14) | 0.90370 (9) | 0.0310 (3) |
| H8A | 0.1747 | 0.0392 | 0.9473 | 0.047* |
| H8B | 0.3984 | 0.0764 | 0.8895 | 0.047* |
| H8C | 0.0861 | 0.0515 | 0.8669 | 0.047* |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|----|------------|------------|------------|-------------|-------------|-------------|
| C1 | 0.0161 (6) | 0.0247 (6) | 0.0211 (6) | -0.0007 (5) | -0.0003 (5) | -0.0036 (5) |
| N1 | 0.0187 (5) | 0.0254 (5) | 0.0276 (6) | -0.0018 (5) | 0.0007 (5) | -0.0083 (5) |
| O1 | 0.0243 (5) | 0.0272 (5) | 0.0380 (6) | 0.0046 (4) | -0.0021 (5) | -0.0092 (4) |
| O2 | 0.0334 (6) | 0.0304 (6) | 0.0408 (6) | -0.0044 (5) | 0.0178 (5) | -0.0053 (5) |
| C2 | 0.0218 (6) | 0.0241 (6) | 0.0242 (6) | -0.0029 (5) | -0.0050 (5) | 0.0001 (5) |
| C3 | 0.0229 (6) | 0.0303 (7) | 0.0203 (6) | -0.0070 (6) | -0.0027 (5) | 0.0046 (5) |
| N2 | 0.0323 (7) | 0.0384 (7) | 0.0262 (6) | -0.0125 (6) | -0.0069 (6) | 0.0095 (5) |
| O3 | 0.0475 (8) | 0.0320 (6) | 0.0489 (7) | -0.0124 (6) | -0.0052 (6) | 0.0114 (5) |
| O4 | 0.0430 (7) | 0.0581 (8) | 0.0374 (6) | -0.0177 (7) | 0.0111 (6) | 0.0105 (6) |
| C4 | 0.0203 (7) | 0.0352 (7) | 0.0203 (6) | -0.0025 (6) | 0.0020 (5) | 0.0001 (6) |
| C5 | 0.0205 (6) | 0.0267 (6) | 0.0221 (6) | 0.0012 (5) | 0.0029 (5) | -0.0024 (5) |
| C6 | 0.0161 (6) | 0.0238 (6) | 0.0200 (6) | -0.0007 (5) | -0.0006 (5) | -0.0014 (5) |
| N3 | 0.0210 (6) | 0.0217 (5) | 0.0301 (6) | 0.0006 (5) | 0.0084 (5) | -0.0019 (5) |
| N4 | 0.0154 (5) | 0.0200 (5) | 0.0312 (6) | 0.0011 (4) | 0.0006 (5) | -0.0004 (5) |
| C7 | 0.0182 (6) | 0.0256 (6) | 0.0228 (6) | -0.0011 (5) | -0.0022 (5) | 0.0029 (5) |
| O5 | 0.0159 (5) | 0.0339 (6) | 0.0375 (6) | -0.0002 (4) | 0.0012 (4) | 0.0046 (5) |
| C8 | 0.0308 (8) | 0.0235 (6) | 0.0389 (8) | -0.0011 (6) | -0.0008 (7) | 0.0019 (6) |

Geometric parameters (Å, °)

| | | | |
|--------|-------------|--------|-------------|
| C1—C2 | 1.3915 (19) | C5—C6 | 1.4178 (18) |
| C1—C6 | 1.4202 (19) | C5—H5 | 0.9500 |
| C1—N1 | 1.4508 (18) | C6—N3 | 1.3477 (18) |
| N1—O1 | 1.2278 (16) | N3—N4 | 1.3913 (17) |
| N1—O2 | 1.2354 (16) | N3—H3 | 0.83 (2) |
| C2—C3 | 1.371 (2) | N4—C7 | 1.3519 (18) |
| C2—H2 | 0.9500 | N4—H4 | 0.85 (2) |
| C3—C4 | 1.397 (2) | C7—O5 | 1.2282 (17) |
| C3—N2 | 1.4543 (19) | C7—C8 | 1.500 (2) |
| N2—O4 | 1.233 (2) | C8—H8A | 0.9800 |
| N2—O3 | 1.2355 (19) | C8—H8B | 0.9800 |
| C4—C5 | 1.367 (2) | C8—H8C | 0.9800 |
| C4—H4A | 0.9500 | | |

