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N-(3,5-Dinitrobenzoyl)-*N*′-phenylhydrazine: sheets built from N—H···O and C—H···O hydrogen bonds

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.003 Å
R factor = 0.052
wR factor = 0.144
Data-to-parameter ratio = 15.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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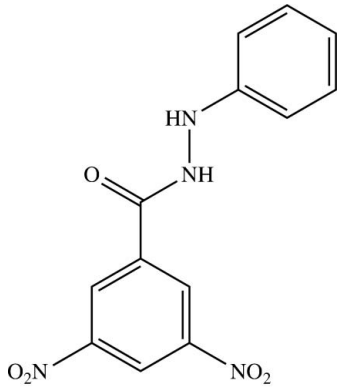
Molecules of the title compound, $C_{13}H_{10}N_4O_5$, are linked into sheets by a combination of two N—H···O hydrogen bonds and one C—H···O hydrogen bond.

Comment

We report here the molecular and supramolecular structure of the title compound, (I) (Fig. 1). The coordination of atom N1 is exactly planar, while that of N2 is markedly pyramidal. The overall molecular conformation is defined by six torsion angles (Table 1), which show that the –C(=O)—NH– portion adopts the usual *trans*-planar conformation. While the nitrated aryl ring is nearly coplanar with the central amide unit, the torsion angle of nearly 90° around the N—N bond is a reflection of the mutually orthogonal orientation of the lone pairs on the two hydrazine N atoms. The molecules thus have no internal symmetry in the solid state and hence are chiral, but the centrosymmetric space group accommodates equal numbers of the two enantiomeric forms.



(I)

The molecules of (I) are linked into sheets by a combination of two N—H···O hydrogen bonds and one C—H···O hydrogen bond (Table 2), and the formation of the sheet is readily analysed in terms of two one-dimensional substructures. Atom N2 in the molecule at (*x*, *y*, *z*) acts as a hydrogen-bond donor to nitro atom O31 in the molecule at (*x*, *y*, 1 + *z*), so generating by translation a *C*(9) (Bernstein *et al.*, 1995) chain running parallel to the [001] direction (Fig. 2). Atoms N1 and C2 in the molecule at (*x*, *y*, *z*) both act as hydrogen-bond donors to carbonyl atom O7 in the molecule at $(-\frac{1}{2}+x, \frac{3}{2}-y, -\frac{1}{2}+z)$, so forming a $C(4)C(5)[R_2^1(7)]$ chain of rings along [101] and generated by the *n*-glide plane at $y = \frac{3}{4}$ (Fig. 3). The combination of the [001] and [101] chains then generates a sheet parallel to (010) (Fig. 4). Two such sheets, generated by

the *n*-glide planes at $y = \frac{1}{4}$ and $y = \frac{3}{4}$, pass through each unit cell, but there are no direction-specific interactions between adjacent sheets.

Experimental

A mixture of equimolar quantities (10 mmol of each component) of 3,5-dinitrobenzoyl chloride and phenylhydrazine in tetrahydrofuran (20 ml) was heated under reflux for 24 h in a dinitrogen atmosphere. The reaction mixture was cooled, and the solvent was removed under reduced pressure. The solid product was washed successively with cold ethanol and diethyl ether, and then recrystallized from ethanol (m.p. 473–475 K; GC/MS *m*/*z* 302 $[M]^+$. IR (KBr disk, χm^{-1}) 3330 and 3280 (NH), 1648 (CO), 1540 and 1344 (NO_2).

Crystal data

$C_{13}H_{10}N_4O_5$
$M_r = 302.25$
Monoclinic, $P2_1/n$
$a = 7.5696$ (3) Å
$b = 22.176$ (2) Å
$c = 8.4099$ (4) Å
$\beta = 110.802$ (3)°
$V = 1319.69$ (15) Å^3
$Z = 4$
$D_x = 1.521$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.12$ mm^{-1}
$T = 120$ (2) K
Lath, yellow
0.44 × 0.08 × 0.02 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.961$, $T_{max} = 0.997$
14875 measured reflections
3022 independent reflections
1961 reflections with $I > 2\sigma(I)$
$R_{int} = 0.067$
$\theta_{max} = 27.5°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.144$
$S = 1.05$
3022 reflections
199 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0578P)^2 + 0.6665P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.24$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-3}

Table 1
Selected torsion angles (°).

