

6-Nitro-1,10-phenanthrolin-5-amine

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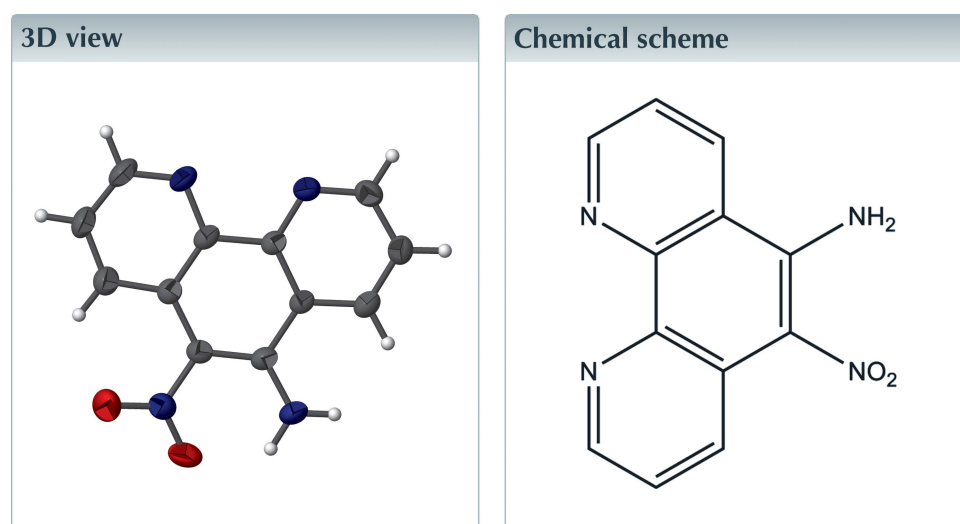
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Keywords: crystal structure; phenanthroline; functionalization; bidentate ligands.

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Structural data: full structural data are available from iucrdata.iucr.org

In the title compound, $C_{12}H_8N_4O_2$, the dihedral angle between the phenanthroline ring system and the nitro group is $23.75(14)^\circ$. The molecule features intramolecular $N-H\cdots O$ and $C-H\cdots O$ hydrogen bonds. In the crystal, $N-H\cdots(N,N)$, $C-H\cdots N$ and $C-H\cdots O$ hydrogen bonds link the molecules into [100] chains.



Structure description

When 1,10-phenanthroline coordinates to transition metals, it forms thermally and chemically stable complexes. The combination of electronic transitions of the metal and the conjugated π -electron system of 1,10-phenanthroline leads to complexes with interesting photophysical, photochemical and electrochemical properties. To expand this chemistry, the synthesis of 1,10-phenanthroline derivatives with substituents on positions 3 to 8 is necessary (Khimich *et al.*, 2006). The title compound is formed by the amination of 5-nitro-1,10-phenanthroline using ethanol and dioxane. The use of phendiamine (1,10-phenanthroline-5,6-diamine) as an N,N' -bidentate ligand was one of the main aims in the study. Phendiamine can be coordinated to two metal centres and can act as a bridging ligand. 5-Amino-6-nitro-1,10-phenanthroline is comparable to phendione (1,10-phenanthroline-5,6-dione) and 5-nitro-1,10-phenanthroline.

The title compound crystallizes in space group $Pbca$ with one molecule in the asymmetric unit (Fig. 1). The nitro group is twisted from the rest of the molecule by $23.75(14)^\circ$. The O atoms of the nitro group accept intramolecular hydrogen bonds from the adjacent NH and CH groups (Table 1).

In the extended structure, there are no π - π stacking interactions but infinite chains are observed propagating along the a -axis direction *via* $N3-H4A\cdots(N1,N2)$, $C3-H3\cdots N1$ and $C9-H7\cdots O1$ interactions (Table 1, Fig. 2). Adjacent molecules in the chain are rotated by approximately 90° with respect to each other (Fig. 3).

