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

# 5-(4-Methylpiperazin-1-yl)-2-nitroaniline

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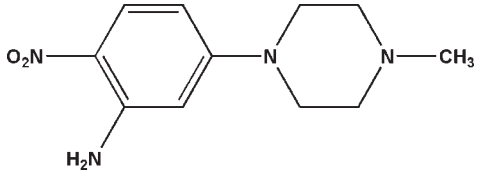
Received 7 April 2010; accepted 30 April 2010

Key indicators: single-crystal X-ray study; $T$ = 293 K; mean $\sigma$(C–C) = 0.004 Å; $R$ factor = 0.064; $wR$ factor = 0.192; data-to-parameter ratio = 13.5.

In the title compound, $C_{11}H_{16}N_4O_2$, the dihedral angle between the benzene ring and the plane of the four carbon atoms in the piperazine ring is 12.17 (3)°; the latter ring adopts a chair conformation. An intramolecular N—H···O hydrogen bond generates an $S$(6) ring. In the crystal, the molecules are linked by N—H···N hydrogen bonds, forming chains.

## Related literature

For bond-length data, see: Allen *et al.* (1987). For the synthetic procedure and use of the title compound as an intermediate in the synthesis of tyrosine kinase inhibitors, see: Renhowe *et al.* (2009).




## Experimental

### Crystal data

$C_{11}H_{16}N_4O_2$
$M_r$ = 236.28
Monoclinic, $P2_1/c$
$a$ = 11.027 (2) Å
$b$ = 6.121 (1) Å
$c$ = 17.524 (4) Å
$\beta$ = 103.79 (3)°
$V$ = 1148.7 (4) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.10 mm$^{-1}$
$T$ = 293 K
0.30 × 0.20 × 0.05 mm

### Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: $\psi$ scan (North *et al.*, 1968)
$T_{min}$ = 0.971, $T_{max}$ = 0.995
2205 measured reflections
2090 independent reflections
1358 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.042
3 standard reflections every 200 reflections
intensity decay: 1%

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.064
$wR(F^2)$ = 0.192
$S$ = 1.01
2090 reflections
155 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.25 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.18 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N3—H3$C$···N1$^{i}$ | 0.86 | 2.39 | 3.156 (4) | 148 |
| N3—H3$D$···O1 | 0.86 | 2.06 | 2.669 (4) | 127 |

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

Data collection: *CAD-4 Software* (Enraf–Nonius, 1985); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); 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*.

The authors thank the Center of Test and Analysis, Nanjing University, for support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2192).

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# supporting information

*Acta Cryst.* (2010). E**66**, o1268 [https://doi.org/10.1107/S1600536810015953]

## 5-(4-Methylpiperazin-1-yl)-2-nitroaniline

**Chang-jun Luan, Cheng Guo, Wei Wang, Jian-qiang Wang and Ren-jun Du**

### S1. Comment

The title compound, (I), has been reported as an intermediate for the synthesis of novel tyrosine kinase inhibitors (Renhowe, P. A. *et al.*, 2009). We herein report its crystal structure.

In the molecular structure of (I), (Fig.1), bond lengths (Allen *et al.*, 1987) and angles are within normal ranges. N2, N3 and N4 atoms are almost coplanar with the benzene ring to which they are bonded [deviations of 0.078 (1), 0.052 (1) and 0.078 (1) Å]. The plane of C2—C3—C4—C5 is nearly parallel with the benzene ring plane (the torsion angle is 12.17 (3) °). By contrast, due to the piperazine moiety adopting a chair conformation N1—C2—C5 and N2—C3—C4 form two separate planes with torsion angle of 45.87 (2) ° and 25.92 (3) °, respectively, with respect to the benzene ring. The crystal structure of the title compound exhibits N—H···O, C—H···O, and N—H···N intra- and intermolecular hydrogen bonds to form a three dimensional network.

As can be seen from the packing diagram, (Fig. 2), the molecules are stacked along the *b* axis.

### S2. Experimental

The title compound, (I) was prepared by a literature method (Renhowe, P. A. *et al.*, 2009). Crystals suitable for X-ray analysis were obtained by dissolving (I) (0.5 g) in methanol (20 ml) and evaporating the solvent slowly at room temperature for about 7 d.

### S3. Refinement

H atoms were positioned geometrically, with N—H = 0.86 Å, C—H = 0.93 Å for aromatic H, 0.97 Å for methylene and 0.96 Å for methyl groups. Refinement was performed using a riding model with $U_{iso}$(H) = $xU_{eq}$(C), where x = 1.5 for methyl and x = 1.2 for all other H atoms.