C1—C7—N1—N2	174.32 (18)	N1—C7—C1—C2	19.8 (3)
C7—N1—N2—C21	84.2 (2)	C2—C3—N3—O31	7.0 (3)
N1—N2—C21—C22	50.8 (3)	C4—C5—N5—O51	−13.6 (3)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O7^{i}	0.88	1.97	2.806 (2)	157
N2—H2*A*···O31^{ii}	0.88	2.16	3.020 (3)	165
C2—H2···O7^{i}	0.95	2.47	3.355 (3)	155

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

All H atoms were located in difference maps and then treated as riding atoms with distances C—H = 0.95 Å and N—H = 0.88 Å, and with $U_{iso}(H) = 1.2U_{eq}(C,N)$.

Data collection: *COLLECT* (Hooft, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); soft-

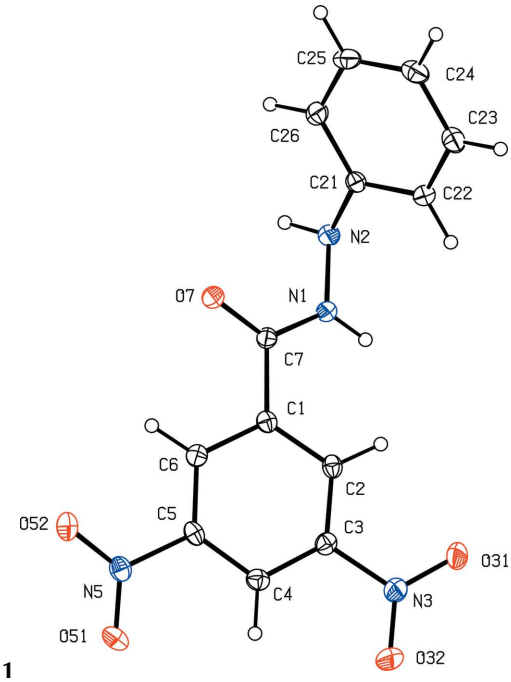


Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

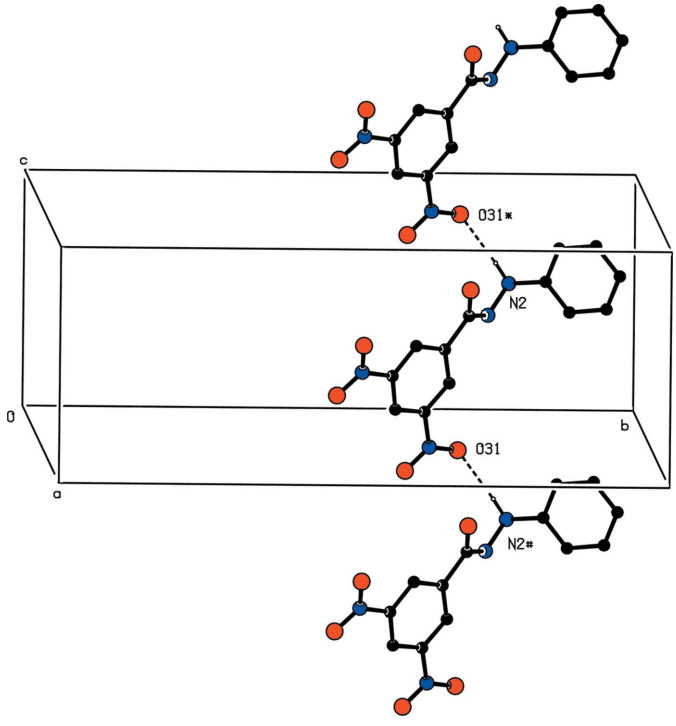


Figure 2
Part of the crystal structure of (I), showing the formation of a $C(9)$ chain parallel to [001]. For the sake of clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(x, y, 1 + z)$ and $(x, y, -1 + z)$, respectively.

