Acta Crystallographica Section E
**Structure Reports**
**Online**
ISSN 1600-5368

# (*E*)-1-(2,4-Dinitrophenyl)-2-pentylidenehydrazine

**Patrícia D. Neunfeldt,[a] Auri R. Duval,[a] Wilson Cunico,[a] Solange M. S. V. Wardell,[b]‡ Edward R. T. Tiekink[c]* and James L. Wardell[d]**

[a]Departamento de Química Orgânica, Universidade Federal de Pelotas (UFPel), Campus Universitário, s/n°, Caixa Postal 354, 96010-900 Pelotas, RS, Brazil, [b]CHEMSOL, 1 Harcourt Road, Aberdeen AB15 5NY, Scotland, [c]Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia, and [d]Centro de Desenvolvimento Tecnológico em Saúde (CDTS), Fundação Oswaldo Cruz (FIOCRUZ), Casa Amarela, Campus de Manguinhos, Av. Brasil 4365, 21040-900 Rio de Janeiro, RJ, Brazil
Correspondence e-mail: edward.tiekink@gmail.com

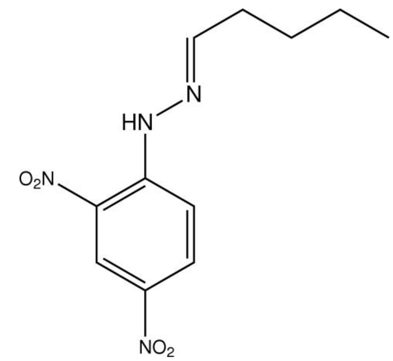
Received 7 January 2010; accepted 17 January 2010

Key indicators: single-crystal X-ray study; $T$ = 120 K; mean $\sigma$(C–C) = 0.006 Å; $R$ factor = 0.078; $wR$ factor = 0.183; data-to-parameter ratio = 12.1.

The title compound, $C_{11}H_{14}N_4O_4$, is essentially planar with an r.m.s. deviation for the 19 non-H atoms of 0.152 Å. The conformation about the C=N bond is *E*, and the molecule has a U-shape as the butyl group folds over towards the aromatic system. An intramolecular C—H···N interaction occurs. The crystal packing is dominated by N—H···O hydrogen bonding and C—H···O contacts, leading to twisted zigzag supramolecular chains along the *c* direction. The crystal packing brings two nitro O atoms into an unusually close proximity of 2.686 (4) Å. While the nature of this interaction is not obvious, there are several precendents for such short nitro–nitro O···O contacts of less than 2.70 Å in the crystallographic literature.

## Related literature

For background to the biological uses of hydrazones, see: Rollas & Küçükgüzel (2007). For background to the synthesis, see: Furniss *et al.* (1999); Neuenfeldt *et al.* (2009). For a description of the Cambridge Structural Database, see: Allen (2002).




## Experimental

### *Crystal data*

$C_{11}H_{14}N_4O_4$
$M_r$ = 266.26
Monoclinic, $C2/c$
$a$ = 31.162 (3) Å
$b$ = 4.4930 (4) Å
$c$ = 18.7329 (14) Å
$\beta$ = 106.159 (4)°
$V$ = 2519.2 (4) Å$^3$
$Z$ = 8
Mo $K\alpha$ radiation
$\mu$ = 0.11 mm$^{-1}$
$T$ = 120 K
0.32 × 0.03 × 0.02 mm

### *Data collection*

-Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2007) $T_{min}$ = 0.628, $T_{max}$ = 1.000
8172 measured reflections
2174 independent reflections
1451 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.115

### *Refinement*

$R[F^2 > 2\sigma(F^2)]$ = 0.078
$wR(F^2)$ = 0.183
$S$ = 1.10
2174 reflections
179 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.28 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.27 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1—H1n···O4 | 0.87 (4) | 1.99 (4) | 2.616 (5) | 128 (3) |
| N1—H1n···O4$^{i}$ | 0.87 (4) | 2.41 (4) | 3.166 (5) | 146 (4) |
| C3—H3···O1$^{ii}$ | 0.95 | 2.39 | 3.335 (5) | 176 |
| C6—H6···N2 | 0.95 | 2.40 | 2.735 (5) | 100 |

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

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

The use of the EPSRC X-ray crystallographic service at the University of Southampton, England and the valuable assistance of the staff there is gratefully acknowledged. JLW acknowledges support from CAPES (Brazil).