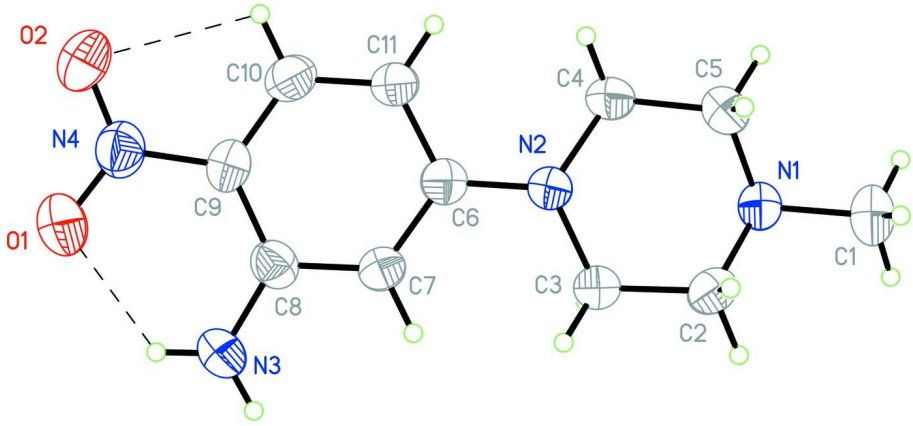


**Figure 1**

The molecular structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

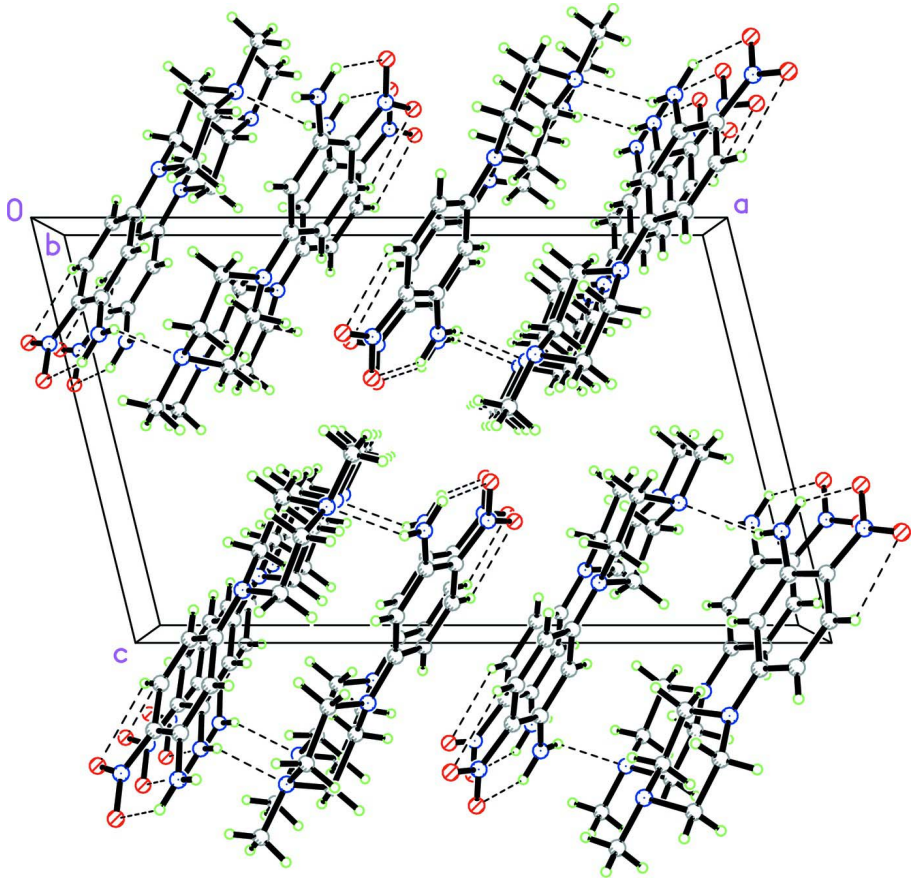


**Figure 2**

A packing diagram of (I). Hydrogen bonds are shown as dashed lines.