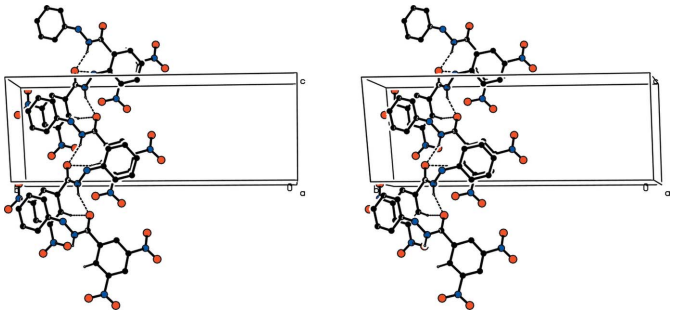


Figure 3
A stereoview of part of the crystal structure of (I), showing the formation of a $C(4)C(5)[R_2^1(7)]$ chain of rings parallel to [101]. For the sake of clarity, H atoms not involved in the motif shown have been omitted.

ware used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, England; the authors thank the staff of the Service for all their help and advice. JLW thanks CNPq and FAPERJ for financial support.

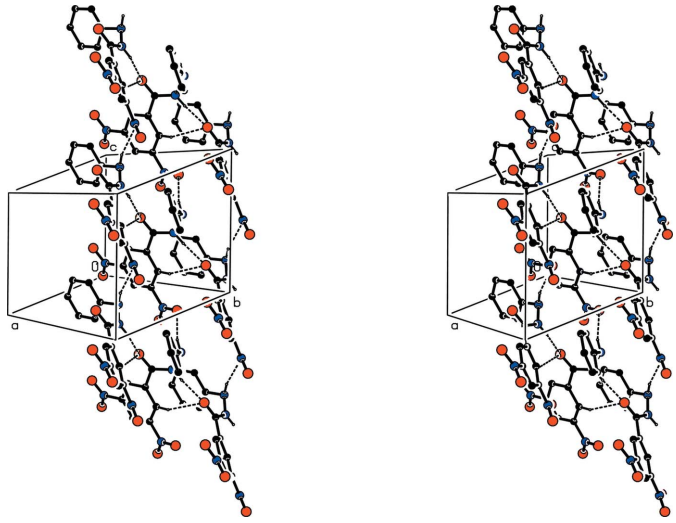


Figure 4
A stereoview of part of the crystal structure of (I), showing the formation of a hydrogen-bonded (010) sheet. For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

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Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 7.5696$ (3) Å
$b = 22.176$ (2) Å
$c = 8.4099$ (4) Å
$\beta = 110.802$ (3)°
$V = 1319.69$ (15) Å^3
$Z = 4$
$F(000) = 624$
$D_x = 1.521$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3022 reflections
$\theta = 3.0$–27.5°
$\mu = 0.12$ mm^{-1}
$T = 120$ K
Lath, yellow
0.44 × 0.08 × 0.02 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Radiation source: Bruker-Nonius FR591 rotating anode
Graphite monochromator
Detector resolution: 9.091 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
$T_{min} = 0.961$, $T_{max} = 0.997$
14875 measured reflections
3022 independent reflections
1961 reflections with $I > 2\sigma(I)$
$R_{int} = 0.067$
$\theta_{max} = 27.5°$, $\theta_{min} = 3.0°$
$h = -9 \rightarrow 9$
$k = -28 \rightarrow 28$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.144$
$S = 1.05$
3022 reflections
199 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-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0578P)^2 + 0.6665P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.24$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-3}