‡ Additional correspondence author, e-mail: j.wardell@abdn.ac.uk.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2271).

## References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Brandenburg, K. (2006). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Furniss, B. S., Hannaford, A. J., Smith, P. W. G. & Tatchell, A. R. (1999). *Vogel's Textbook of Practical Organic Chemistry*, 5th ed. London: Longmans.
Hooft, R. W. W. (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
Neuenfeldt, P. D., Drawanz, B. B., Cunico, W., Tiekink, E. R. T., Wardell, J. L. & Wardell, S. M. S. V. (2009). *Acta Cryst.* E**65**, o3190–o3191.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Rollas, S. & Küçükgüzel, G. S. (2007). *Molecules*, **12**, 1910–1939.
Sheldrick, G. M. (2007). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Westrip, S. P. (2010). *publCIF*. In preparation.

# supporting information

*Acta Cryst.* (2010). E**66**, o483–o484 [https://doi.org/10.1107/S1600536810002102]

## (*E*)-1-(2,4-Dinitrophenyl)-2-pentylidenehydrazine

**Patrícia D. Neunfeldt, Auri R. Duval, Wilson Cunico, Solange M. S. V. Wardell, Edward R. T. Tiekink and James L. Wardell**

### S1. Comment

2,4-Dinitrophenylhydrazine is a frequently used reagent for the characterization of aldehydes and ketones (Furniss *et al.*, 1999). The 2,4-dinitrophenylhydrazone products are generally formed readily in good yield and purity. The ready formation of 2,4-dinitrophenyl hydrazones of carbonyl compounds can be a disadvantage as found during the attempted formation of a thiazolidinone from 2,4-dinitrophenylhydrazine, pentanal and mercaptoacetic acid, using a similar one-pot synthesis to that used successfully with amines, carbonyl compounds and mercaptoacetic acid (Neuenfeldt *et al.*, 2009). Instead of the targeted thiazolidinone derivative, the 2,4-dinitrophenylhydrazone of pentanal was isolated in very high yield: as shown below, this compound was efficiently produced from a reaction mixture reaction just involving 2,4-dinitrophenylhydrazine and pentanal. Hydrazones containing the –NHN=CH moiety constitute an important class of antimicrobial, anticonvulsant, analgesic, antiinflammatory, antiplatelet, antitubercular and antitumoral agents. (Rollas & Küçükgüzel, 2007).

To a first approximation, the molecule of (I), Fig. 1, is flat with the maximum deviations of torsion angles from the ideal 0 or 180 ° being 9.0 (7) ° for N2–C7–C8–C9, and -170.7 (4) ° for C1–N1–N2–C7; the r.m.s. deviation of the non-hydrogen atoms = 0.152 Å. The *n*-butyl side-chain folds over to be oriented towards the benzene ring. The conformation about the C7═N3 bond [1.270 (5) Å] is *E*. In the crystal packing, supramolecular chains are formed along the *c* direction. These are sustained by four-membered $\{\cdots H\cdots O\}_2$ synthons as the amine-H1n atom is bifurcated forming intra- and intermolecular *N–H*···Onitro hydrogen bonds, Fig. 2 and Table 1. Additional stabilization to the chain is afforded by ten-membered $\{\cdots ONC_2H\}_2$ synthons, Fig. 2 and Table 1. Whereas the smaller of the synthons is disposed about a centre of inversion, the larger has crystallographic 2-fold symmetry and has a distinct folded conformation. The latter induces considerable kinks in the chain as emphasized in Fig. 3 which illustrates the formation of 2-D arrays *via* N–O···$\pi$ interactions [N–O3···$Cg$(C1–C6)$^i$ = 3.163 (3) Å with an angle at O3 = 89.9 (2) ° where $Cg$ is the ring centroid of the C1–C6 ring and symmetry operation $i = x, -1 + y, z$]. Globally, the layers formed in the *bc* plane stack along the *a* direction with interdigitation of the saturated residues. It is noted that the packing of molecules brings into close proximity two nitro-O atoms, *i.e.* O4···O4$^{ii}$ = 2.686 (4) Å for *ii*: $-x, 1 - y, 1 - z$. While the nature of this interaction is not obvious, there are approximately 50 precendents for such $O_{nitro}\cdots O_{nitro}$ contacts < 2.70 Å in the crystallographic literature (Allen, 2002).