## 5-(4-Methylpiperazin-1-yl)-2-nitroaniline

*Crystal data*

$C_{11}H_{16}N_4O_2$
$M_r = 236.28$
Monoclinic, $P2_1/c$
$a = 11.027$ (2) Å
$b = 6.121$ (1) Å
$c = 17.524$ (4) Å
$\beta = 103.79$ (3)°
$V = 1148.7$ (4) Å$^3$
$Z = 4$
$F(000) = 504$
$D_x = 1.366$ Mg m$^{-3}$
Melting point: 428 K
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 9$–13°
$\mu = 0.10$ mm$^{-1}$
$T = 293$ K
Block, yellow
0.30 × 0.20 × 0.05 mm

*Data collection*

Enraf–Nonius CAD-4 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\omega/2\theta$ scans
Absorption correction: $\psi$ scan (North *et al.*, 1968)
$T_{min} = 0.971$, $T_{max} = 0.995$
2205 measured reflections
2090 independent reflections
1358 reflections with $I > 2\sigma(I)$
$R_{int} = 0.042$
$\theta_{max} = 25.3°$, $\theta_{min} = 1.9°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 7$
$l = -21 \rightarrow 20$
3 standard reflections every 200 reflections
intensity decay: 1%

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.064$
$wR(F^2) = 0.192$
$S = 1.01$
2090 reflections
155 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
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2 + 0.3P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.25$ e Å$^{-3}$
$\Delta\rho_{min} = -0.18$ e Å$^{-3}$
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.038 (6)

*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**. 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.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)*

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| N1 | 0.6711 (2) | 0.0465 (4) | 0.16875 (13) | 0.0438 (6) |
| O1 | 1.3775 (2) | −0.0656 (4) | 0.56703 (14) | 0.0774 (8) |