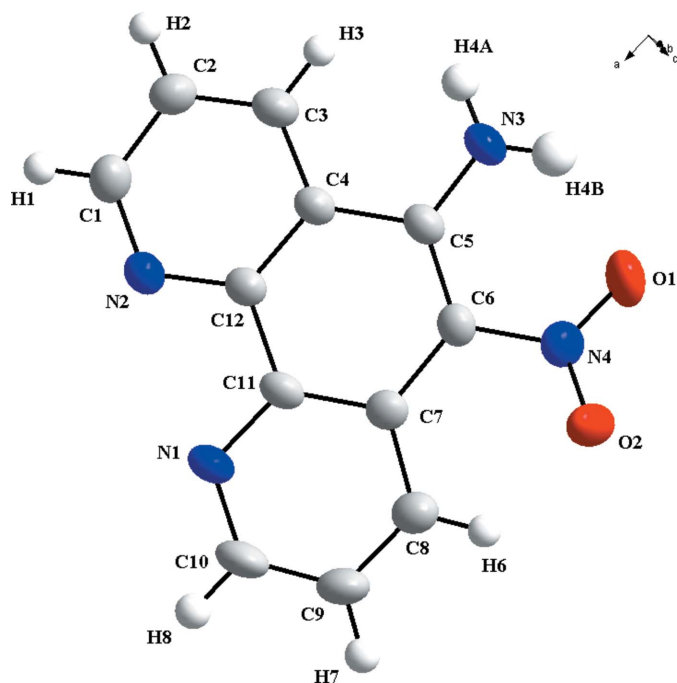


Figure 1
The molecular structure of the title compound showing 50% displacement ellipsoids.

A search of the Cambridge Structural Database (Version 5.32, update Feb 2011, Groom *et al.*, 2016) for 1,10-phenanthroline derivatives with nitrogen atoms on positions 5 and 6 gave 136 hits, with a variety of substituents on the nitrogen atoms. One of these structures, *N''',N'''-1,10-phenanthroline-5,6-diylbis (N,N,N',N'-tetramethylguanidine)* reported by Ortmeier *et al.*, (2017) (refcode ZEQREV) has similar bond distances and angles to those in the title compound.

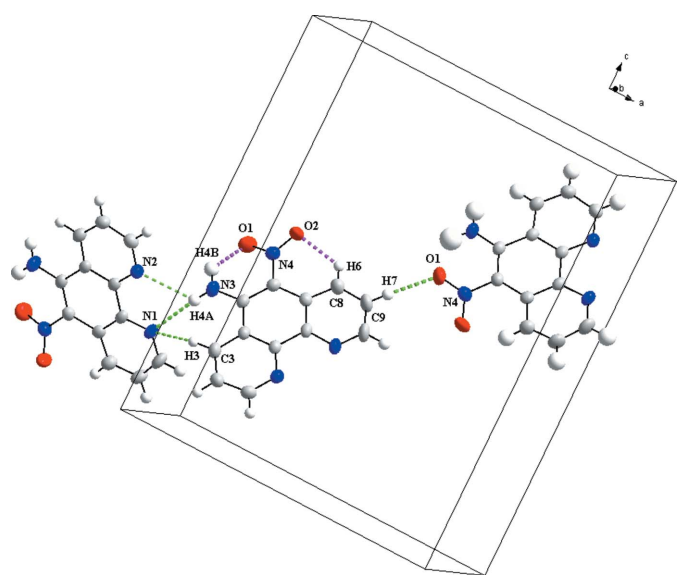


Figure 2
Illustration of the hydrogen-bonding interactions observed in 5-amino-6-nitro-1,10-phenanthroline. Intermolecular interactions are illustrated in green dashed lines while intramolecular interactions are illustrated by purple dashed lines.

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

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N3—H4A···N1 ⁱ	0.89 (3)	2.34 (3)	3.092 (4)	143 (3)
N3—H4A···N2 ⁱ	0.89 (3)	2.55 (3)	3.111 (4)	122 (2)
N3—H4B···O1	0.93 (4)	1.90 (4)	2.571 (4)	127 (3)
C3—H3···N1 ⁱ	0.95	2.61	3.438 (4)	145
C8—H6···O2	0.95	2.12	2.716 (4)	119
C9—H7···O1 ⁱⁱ	0.95	2.46	3.395 (4)	167