### S2. Experimental

A mixture of 2,4-dinitrophenylhydrazine 1 (3 mmol) and pentanal 2 (3 mmol) in toluene (35 ml) was heated at 403 K with a Dean-Stark trap for 3 h. The reaction was cooled and the crude product was recrystallized from ethanol, yield 69%. m.p. 371–372 K. $^1$H NMR (400 MHz, $CDCl_3$): d 11.00 (br, 1H, NH), 9.11 (d, 1H, J = 2.4 Hz), 8.29 (dd, 1H, J = 9.6 and 2.4 Hz), 7.93 (d, 1H, J = 9.6 Hz), 7.54 (t, 1H, J = 5.2 Hz), 2.43 (m, 2H), 1.60 (m, 2H), 1.43 (sext, 2H, J = 7.6 Hz), 0.97 (t, 3H, J = 7.6 Hz) p.p.m.

## S3. Refinement

The C-bound H atoms were geometrically placed (C–H = 0.95–0.99 Å) and refined as riding with $U_{iso}$(H) = 1.2–1.5$U_{eq}$(C). The methyl H atoms were rotated to fit the electron density. The N–H atom was located in a difference map and refined with $U_{iso}$(H) = 1.2$U_{eq}$(N). The reported structure, while unambiguous, is not optimal owing to the poor quality of the crystals available for analysis.

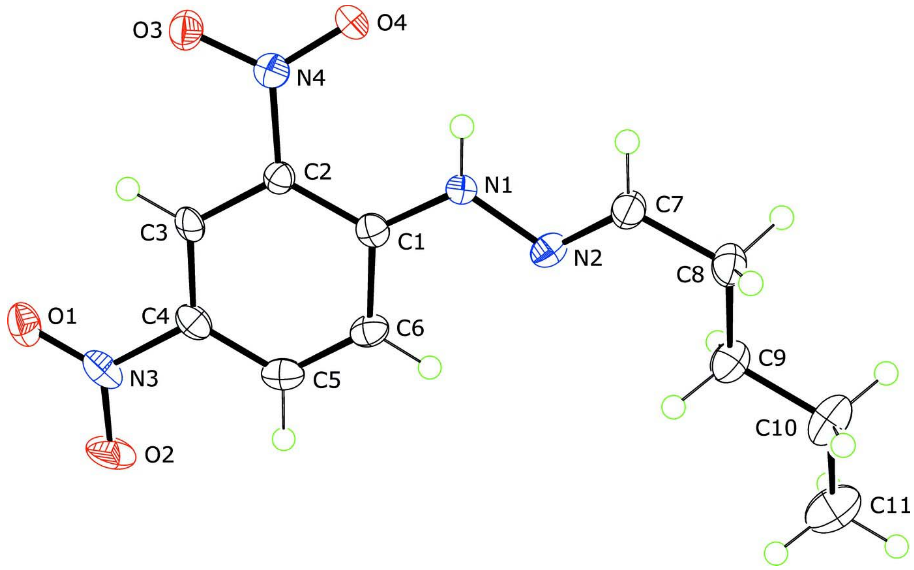



**Figure 1**

The molecular structure of (I) showing the atom-labelling scheme and displacement ellipsoids at the 50% probability level.