| | | | | |
|---|---|---|---|---|
| C1 | 0.5525 (3) | 0.1090 (6) | 0.11543 (19) | 0.0603 (9) |
| H1A | 0.5683 | 0.2064 | 0.0760 | 0.090* |
| H1B | 0.5007 | 0.1809 | 0.1447 | 0.090* |
| H1C | 0.5107 | −0.0193 | 0.0907 | 0.090* |
| N2 | 0.8586 (2) | 0.0019 (4) | 0.31264 (13) | 0.0397 (6) |
| O2 | 1.2787 (2) | −0.3532 (4) | 0.58981 (13) | 0.0662 (7) |
| C2 | 0.7330 (3) | 0.2397 (5) | 0.20898 (17) | 0.0484 (8) |
| H2A | 0.6826 | 0.3007 | 0.2422 | 0.058* |
| H2B | 0.7409 | 0.3493 | 0.1705 | 0.058* |
| C3 | 0.8606 (3) | 0.1827 (5) | 0.25841 (16) | 0.0466 (8) |
| H3A | 0.9143 | 0.1440 | 0.2240 | 0.056* |
| H3B | 0.8960 | 0.3103 | 0.2883 | 0.056* |
| N3 | 1.2683 (2) | 0.2156 (4) | 0.45524 (16) | 0.0613 (8) |
| H3C | 1.2595 | 0.3315 | 0.4267 | 0.074* |
| H3D | 1.3359 | 0.1954 | 0.4909 | 0.074* |
| C4 | 0.7741 (3) | −0.1801 (5) | 0.28094 (18) | 0.0478 (8) |
| H4A | 0.7577 | −0.2645 | 0.3242 | 0.057* |
| H4B | 0.8149 | −0.2755 | 0.2506 | 0.057* |
| N4 | 1.2841 (2) | −0.1869 (5) | 0.55073 (15) | 0.0527 (7) |
| C5 | 0.6513 (3) | −0.1026 (5) | 0.22932 (17) | 0.0506 (8) |
| H5A | 0.6035 | −0.2276 | 0.2048 | 0.061* |
| H5B | 0.6033 | −0.0292 | 0.2615 | 0.061* |
| C6 | 0.9667 (2) | −0.0433 (4) | 0.36840 (15) | 0.0367 (7) |
| C7 | 1.0669 (2) | 0.1023 (5) | 0.38534 (15) | 0.0398 (7) |
| H7A | 1.0610 | 0.2307 | 0.3563 | 0.048* |
| C8 | 1.1758 (2) | 0.0647 (5) | 0.44396 (16) | 0.0415 (7) |
| C9 | 1.1820 (2) | −0.1317 (5) | 0.48727 (15) | 0.0422 (7) |
| C10 | 1.0839 (3) | −0.2817 (5) | 0.46870 (17) | 0.0475 (8) |
| H10A | 1.0901 | −0.4120 | 0.4966 | 0.057* |
| C11 | 0.9799 (3) | −0.2428 (5) | 0.41112 (17) | 0.0444 (7) |
| H11A | 0.9169 | −0.3471 | 0.3995 | 0.053* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| N1 | 0.0385 (13) | 0.0422 (14) | 0.0464 (13) | −0.0004 (11) | 0.0017 (10) | 0.0030 (11) |
| O1 | 0.0545 (14) | 0.0794 (18) | 0.0820 (17) | −0.0125 (13) | −0.0158 (12) | 0.0122 (14) |
| C1 | 0.0411 (17) | 0.067 (2) | 0.065 (2) | 0.0050 (16) | −0.0025 (15) | 0.0064 (18) |
| N2 | 0.0357 (12) | 0.0346 (12) | 0.0458 (13) | −0.0029 (10) | 0.0040 (10) | 0.0048 (11) |
| O2 | 0.0610 (15) | 0.0616 (15) | 0.0674 (15) | 0.0125 (12) | −0.0015 (12) | 0.0190 (12) |
| C2 | 0.0527 (18) | 0.0375 (16) | 0.0502 (17) | 0.0004 (14) | 0.0030 (14) | 0.0085 (14) |
| C3 | 0.0449 (17) | 0.0396 (16) | 0.0503 (17) | −0.0067 (14) | 0.0016 (14) | 0.0084 (14) |
| N3 | 0.0486 (15) | 0.0509 (16) | 0.0724 (17) | −0.0149 (13) | −0.0094 (13) | 0.0073 (14) |
| C4 | 0.0440 (16) | 0.0354 (15) | 0.0605 (18) | −0.0053 (13) | 0.0057 (14) | 0.0075 (14) |
| N4 | 0.0484 (15) | 0.0537 (17) | 0.0516 (15) | 0.0041 (14) | 0.0033 (12) | 0.0020 (13) |
| C5 | 0.0383 (16) | 0.0456 (17) | 0.0636 (19) | −0.0060 (14) | 0.0036 (14) | 0.0058 (16) |
| C6 | 0.0354 (14) | 0.0369 (15) | 0.0393 (14) | 0.0018 (12) | 0.0118 (12) | −0.0007 (12) |
| C7 | 0.0414 (15) | 0.0320 (15) | 0.0443 (15) | 0.0013 (12) | 0.0071 (12) | 0.0025 (12) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C8 | 0.0391 (15) | 0.0386 (16) | 0.0455 (16) | −0.0015 (13) | 0.0075 (13) | −0.0057 (13) |
| C9 | 0.0398 (15) | 0.0469 (17) | 0.0377 (15) | 0.0063 (13) | 0.0051 (12) | 0.0029 (13) |
| C10 | 0.0470 (17) | 0.0444 (18) | 0.0510 (17) | 0.0014 (14) | 0.0116 (14) | 0.0123 (14) |
| C11 | 0.0391 (15) | 0.0395 (16) | 0.0527 (17) | −0.0031 (13) | 0.0071 (13) | 0.0101 (14) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| N1—C5 | 1.455 (3) | N3—H3C | 0.8600 |
| N1—C2 | 1.460 (4) | N3—H3D | 0.8600 |
| N1—C1 | 1.466 (3) | C4—C5 | 1.514 (4) |
| O1—N4 | 1.246 (3) | C4—H4A | 0.9700 |
| C1—H1A | 0.9600 | C4—H4B | 0.9700 |
| C1—H1B | 0.9600 | N4—C9 | 1.422 (4) |
| C1—H1C | 0.9600 | C5—H5A | 0.9700 |
| N2—C6 | 1.377 (3) | C5—H5B | 0.9700 |
| N2—C3 | 1.462 (3) | C6—C7 | 1.395 (4) |
| N2—C4 | 1.473 (3) | C6—C11 | 1.421 (4) |
| O2—N4 | 1.236 (3) | C7—C8 | 1.401 (4) |
| C2—C3 | 1.507 (4) | C7—H7A | 0.9300 |
| C2—H2A | 0.9700 | C8—C9 | 1.415 (4) |
| C2—H2B | 0.9700 | C9—C10 | 1.396 (4) |
| C3—H3A | 0.9700 | C10—C11 | 1.356 (4) |
| C3—H3B | 0.9700 | C10—H10A | 0.9300 |
| N3—C8 | 1.355 (3) | C11—H11A | 0.9300 |
| | | | |
| C5—N1—C2 | 106.8 (2) | N2—C4—H4B | 109.1 |
| C5—N1—C1 | 111.2 (2) | C5—C4—H4B | 109.1 |
| C2—N1—C1 | 109.8 (2) | H4A—C4—H4B | 107.8 |
| N1—C1—H1A | 109.5 | O2—N4—O1 | 120.6 (3) |
| N1—C1—H1B | 109.5 | O2—N4—C9 | 119.7 (3) |
| H1A—C1—H1B | 109.5 | O1—N4—C9 | 119.7 (3) |
| N1—C1—H1C | 109.5 | N1—C5—C4 | 111.3 (2) |
| H1A—C1—H1C | 109.5 | N1—C5—H5A | 109.4 |
| H1B—C1—H1C | 109.5 | C4—C5—H5A | 109.4 |
| C6—N2—C3 | 118.0 (2) | N1—C5—H5B | 109.4 |
| C6—N2—C4 | 118.6 (2) | C4—C5—H5B | 109.4 |
| C3—N2—C4 | 115.7 (2) | H5A—C5—H5B | 108.0 |
| N1—C2—C3 | 110.8 (2) | N2—C6—C7 | 122.0 (2) |
| N1—C2—H2A | 109.5 | N2—C6—C11 | 120.6 (2) |
| C3—C2—H2A | 109.5 | C7—C6—C11 | 117.4 (2) |
| N1—C2—H2B | 109.5 | C6—C7—C8 | 123.2 (3) |
| C3—C2—H2B | 109.5 | C6—C7—H7A | 118.4 |
| H2A—C2—H2B | 108.1 | C8—C7—H7A | 118.4 |
| N2—C3—C2 | 113.1 (2) | N3—C8—C7 | 118.6 (3) |
| N2—C3—H3A | 109.0 | N3—C8—C9 | 124.2 (2) |
| C2—C3—H3A | 109.0 | C7—C8—C9 | 117.2 (2) |
| N2—C3—H3B | 109.0 | C10—C9—C8 | 119.9 (2) |
| C2—C3—H3B | 109.0 | C10—C9—N4 | 116.8 (3) |