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

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₁₂ H ₈ N ₄ O ₂
<i>M_r</i>	240.22
Crystal system, space group	Orthorhombic, <i>Pbca</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	14.265 (8), 8.060 (4), 17.564 (9)
<i>V</i> (Å ³)	2019.4 (19)
<i>Z</i>	8
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.11
Crystal size (mm)	0.37 × 0.12 × 0.09
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2012)
<i>T_{min}</i> , <i>T_{max}</i>	0.984, 0.99
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	13477, 2426, 1204
<i>R_{int}</i>	0.093
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.058, 0.176, 1.03
No. of reflections	2426
No. of parameters	172
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.36, -0.39

Computer programs: *APEX2* and *SAINT* (Bruker, 2012), *SIR92* (Altomare *et al.*, 1994), *SHELXL2018/3* (Sheldrick, 2015), *DIAMOND* (Brandenburg, 2006) and *OLEX2* (Dolomanov *et al.*, 2009).

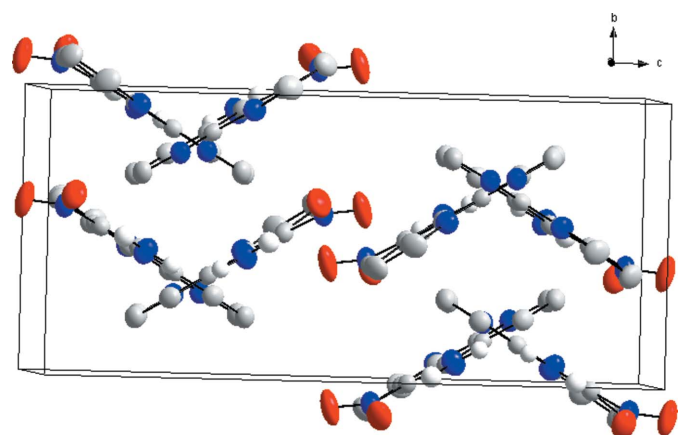


Figure 3
Representation of the packing of 5-amino-6-nitro-1,10-phenanthroline along the *a* axis.

Synthesis and crystallization

The synthesis of the title compound was achieved according to the literature method of Bolger *et al.* (1996). 5-Nitro-1,10-phenanthroline (3.49 g, 15.5 mmol) was dissolved in a mixture of 100 ml of ethanol/dioxane (3:2) and heated to 60°C until all the solids were dissolved. It was rapidly cooled to 4°C and formed a fine suspension. Powdered hydroxyl amine hydrochloride (6.84 g, 9.84 mmol) was added, followed by the dropwise addition of KOH (7.27 g, 129.5 mmol) in methanol (100 ml). The solution was stirred at 4°C for one hour and then heated to 60°C for another hour. The solution was poured onto ice and resulted in the formation of a yellow precipitate, which was washed with water and methanol after filtration. Yellow single crystals suitable for X-ray diffraction were obtained in chloroform at room temperature. Yield: 0.5441 g (14%). IR (ATR, cm^{-1}): 1626, 1523, 1486, 1433, 1383, 1302, 1260, 1172, 1095, 827, 796, 734, 670. ^1H NMR (300 MHz, $\text{DMSO-}d_6$): δ 9.2 (*dd*, $J = 1.35, 4.26$ Hz, 1H), 9.1 (*dd*, $J = 1.36, 8.44$ Hz, 1H), 8.8 (*dd*, $J = 1.47, 4.27$ Hz, 1H), 8.7 (*dd*, $J = 1.48, 8.58$ Hz, 1H), 8.6 (*s*, 2H), 7.9 (*dd*, $J = 4.27, 8.46$ Hz, 1H) and 7.7 (*dd*, $J = 4.15, 8.46$ Hz, 1H). ^{13}C NMR (600 MHz, $\text{DMSO-}d_6$): δ 154, 148, 147, 144, 140, 137, 134, 131, 125, 124, 123, 121. UV/Vis: ε ($\lambda_{\text{max}} = 419$ nm) = $19985 \text{ M}^{-1} \text{ cm}^{-1}$.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Funding information

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References

- Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
- Bolger, J., Gourdon, A., Ishow, E. & Launay, J. (1996). *Inorg. Chem.* **35**, 2937–2944.
- Brandenburg, K. (2006). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
- Bruker (2012). *APEX2, SAINT and SADABS*. Bruker AXS Inc, Madison, Wisconsin, USA.
- Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- Khimich, N. N., Obrezkov, N. P. & Koptelova, L. A. (2006). *Russ. J. Org. Chem.* **42**, 555–557.
- Ortmeyer, J., Vukadinovic, Y., Neuba, A., Egold, H., Flörke, U. & Henkel, G. (2017). *Eur. J. Org. Chem.* pp. 6085–6095.
- Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.