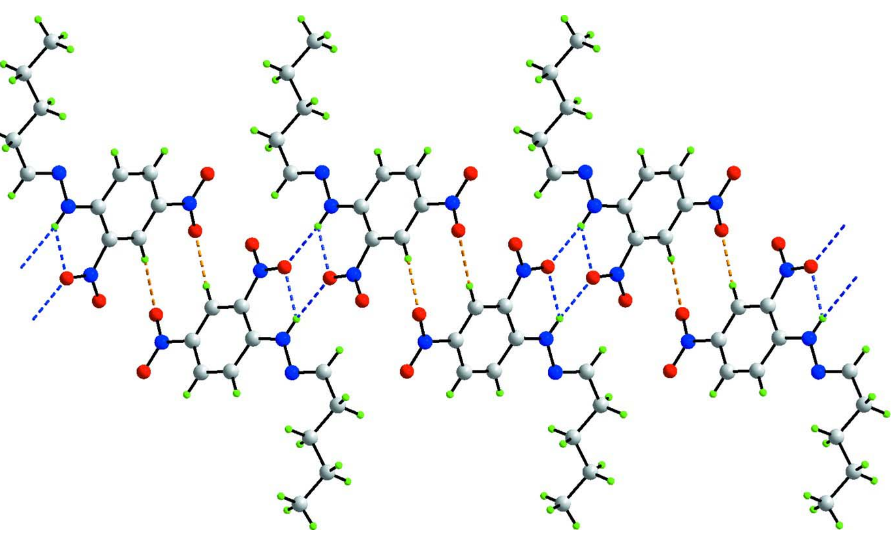


**Figure 2**

A view of the supramolecular chain in (I) mediated by N–H···O hydrogen bonding and C–H···O contacts, shown as blue and orange dashed lines, respectively. Colour code: O, red; N, blue; C, grey; and H, green.

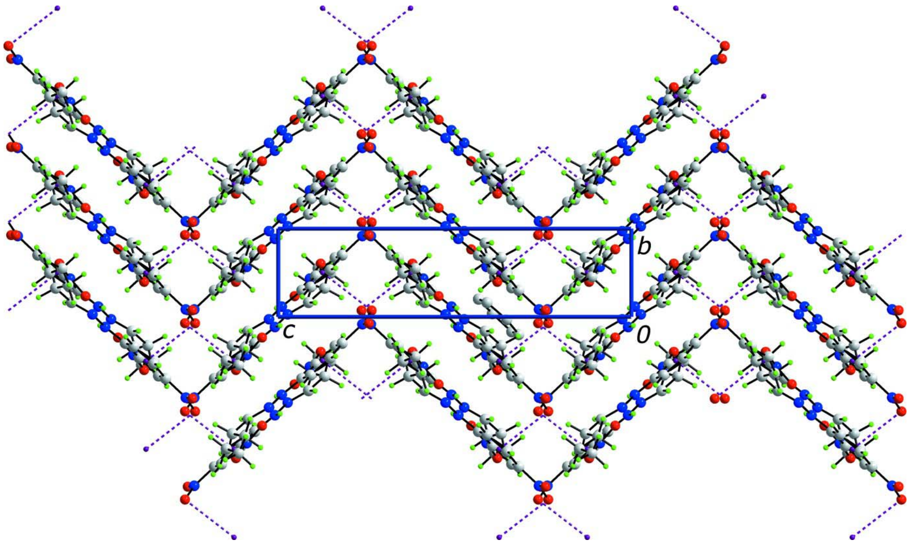



**Figure 3**

A view of the supramolecular 2-D array in (I) with N–O···$\pi$ interactions shown as purple dashed lines. This figure highlights the zigzag topology of the chains shown in Fig. 2. Colour code: O, red; N, blue; C, grey; and H, green.

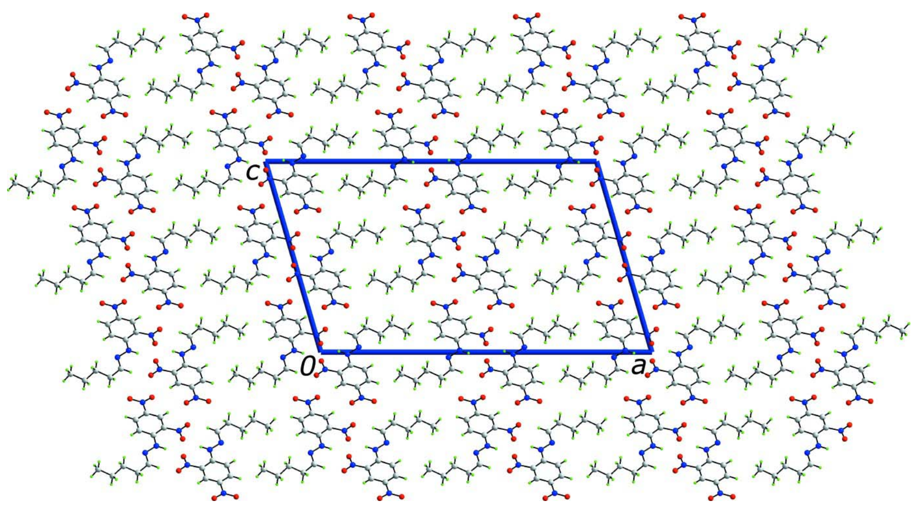



**Figure 4**

A view of the stacking of layers (illustrated in Fig. 3) in (I) with the interdigitation of the *n*-butyl residues. Colour code: O, red; N, blue; C, grey; and H, green.