| | | | |
|---|---|---|---|
| H3A—C3—H3B | 107.8 | C8—C9—N4 | 123.3 (3) |
| C8—N3—H3C | 120.0 | C11—C10—C9 | 121.9 (3) |
| C8—N3—H3D | 120.0 | C11—C10—H10A | 119.0 |
| H3C—N3—H3D | 120.0 | C9—C10—H10A | 119.0 |
| N2—C4—C5 | 112.5 (2) | C10—C11—C6 | 120.3 (3) |
| N2—C4—H4A | 109.1 | C10—C11—H11A | 119.8 |
| C5—C4—H4A | 109.1 | C6—C11—H11A | 119.8 |

| | | | |
|---|---|---|---|
| C5—N1—C2—C3 | 64.5 (3) | C6—C7—C8—N3 | 179.3 (3) |
| C1—N1—C2—C3 | −174.7 (2) | C6—C7—C8—C9 | −0.1 (4) |
| C6—N2—C3—C2 | −170.8 (2) | N3—C8—C9—C10 | −177.0 (3) |
| C4—N2—C3—C2 | 40.4 (3) | C7—C8—C9—C10 | 2.4 (4) |
| N1—C2—C3—N2 | −53.1 (3) | N3—C8—C9—N4 | 3.6 (4) |
| C6—N2—C4—C5 | 171.8 (2) | C7—C8—C9—N4 | −177.1 (2) |
| C3—N2—C4—C5 | −39.5 (3) | O2—N4—C9—C10 | −5.1 (4) |
| C2—N1—C5—C4 | −64.2 (3) | O1—N4—C9—C10 | 175.8 (3) |
| C1—N1—C5—C4 | 175.9 (3) | O2—N4—C9—C8 | 174.4 (3) |
| N2—C4—C5—N1 | 52.0 (3) | O1—N4—C9—C8 | −4.8 (4) |
| C3—N2—C6—C7 | 13.8 (4) | C8—C9—C10—C11 | −1.8 (4) |
| C4—N2—C6—C7 | 161.8 (2) | N4—C9—C10—C11 | 177.7 (3) |
| C3—N2—C6—C11 | −166.2 (2) | C9—C10—C11—C6 | −1.2 (5) |
| C4—N2—C6—C11 | −18.2 (4) | N2—C6—C11—C10 | −176.7 (3) |
| N2—C6—C7—C8 | 177.3 (2) | C7—C6—C11—C10 | 3.3 (4) |
| C11—C6—C7—C8 | −2.7 (4) | | |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N3—H3*C*···N1$^{i}$ | 0.86 | 2.39 | 3.156 (4) | 148 |
| N3—H3*D*···O1 | 0.86 | 2.06 | 2.669 (4) | 127 |
| C10—H10*A*···O2 | 0.93 | 2.35 | 2.671 (4) | 100 |

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