full crystallographic data

IUCrData (2019). 4, x191016 [https://doi.org/10.1107/S2414314619010162]

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Crystal data

$C_{12}H_8N_4O_2$	$F(000) = 992$
$M_r = 240.22$	$D_x = 1.58 \text{ Mg m}^{-3}$
Orthorhombic, <i>Pbca</i>	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Hall symbol: -P 2ac 2ab	Cell parameters from 1396 reflections
$a = 14.265 (8) \text{ \AA}$	$\theta = 3.7\text{--}23.4^\circ$
$b = 8.060 (4) \text{ \AA}$	$\mu = 0.11 \text{ mm}^{-1}$
$c = 17.564 (9) \text{ \AA}$	$T = 100 \text{ K}$
$V = 2019.4 (19) \text{ \AA}^3$	Cuboid, yellow
$Z = 8$	$0.37 \times 0.12 \times 0.09 \text{ mm}$

Data collection

Bruker APEXII CCD diffractometer	2426 independent reflections
φ and ω scans	1204 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 2012)	$R_{\text{int}} = 0.093$
$T_{\text{min}} = 0.984$, $T_{\text{max}} = 0.99$	$\theta_{\text{max}} = 28.0^\circ$, $\theta_{\text{min}} = 4.0^\circ$
13477 measured reflections	$h = -18 \rightarrow 18$
	$k = -7 \rightarrow 10$
	$l = -22 \rightarrow 23$

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0669P)^2 + 0.4998P]$
$R[F^2 > 2\sigma(F^2)] = 0.058$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.176$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.03$	$\Delta\rho_{\text{max}} = 0.36 \text{ e \AA}^{-3}$
2426 reflections	$\Delta\rho_{\text{min}} = -0.39 \text{ e \AA}^{-3}$
172 parameters	Extinction correction: SHELXL-2018/3 (Sheldrick 2015)
0 restraints	Extinction coefficient: 0.0047 (14)
Hydrogen site location: mixed	