**(*E*)-1-(2,4-Dinitrophenyl)-2-pentylidenehydrazine**

*Crystal data*

$C_{11}H_{14}N_4O_4$
$M_r$ = 266.26
Monoclinic, *C*2/*c*
Hall symbol: -C 2yc
*a* = 31.162 (3) Å
*b* = 4.4930 (4) Å
*c* = 18.7329 (14) Å
$\beta$ = 106.159 (4)°
*V* = 2519.2 (4) $Å^3$
*Z* = 8
*F*(000) = 1120
$D_x$ = 1.404 Mg $m^{-3}$
Mo *Kα* radiation, $\lambda$ = 0.71073 Å
Cell parameters from 14843 reflections
$\theta$ = 2.9–27.5°
$\mu$ = 0.11 $mm^{-1}$

$T$ = 120 K
Needle, yellow

0.32 × 0.03 × 0.02 mm

*Data collection*

-Nonius KappaCCD area-detector diffractometer
Radiation source: Enraf Nonius FR591 rotating anode
10 cm confocal mirrors monochromator
Detector resolution: 9.091 pixels mm$^{-1}$
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2007)

$T_{min}$ = 0.628, $T_{max}$ = 1.000
8172 measured reflections
2174 independent reflections
1451 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.115
$\theta_{max}$ = 25.0°, $\theta_{min}$ = 3.0°
$h = -36 \rightarrow 36$
$k = -5 \rightarrow 5$
$l = -22 \rightarrow 22$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.078$
$wR(F^2) = 0.183$
$S$ = 1.10
2174 reflections
179 parameters
0 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
$w = 1/[\sigma^2(F_o^2) + (0.0406P)^2 + 14.6755P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.28 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.27 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 (Å$^2$)*

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| O1 | 0.04985 (11) | −0.5722 (7) | 0.23571 (16) | 0.0294 (8) |
| O2 | 0.11770 (10) | −0.4264 (8) | 0.24360 (16) | 0.0360 (9) |
| O3 | −0.03340 (10) | −0.1033 (7) | 0.37999 (16) | 0.0263 (8) |
| O4 | −0.00644 (9) | 0.2652 (7) | 0.45386 (15) | 0.0240 (7) |
| N1 | 0.07910 (11) | 0.3841 (8) | 0.49031 (18) | 0.0194 (8) |
| H1N | 0.0551 (14) | 0.401 (10) | 0.505 (2) | 0.023* |
| N2 | 0.11897 (11) | 0.5276 (8) | 0.52633 (18) | 0.0224 (9) |
| N3 | 0.08254 (13) | −0.4163 (9) | 0.26201 (19) | 0.0267 (9) |
| N4 | −0.00244 (11) | 0.0661 (8) | 0.41033 (19) | 0.0213 (8) |
| C1 | 0.07833 (13) | 0.2003 (10) | 0.4333 (2) | 0.0197 (10) |
| C2 | 0.04022 (13) | 0.0353 (10) | 0.3940 (2) | 0.0185 (9) |
| C3 | 0.04158 (14) | −0.1701 (9) | 0.3391 (2) | 0.0191 (9) |
| H3 | 0.0161 | −0.2868 | 0.3159 | 0.023* |