| | | | |
|-------------|--------------|-------------|--------------|
| C2—C1—C6 | 121.96 (13) | C6—C5—H5 | 119.2 |
| C2—C1—N1 | 116.25 (12) | N3—C6—C5 | 120.61 (13) |
| C6—C1—N1 | 121.79 (12) | N3—C6—C1 | 122.76 (12) |
| O1—N1—O2 | 122.79 (12) | C5—C6—C1 | 116.59 (12) |
| O1—N1—C1 | 118.74 (12) | C6—N3—N4 | 121.01 (12) |
| O2—N1—C1 | 118.47 (12) | C6—N3—H3 | 120.3 (12) |
| C3—C2—C1 | 118.50 (13) | N4—N3—H3 | 115.2 (12) |
| C3—C2—H2 | 120.8 | C7—N4—N3 | 116.14 (12) |
| C1—C2—H2 | 120.8 | C7—N4—H4 | 119.2 (12) |
| C2—C3—C4 | 121.83 (13) | N3—N4—H4 | 116.0 (13) |
| C2—C3—N2 | 118.65 (14) | O5—C7—N4 | 121.37 (13) |
| C4—C3—N2 | 119.49 (13) | O5—C7—C8 | 123.55 (14) |
| O4—N2—O3 | 123.81 (14) | N4—C7—C8 | 115.07 (13) |
| O4—N2—C3 | 117.56 (14) | C7—C8—H8A | 109.5 |
| O3—N2—C3 | 118.63 (15) | C7—C8—H8B | 109.5 |
| C5—C4—C3 | 119.47 (13) | H8A—C8—H8B | 109.5 |
| C5—C4—H4A | 120.3 | C7—C8—H8C | 109.5 |
| C3—C4—H4A | 120.3 | H8A—C8—H8C | 109.5 |
| C4—C5—C6 | 121.60 (13) | H8B—C8—H8C | 109.5 |
| C4—C5—H5 | 119.2 | | |
| | | | |
| C2—C1—N1—O1 | 9.02 (18) | N2—C3—C4—C5 | 176.53 (13) |
| C6—C1—N1—O1 | -170.04 (13) | C3—C4—C5—C6 | -0.2 (2) |
| C2—C1—N1—O2 | -171.10 (12) | C4—C5—C6—N3 | -175.76 (14) |
| C6—C1—N1—O2 | 9.84 (19) | C4—C5—C6—C1 | 2.1 (2) |
| C6—C1—C2—C3 | 1.1 (2) | C2—C1—C6—N3 | 175.25 (13) |
| N1—C1—C2—C3 | -177.94 (12) | N1—C1—C6—N3 | -5.7 (2) |
| C1—C2—C3—C4 | 0.9 (2) | C2—C1—C6—C5 | -2.53 (19) |
| C1—C2—C3—N2 | -177.00 (13) | N1—C1—C6—C5 | 176.47 (12) |
| C2—C3—N2—O4 | 179.13 (13) | C5—C6—N3—N4 | -13.1 (2) |
| C4—C3—N2—O4 | 1.2 (2) | C1—C6—N3—N4 | 169.18 (13) |
| C2—C3—N2—O3 | -0.3 (2) | C6—N3—N4—C7 | -142.12 (14) |
| C4—C3—N2—O3 | -178.27 (14) | N3—N4—C7—O5 | 7.5 (2) |
| C2—C3—C4—C5 | -1.3 (2) | N3—N4—C7—C8 | -171.84 (12) |

Hydrogen-bond geometry (\AA , $^\circ$)

| <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> |
|-----------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| N3—H3 \cdots O2 | 0.83 (2) | 2.001 (18) | 2.5942 (16) | 127.9 (16) |
| N4—H4 \cdots O5 ⁱ | 0.85 (2) | 1.95 (2) | 2.7748 (16) | 164.0 (17) |
| C5—H5 \cdots O4 ⁱⁱ | 0.95 | 2.44 | 3.249 (2) | 143 |
| C8—H8A \cdots O2 ⁱⁱⁱ | 0.98 | 2.58 | 3.269 (2) | 128 |
| C8—H8C \cdots O3 ^{iv} | 0.98 | 2.57 | 3.527 (2) | 165 |

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