Special details

Experimental. NMR (DMSO-d_6): δ(H) 11.08 (1*H*, *s*, NH), 9.12 (2*H*, *d*, *J* = 2.0 Hz), 9.01 (1*H*, *d*, 2.0), 7.18 (2*H*, *dd*, *J* = 7.5 and 8.0 Hz), 6.84 (2*H*, *d*, *J* = 7.5 Hz), 6.76 (1*H*, *dd*, *J* = 7.0 and 7.5 Hz); δ(C) 162.3, 148.7, 148.2, 135.4, 128.7, 127.6, 121.1, 119.0, 112.4.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.3507 (3)	0.66944 (9)	0.3671 (3)	0.0219 (5)
C2	0.2617 (3)	0.68260 (10)	0.1953 (3)	0.0238 (5)
C3	0.2731 (3)	0.64172 (10)	0.0765 (3)	0.0246 (5)
N3	0.1766 (3)	0.65608 (9)	−0.1038 (2)	0.0343 (5)
O31	0.1060 (3)	0.70687 (8)	−0.1391 (2)	0.0398 (5)
O32	0.1661 (3)	0.61737 (9)	−0.2088 (2)	0.0568 (6)
C4	0.3710 (3)	0.58807 (10)	0.1178 (3)	0.0257 (5)
C5	0.4630 (3)	0.57717 (9)	0.2893 (3)	0.0231 (5)
N5	0.5719 (3)	0.52110 (8)	0.3400 (2)	0.0277 (5)
O51	0.5481 (2)	0.48150 (7)	0.2329 (2)	0.0390 (5)
O52	0.6815 (2)	0.51683 (7)	0.4883 (2)	0.0332 (4)
C6	0.4550 (3)	0.61626 (9)	0.4147 (3)	0.0236 (5)
C7	0.3390 (3)	0.70940 (10)	0.5064 (3)	0.0234 (5)
O7	0.4536 (2)	0.70439 (7)	0.65282 (19)	0.0306 (4)
N1	0.1957 (3)	0.74860 (8)	0.4635 (2)	0.0244 (4)
N2	0.1620 (3)	0.78444 (8)	0.5875 (2)	0.0271 (5)
C21	0.2694 (3)	0.83829 (10)	0.6312 (3)	0.0242 (5)
C22	0.2748 (3)	0.87735 (10)	0.5041 (3)	0.0283 (5)
C23	0.3666 (3)	0.93227 (11)	0.5482 (3)	0.0321 (6)
C24	0.4539 (3)	0.94840 (11)	0.7171 (3)	0.0344 (6)
C25	0.4493 (3)	0.90925 (11)	0.8429 (3)	0.0334 (6)
C26	0.3579 (3)	0.85433 (11)	0.8015 (3)	0.0288 (5)
H2	0.1942	0.7193	0.1607	0.029*
H4	0.3750	0.5602	0.0332	0.031*
H6	0.5195	0.6071	0.5314	0.028*
H1	0.1121	0.7528	0.3601	0.029*
H2A	0.1693	0.7622	0.6762	0.033*
H22	0.2160	0.8665	0.3878	0.034*
H23	0.3697	0.9592	0.4613	0.039*
H24	0.5164	0.9862	0.7461	0.041*
H25	0.5096	0.9201	0.9590	0.040*
H26	0.3553	0.8276	0.8889	0.035*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0203 (11)	0.0199 (11)	0.0258 (11)	−0.0031 (9)	0.0085 (9)	0.0011 (9)
C2	0.0211 (11)	0.0218 (11)	0.0269 (12)	−0.0009 (9)	0.0066 (9)	0.0035 (9)
C3	0.0260 (12)	0.0259 (12)	0.0237 (11)	−0.0033 (9)	0.0112 (10)	0.0020 (9)
N3	0.0436 (13)	0.0337 (12)	0.0276 (11)	0.0061 (10)	0.0152 (9)	0.0031 (9)