| | | | | |
|---|---|---|---|---|
| C4 | 0.08074 (14) | −0.2003 (10) | 0.3192 (2) | 0.0222 (10) |
| C5 | 0.11852 (14) | −0.0324 (10) | 0.3534 (2) | 0.0242 (10) |
| H5 | 0.1450 | −0.0528 | 0.3381 | 0.029* |
| C6 | 0.11736 (14) | 0.1613 (10) | 0.4090 (2) | 0.0230 (10) |
| H6 | 0.1434 | 0.2733 | 0.4321 | 0.028* |
| C7 | 0.11826 (14) | 0.6629 (11) | 0.5855 (2) | 0.0248 (10) |
| H7 | 0.0922 (15) | 0.660 (11) | 0.604 (2) | 0.030* |
| C8 | 0.15800 (14) | 0.8254 (11) | 0.6307 (2) | 0.0281 (11) |
| H8A | 0.1693 | 0.7207 | 0.6788 | 0.034* |
| H8B | 0.1485 | 1.0266 | 0.6415 | 0.034* |
| C9 | 0.19629 (14) | 0.8581 (12) | 0.5957 (2) | 0.0292 (11) |
| H9A | 0.2041 | 0.6593 | 0.5802 | 0.035* |
| H9B | 0.1863 | 0.9830 | 0.5505 | 0.035* |
| C10 | 0.23763 (15) | 0.9966 (13) | 0.6476 (3) | 0.0382 (13) |
| H10A | 0.2293 | 1.1896 | 0.6655 | 0.046* |
| H10B | 0.2485 | 0.8654 | 0.6914 | 0.046* |
| C11 | 0.27528 (16) | 1.0479 (14) | 0.6126 (3) | 0.0481 (15) |
| H11A | 0.2826 | 0.8602 | 0.5921 | 0.072* |
| H11B | 0.3016 | 1.1216 | 0.6503 | 0.072* |
| H11C | 0.2660 | 1.1951 | 0.5727 | 0.072* |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O1 | 0.0374 (18) | 0.0244 (18) | 0.0233 (16) | 0.0013 (17) | 0.0035 (14) | −0.0058 (15) |
| O2 | 0.0333 (18) | 0.050 (2) | 0.0308 (17) | 0.0130 (18) | 0.0186 (15) | −0.0036 (17) |
| O3 | 0.0273 (16) | 0.0281 (19) | 0.0246 (15) | −0.0065 (15) | 0.0090 (13) | −0.0059 (15) |
| O4 | 0.0244 (16) | 0.0223 (18) | 0.0265 (15) | 0.0017 (13) | 0.0093 (13) | −0.0074 (15) |
| N1 | 0.0163 (18) | 0.019 (2) | 0.0236 (18) | 0.0000 (16) | 0.0061 (15) | −0.0035 (17) |
| N2 | 0.0181 (17) | 0.026 (2) | 0.0231 (19) | −0.0029 (16) | 0.0052 (15) | 0.0018 (17) |
| N3 | 0.037 (2) | 0.023 (2) | 0.0218 (19) | 0.010 (2) | 0.0108 (18) | 0.0006 (17) |
| N4 | 0.0228 (19) | 0.020 (2) | 0.0219 (18) | 0.0005 (17) | 0.0078 (16) | 0.0023 (18) |
| C1 | 0.022 (2) | 0.017 (2) | 0.019 (2) | 0.0026 (19) | 0.0042 (18) | 0.0026 (19) |
| C2 | 0.019 (2) | 0.017 (2) | 0.019 (2) | −0.0002 (18) | 0.0047 (18) | 0.0006 (19) |
| C3 | 0.024 (2) | 0.010 (2) | 0.021 (2) | 0.0042 (18) | 0.0025 (18) | 0.0015 (18) |
| C4 | 0.029 (2) | 0.018 (2) | 0.021 (2) | 0.005 (2) | 0.0091 (19) | 0.0028 (19) |
| C5 | 0.022 (2) | 0.025 (3) | 0.028 (2) | 0.005 (2) | 0.0105 (19) | 0.009 (2) |
| C6 | 0.019 (2) | 0.022 (3) | 0.028 (2) | −0.0008 (19) | 0.0082 (19) | 0.006 (2) |
| C7 | 0.023 (2) | 0.027 (3) | 0.024 (2) | −0.004 (2) | 0.0054 (19) | −0.003 (2) |
| C8 | 0.030 (2) | 0.028 (3) | 0.027 (2) | −0.008 (2) | 0.009 (2) | −0.005 (2) |
| C9 | 0.027 (2) | 0.033 (3) | 0.027 (2) | −0.006 (2) | 0.006 (2) | 0.001 (2) |
| C10 | 0.032 (3) | 0.043 (4) | 0.033 (3) | −0.010 (2) | −0.002 (2) | 0.004 (3) |
| C11 | 0.032 (3) | 0.056 (4) | 0.054 (3) | −0.008 (3) | 0.009 (3) | 0.010 (3) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| O1—N3 | 1.221 (5) | C5—H5 | 0.9500 |
| O2—N3 | 1.238 (4) | C6—H6 | 0.9500 |