Special details

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

Refinement. Aromatic H atoms were positioned geometrically with a C—H distance of 0.95 Å and constrained to ride on their parent atoms with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.40826 (14)	0.4435 (3)	0.33237 (13)	0.0383 (6)
C12	0.26583 (16)	0.3587 (3)	0.27163 (14)	0.0286 (6)
C6	0.15781 (17)	0.5134 (3)	0.38771 (14)	0.0309 (6)
C7	0.25963 (17)	0.5190 (3)	0.39240 (14)	0.0300 (6)
C11	0.31313 (17)	0.4415 (3)	0.33443 (15)	0.0305 (6)
C4	0.16718 (16)	0.3585 (3)	0.26734 (14)	0.0284 (6)
N2	0.32090 (15)	0.2864 (3)	0.21825 (13)	0.0356 (6)
N3	0.01725 (16)	0.4325 (3)	0.31972 (18)	0.0445 (7)
C5	0.11029 (17)	0.4399 (3)	0.32623 (15)	0.0311 (6)
O1	0.02003 (14)	0.6244 (3)	0.43663 (12)	0.0562 (7)
N4	0.10335 (16)	0.5857 (3)	0.44757 (14)	0.0421 (6)
C9	0.40771 (19)	0.6088 (4)	0.44486 (17)	0.0458 (8)
H7	0.442575	0.66799	0.482097	0.055*
C8	0.31192 (19)	0.6052 (4)	0.44809 (16)	0.0404 (7)
H6	0.280266	0.661066	0.488166	0.048*
C1	0.27861 (19)	0.2137 (4)	0.15956 (15)	0.0393 (7)
H1	0.316626	0.164069	0.121416	0.047*
C3	0.12573 (19)	0.2785 (3)	0.20499 (15)	0.0364 (7)
H3	0.059429	0.274357	0.200254	0.044*
C2	0.18162 (19)	0.2063 (4)	0.15100 (16)	0.0383 (7)
H2	0.154655	0.151906	0.108296	0.046*
C10	0.4533 (2)	0.5254 (4)	0.38678 (18)	0.0471 (8)
H8	0.51987	0.526878	0.385799	0.057*
O2	0.13845 (16)	0.6016 (4)	0.51179 (13)	0.0786 (9)
H4A	-0.009 (2)	0.385 (4)	0.2794 (19)	0.062 (11)*
H4B	-0.020 (3)	0.483 (5)	0.356 (2)	0.089 (13)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0250 (12)	0.0449 (14)	0.0449 (15)	-0.0012 (10)	-0.0059 (10)	-0.0005 (11)
C12	0.0267 (13)	0.0276 (13)	0.0316 (15)	0.0004 (10)	-0.0020 (11)	0.0042 (11)
C6	0.0295 (14)	0.0318 (15)	0.0314 (16)	0.0029 (11)	0.0023 (11)	0.0023 (11)
C7	0.0311 (13)	0.0289 (13)	0.0299 (15)	0.0011 (10)	-0.0031 (11)	0.0039 (11)
C11	0.0241 (13)	0.0319 (14)	0.0357 (17)	-0.0018 (10)	-0.0045 (11)	0.0059 (12)
C4	0.0250 (13)	0.0297 (13)	0.0305 (15)	-0.0010 (11)	-0.0015 (11)	0.0049 (11)
N2	0.0286 (12)	0.0423 (14)	0.0359 (14)	0.0018 (10)	0.0011 (10)	-0.0001 (11)
N3	0.0244 (12)	0.0594 (17)	0.0496 (18)	0.0033 (11)	-0.0012 (12)	-0.0095 (14)
C5	0.0249 (13)	0.0335 (14)	0.0349 (16)	-0.0005 (10)	0.0005 (11)	0.0040 (12)
O1	0.0419 (12)	0.0726 (16)	0.0540 (15)	0.0196 (11)	0.0072 (10)	-0.0093 (11)
N4	0.0380 (14)	0.0534 (16)	0.0349 (15)	-0.0023 (12)	0.0047 (12)	-0.0033 (11)
C9	0.0395 (17)	0.0499 (19)	0.048 (2)	-0.0064 (14)	-0.0132 (14)	-0.0088 (15)
C8	0.0392 (16)	0.0405 (16)	0.0415 (18)	-0.0008 (13)	-0.0048 (13)	-0.0052 (13)
C1	0.0400 (16)	0.0447 (17)	0.0331 (17)	0.0039 (13)	0.0041 (13)	0.0003 (13)
C3	0.0293 (14)	0.0395 (16)	0.0405 (17)	-0.0023 (12)	-0.0049 (12)	0.0011 (13)

C2	0.0392 (15)	0.0423 (17)	0.0333 (17)	-0.0042 (13)	-0.0035 (12)	-0.0008 (13)
C10	0.0269 (14)	0.0532 (19)	0.061 (2)	-0.0059 (13)	-0.0116 (14)	-0.0047 (16)
O2	0.0519 (15)	0.142 (3)	0.0419 (15)	-0.0144 (15)	0.0048 (12)	-0.0285 (14)

Geometric parameters (Å, °)