O31	0.0574 (12)	0.0348 (10)	0.0305 (9)	0.0131 (9)	0.0196 (9)	0.0109 (8)
O32	0.0876 (16)	0.0517 (12)	0.0266 (10)	0.0251 (11)	0.0146 (10)	−0.0054 (9)
C4	0.0278 (12)	0.0237 (12)	0.0277 (12)	−0.0037 (9)	0.0125 (10)	−0.0018 (9)
C5	0.0194 (11)	0.0180 (10)	0.0335 (12)	−0.0012 (9)	0.0113 (9)	0.0033 (9)
N5	0.0264 (10)	0.0252 (10)	0.0333 (11)	0.0009 (8)	0.0128 (9)	0.0038 (9)
O51	0.0480 (11)	0.0246 (9)	0.0440 (10)	0.0065 (8)	0.0157 (9)	−0.0047 (8)
O52	0.0293 (9)	0.0328 (9)	0.0352 (9)	0.0046 (7)	0.0087 (8)	0.0087 (8)
C6	0.0211 (11)	0.0234 (11)	0.0247 (11)	−0.0047 (9)	0.0061 (9)	0.0007 (9)
C7	0.0242 (12)	0.0209 (11)	0.0220 (11)	−0.0033 (9)	0.0044 (9)	0.0001 (9)
O7	0.0319 (9)	0.0277 (9)	0.0251 (9)	0.0014 (7)	0.0014 (7)	−0.0022 (7)
N1	0.0257 (10)	0.0241 (9)	0.0210 (9)	0.0017 (8)	0.0052 (8)	−0.0012 (8)
N2	0.0339 (11)	0.0252 (10)	0.0239 (10)	0.0021 (8)	0.0123 (9)	0.0003 (8)
C21	0.0227 (12)	0.0241 (11)	0.0245 (11)	0.0066 (9)	0.0069 (9)	−0.0006 (9)
C22	0.0335 (13)	0.0262 (12)	0.0224 (11)	0.0014 (10)	0.0066 (10)	−0.0021 (10)
C23	0.0300 (13)	0.0265 (12)	0.0374 (14)	0.0020 (10)	0.0088 (11)	0.0015 (11)
C24	0.0269 (13)	0.0292 (13)	0.0427 (15)	0.0025 (10)	0.0070 (11)	−0.0102 (12)
C25	0.0245 (13)	0.0402 (14)	0.0299 (13)	0.0073 (11)	0.0028 (10)	−0.0131 (11)
C26	0.0241 (12)	0.0351 (13)	0.0258 (12)	0.0106 (10)	0.0072 (10)	0.0007 (10)

Geometric parameters (Å, º)

C1—C2	1.391 (3)	C7—N1	1.336 (3)
C1—C6	1.396 (3)	N1—N2	1.405 (2)
C1—C7	1.496 (3)	N1—H1	0.88
C2—C3	1.374 (3)	N2—C21	1.418 (3)
C2—H2	0.95	N2—H2A	0.88
C3—C4	1.379 (3)	C21—C22	1.388 (3)
C3—N3	1.465 (3)	C21—C26	1.395 (3)
N3—O32	1.214 (3)	C22—C23	1.386 (3)
N3—O31	1.237 (2)	C22—H22	0.95
C4—C5	1.382 (3)	C23—C24	1.385 (3)
C4—H4	0.95	C23—H23	0.95
C5—C6	1.383 (3)	C24—C25	1.378 (3)
C5—N5	1.469 (3)	C24—H24	0.95
N5—O51	1.225 (2)	C25—C26	1.383 (3)
N5—O52	1.232 (2)	C25—H25	0.95
C6—H6	0.95	C26—H26	0.95
C7—O7	1.234 (2)		
C2—C1—C6	119.4 (2)	N1—C7—C1	116.21 (18)
C2—C1—C7	123.19 (19)	C7—N1—N2	120.76 (18)
C6—C1—C7	117.43 (19)	C7—N1—H1	124.5
C3—C2—C1	119.0 (2)	N2—N1—H1	114.7
C3—C2—H2	120.5	N1—N2—C21	115.50 (18)
C1—C2—H2	120.5	N1—N2—H2A	109.8
C2—C3—C4	123.6 (2)	C21—N2—H2A	113.3
C2—C3—N3	118.16 (19)	C22—C21—C26	119.8 (2)
C4—C3—N3	118.3 (2)	C22—C21—N2	119.80 (19)