| | | | |
|---|---|---|---|
| O3—N4 | 1.236 (4) | C7—C8 | 1.483 (6) |
| O4—N4 | 1.240 (4) | C7—H7 | 0.96 (4) |
| N1—C1 | 1.345 (5) | C8—C9 | 1.521 (6) |
| N1—N2 | 1.396 (5) | C8—H8A | 0.9900 |
| N1—H1N | 0.87 (4) | C8—H8B | 0.9900 |
| N2—C7 | 1.270 (5) | C9—C10 | 1.515 (6) |
| N3—C4 | 1.458 (5) | C9—H9A | 0.9900 |
| N4—C2 | 1.451 (5) | C9—H9B | 0.9900 |
| C1—C2 | 1.420 (6) | C10—C11 | 1.513 (6) |
| C1—C6 | 1.423 (5) | C10—H10A | 0.9900 |
| C2—C3 | 1.391 (6) | C10—H10B | 0.9900 |
| C3—C4 | 1.378 (5) | C11—H11A | 0.9800 |
| C3—H3 | 0.9500 | C11—H11B | 0.9800 |
| C4—C5 | 1.395 (6) | C11—H11C | 0.9800 |
| C5—C6 | 1.365 (6) | | |

| | | | |
|---|---|---|---|
| C1—N1—N2 | 118.9 (3) | N2—C7—C8 | 121.3 (4) |
| C1—N1—H1N | 119 (3) | N2—C7—H7 | 122 (3) |
| N2—N1—H1N | 122 (3) | C8—C7—H7 | 117 (3) |
| C7—N2—N1 | 114.4 (3) | C7—C8—C9 | 115.5 (4) |
| O1—N3—O2 | 124.8 (4) | C7—C8—H8A | 108.4 |
| O1—N3—C4 | 118.7 (3) | C9—C8—H8A | 108.4 |
| O2—N3—C4 | 116.6 (4) | C7—C8—H8B | 108.4 |
| O3—N4—O4 | 122.6 (3) | C9—C8—H8B | 108.4 |
| O3—N4—C2 | 119.2 (3) | H8A—C8—H8B | 107.5 |
| O4—N4—C2 | 118.2 (3) | C10—C9—C8 | 113.0 (4) |
| N1—C1—C2 | 124.0 (4) | C10—C9—H9A | 109.0 |
| N1—C1—C6 | 120.1 (4) | C8—C9—H9A | 109.0 |
| C2—C1—C6 | 115.8 (4) | C10—C9—H9B | 109.0 |
| C3—C2—C1 | 122.5 (4) | C8—C9—H9B | 109.0 |
| C3—C2—N4 | 115.9 (4) | H9A—C9—H9B | 107.8 |
| C1—C2—N4 | 121.6 (4) | C11—C10—C9 | 114.0 (4) |
| C4—C3—C2 | 118.5 (4) | C11—C10—H10A | 108.7 |
| C4—C3—H3 | 120.8 | C9—C10—H10A | 108.7 |
| C2—C3—H3 | 120.8 | C11—C10—H10B | 108.7 |
| C3—C4—C5 | 121.3 (4) | C9—C10—H10B | 108.7 |
| C3—C4—N3 | 118.8 (4) | H10A—C10—H10B | 107.6 |
| C5—C4—N3 | 119.8 (4) | C10—C11—H11A | 109.5 |
| C6—C5—C4 | 119.8 (4) | C10—C11—H11B | 109.5 |
| C6—C5—H5 | 120.1 | H11A—C11—H11B | 109.5 |
| C4—C5—H5 | 120.1 | C10—C11—H11C | 109.5 |
| C5—C6—C1 | 121.9 (4) | H11A—C11—H11C | 109.5 |
| C5—C6—H6 | 119.0 | H11B—C11—H11C | 109.5 |
| C1—C6—H6 | 119.0 | | |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1n···O4 | 0.87 (4) | 1.99 (4) | 2.616 (5) | 128 (3) |
| N1—H1n···O4$^{i}$ | 0.87 (4) | 2.41 (4) | 3.166 (5) | 146 (4) |
| C3—H3···O1$^{ii}$ | 0.95 | 2.39 | 3.335 (5) | 176 |
| C6—H6···N2 | 0.95 | 2.40 | 2.735 (5) | 100 |

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