N1—C10	1.327 (3)	N3—H4A	0.89 (3)
N1—C11	1.358 (3)	N3—H4B	0.93 (4)
C12—N2	1.355 (3)	O1—N4	1.244 (3)
C12—C4	1.409 (3)	N4—O2	1.241 (3)
C12—C11	1.455 (3)	C9—C8	1.368 (4)
C6—C5	1.406 (4)	C9—C10	1.384 (4)
C6—N4	1.431 (3)	C9—H7	0.95
C6—C7	1.456 (3)	C8—H6	0.95
C7—C8	1.413 (4)	C1—C2	1.393 (4)
C7—C11	1.418 (4)	C1—H1	0.95
C4—C3	1.402 (4)	C3—C2	1.369 (4)
C4—C5	1.469 (4)	C3—H3	0.95
N2—C1	1.331 (3)	C2—H2	0.95
N3—C5	1.333 (3)	C10—H8	0.95
C10—N1—C11	118.1 (2)	C6—C5—C4	117.5 (2)
N2—C12—C4	122.8 (2)	O2—N4—O1	120.0 (2)
N2—C12—C11	116.9 (2)	O2—N4—C6	119.4 (2)
C4—C12—C11	120.3 (2)	O1—N4—C6	120.5 (2)
C5—C6—N4	118.3 (2)	C8—C9—C10	119.3 (3)
C5—C6—C7	122.5 (2)	C8—C9—H7	120.4
N4—C6—C7	119.2 (2)	C10—C9—H7	120.4
C8—C7—C11	115.5 (2)	C9—C8—C7	120.6 (3)
C8—C7—C6	125.6 (2)	C9—C8—H6	119.7
C11—C7—C6	118.9 (2)	C7—C8—H6	119.7
N1—C11—C7	123.5 (2)	N2—C1—C2	123.6 (3)
N1—C11—C12	116.7 (2)	N2—C1—H1	118.2
C7—C11—C12	119.8 (2)	C2—C1—H1	118.2
C3—C4—C12	117.6 (2)	C2—C3—C4	119.4 (2)
C3—C4—C5	121.5 (2)	C2—C3—H3	120.3
C12—C4—C5	120.9 (2)	C4—C3—H3	120.3
C1—N2—C12	117.6 (2)	C3—C2—C1	119.1 (3)
C5—N3—H4A	121 (2)	C3—C2—H2	120.5
C5—N3—H4B	119 (2)	C1—C2—H2	120.5
H4A—N3—H4B	120 (3)	N1—C10—C9	123.0 (3)
N3—C5—C6	124.4 (3)	N1—C10—H8	118.5
N3—C5—C4	118.0 (3)	C9—C10—H8	118.5
C5—C6—C7—C8	173.1 (3)	C7—C6—C5—N3	-179.8 (2)
N4—C6—C7—C8	-6.7 (4)	N4—C6—C5—C4	-176.8 (2)
C5—C6—C7—C11	-2.7 (4)	C7—C6—C5—C4	3.4 (4)
N4—C6—C7—C11	177.5 (2)	C3—C4—C5—N3	1.4 (4)

C10—N1—C11—C7	-1.4 (4)	C12—C4—C5—N3	-178.7 (2)
C10—N1—C11—C12	176.6 (2)	C3—C4—C5—C6	178.4 (2)
C8—C7—C11—N1	1.9 (4)	C12—C4—C5—C6	-1.7 (4)
C6—C7—C11—N1	178.2 (2)	C5—C6—N4—O2	156.5 (3)
C8—C7—C11—C12	-176.0 (2)	C7—C6—N4—O2	-23.7 (4)
C6—C7—C11—C12	0.2 (3)	C5—C6—N4—O1	-19.7 (4)
N2—C12—C11—N1	2.2 (3)	C7—C6—N4—O1	160.1 (3)
C4—C12—C11—N1	-176.7 (2)	C10—C9—C8—C7	-0.7 (4)
N2—C12—C11—C7	-179.7 (2)	C11—C7—C8—C9	-0.8 (4)
C4—C12—C11—C7	1.4 (4)	C6—C7—C8—C9	-176.7 (3)
N2—C12—C4—C3	0.4 (4)	C12—N2—C1—C2	-1.0 (4)
C11—C12—C4—C3	179.2 (2)	C12—C4—C3—C2	-0.7 (4)
N2—C12—C4—C5	-179.4 (2)	C5—C4—C3—C2	179.1 (2)
C11—C12—C4—C5	-0.6 (4)	C4—C3—C2—C1	0.2 (4)
C4—C12—N2—C1	0.4 (4)	N2—C1—C2—C3	0.6 (4)
C11—C12—N2—C1	-178.4 (2)	C11—N1—C10—C9	-0.3 (4)
N4—C6—C5—N3	-0.1 (4)	C8—C9—C10—N1	1.4 (5)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N3—H4 <i>A</i> ...N1 ⁱ	0.89 (3)	2.34 (3)	3.092 (4)	143 (3)
N3—H4 <i>A</i> ...N2 ⁱ	0.89 (3)	2.55 (3)	3.111 (4)	122 (2)
N3—H4 <i>B</i> ...O1	0.93 (4)	1.90 (4)	2.571 (4)	127 (3)
C3—H3...N1 ⁱ	0.95	2.61	3.438 (4)	145
C8—H6...O2	0.95	2.12	2.716 (4)	119
C9—H7...O1 ⁱⁱ	0.95	2.46	3.395 (4)	167

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