O32—N3—O31	123.9 (2)	C26—C21—N2	120.2 (2)
O32—N3—C3	118.6 (2)	C23—C22—C21	119.4 (2)
O31—N3—C3	117.42 (19)	C23—C22—H22	120.3
C3—C4—C5	116.1 (2)	C21—C22—H22	120.3
C3—C4—H4	122.0	C24—C23—C22	120.9 (2)
C5—C4—H4	122.0	C24—C23—H23	119.6
C4—C5—C6	123.0 (2)	C22—C23—H23	119.6
C4—C5—N5	118.3 (2)	C25—C24—C23	119.5 (2)
C6—C5—N5	118.74 (19)	C25—C24—H24	120.3
O51—N5—O52	124.02 (19)	C23—C24—H24	120.3
O51—N5—C5	118.21 (18)	C24—C25—C26	120.5 (2)
O52—N5—C5	117.78 (18)	C24—C25—H25	119.7
C5—C6—C1	119.0 (2)	C26—C25—H25	119.7
C5—C6—H6	120.5	C25—C26—C21	119.9 (2)
C1—C6—H6	120.5	C25—C26—H26	120.1
O7—C7—N1	123.0 (2)	C21—C26—H26	120.1
O7—C7—C1	120.8 (2)		

C1—C7—N1—N2	174.32 (18)	C6—C5—N5—O52	−14.4 (3)
C7—N1—N2—C21	84.2 (2)	C4—C5—C6—C1	−0.4 (3)
N1—N2—C21—C22	50.8 (3)	N5—C5—C6—C1	−179.55 (18)
N1—C7—C1—C2	19.8 (3)	C2—C1—C6—C5	−1.7 (3)
C6—C1—C2—C3	2.4 (3)	C7—C1—C6—C5	177.64 (19)
C7—C1—C2—C3	−176.9 (2)	C2—C1—C7—O7	−162.2 (2)
C1—C2—C3—C4	−1.0 (3)	C6—C1—C7—O7	18.4 (3)
C1—C2—C3—N3	179.3 (2)	C6—C1—C7—N1	−159.5 (2)
C2—C3—N3—O32	−171.1 (2)	O7—C7—N1—N2	−3.6 (3)
C4—C3—N3—O32	9.1 (3)	N1—N2—C21—C26	−134.1 (2)
C2—C3—N3—O31	7.0 (3)	C26—C21—C22—C23	−0.7 (3)
C4—C3—N3—O31	−172.8 (2)	N2—C21—C22—C23	174.5 (2)
C2—C3—C4—C5	−1.1 (3)	C21—C22—C23—C24	0.4 (4)
N3—C3—C4—C5	178.66 (19)	C22—C23—C24—C25	0.1 (4)
C3—C4—C5—C6	1.8 (3)	C23—C24—C25—C26	−0.3 (4)
C3—C4—C5—N5	−179.08 (19)	C24—C25—C26—C21	0.0 (3)
C4—C5—N5—O51	−13.6 (3)	C22—C21—C26—C25	0.5 (3)
C6—C5—N5—O51	165.6 (2)	N2—C21—C26—C25	−174.7 (2)
C4—C5—N5—O52	166.47 (19)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O7^{i}	0.88	1.97	2.806 (2)	157
N2—H2*A*···O31^{ii}	0.88	2.16	3.020 (3)	165
C2—H2···O7^{i}	0.95	2.47	3.355 (3)	155

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