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1-(3-Bromo-6-nitro-1*H*-indazol-1-yl)ethan-1-one

Mohamed Mokhtar Mohamed Abdelahi,[a]* Youness El Bakri,[a] Mohamed Said Minnih,[b] Mohammed Benchidmi,[a] El Mokhtar Essassi[a] and Joel T. Mague[c]

[a]Laboratoire de Chimie Organique Hétérocyclique, URAC 21, Pôle de Compétence Pharmacochimie, Av Ibn Battouta, BP 1014, Faculté des Sciences, Mohammed V University, Rabat, Morocco, [b]Faculté des Sciences et Techniques, Université de Sciences, de Technologie, et de Medecine Nouakchott, Mauritania, and [c]Department of Chemistry, Tulane University, New Orleans, LA 70118, USA. *Correspondence e-mail: mmohamedabdelahi@gmail.com

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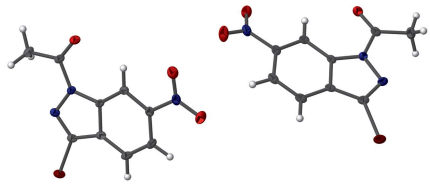
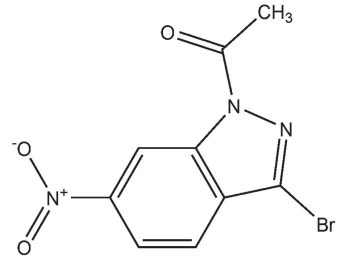
The asymmetric unit of the title compound, $C_9H_6BrN_3O_3$, consists of two independent molecules differing in the rotational orientations of the nitro and acetyl substituents. In the crystal, head-to-head π-stacking between pairs of adjacent molecules forms dimers which are associated into stacks by C—Br$\cdots\pi$(ring) interactions. C—H$\cdots$O hydrogen bonds tie the stacks together.

3D view



Chemical scheme



Structure description

Among heterocyclic frameworks, indazole derivatives have been widely used in medicinal chemistry and drug discovery including anti-inflammatory, anti-tumor, or HIV protease inhibition (Boulouard *et al.*, 2007), as well as exhibiting estrogen receptor binding (Steffan *et al.*, 2004), antifungal and antibacterial activities (Tandon *et al.*, 2005). Following this line of research, we now report a new acetylation of 6-nitro-1*H*-indazole using acetic anhydride in the presence of a catalytic amount of acetic acid.

The asymmetric unit (Fig. 1) consists of two independent molecules which differ in the rotational orientations of the nitro and acetyl groups. Thus the C6—C5—N3—O2 and C15—C14—N6—O5 torsion angles are, respectively, 7.1 (2) and 18.8 (2)° while the N2—N1—C8—C9 and N5—N4—C17—C18 torsion angles are, respectively, −0.8 (2) and −1.6 (2)°.

In the crystal, head-to-head π-stacking between pairs of adjacent molecules [centroid–centroid distance for the five-membered rings = 3.6509 (9) Å and for the six-membered rings = 3.7419 (9) Å, with dihedral angles, respectively, of 1.00 (8) and 1.57 (7)°] forms dimers which are associated into stacks by C1—Br1$\cdots\pi$(ring) interactions [ring = C10–C16/N4/N5 at $\frac{3}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$ with Br1$\cdots$centroid = 3.660 (7) Å] (Figs. 2 and 3). The mean planes of the molecules in the stacks are inclined at ±30.19 (1)° to (010). Tying the

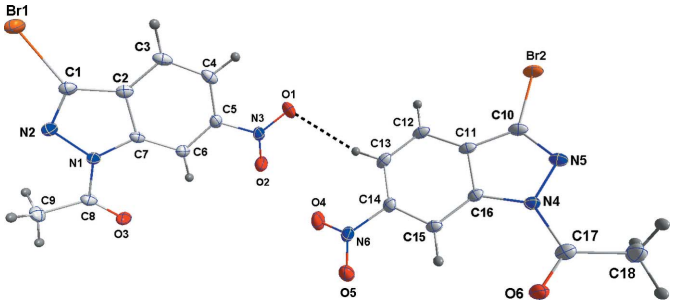


Figure 1
The asymmetric unit with the atom-labelling scheme and 50% probability ellipsoids. The intermolecular C—H···O hydrogen bond is shown as a dashed line.

stacks together are C9—H9*B*···O1 and C13—H13···O1 hydrogen bonds (Table 1 and Figs. 2 and 3). Between the stacks are Br1···O5($x+\frac{1}{2}$, $-y+\frac{3}{2}$, $z-\frac{1}{2}$) and Br2···O2($x+\frac{1}{2}$, $-y+\frac{1}{2}$, $z-\frac{1}{2}$) contacts of 2.966 (1) and 3.039 (1) Å, respectively, which are significantly less than the sum of the van der Waals radii (3.37 Å) and so may be additional attractive interactions binding the stacks together.

Synthesis and crystallization

A mixture of 3-bromo-6-nitro-1*H*-indazole (0.6 g, 3.68 mmol), acetic acid (2 ml) and acetic anhydride (10 ml) were heated under reflux for 24 h. After completion of the reaction (monitored by TLC), the solvent was removed under vacuum. The residue obtained was recrystallized from ethanol solution to afford the title compound as colorless crystals (yield 62%; m.p. 429–431 K).

Refinement

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

Acknowledgements

JTM thanks Tulane University for support of the Tulane Crystallography Laboratory.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C9—H9*B*···O1^{i}	0.98	2.47	3.301 (2)	142
C13—H13···O1	0.95	2.49	3.380 (2)	157

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_9H_6BrN_3O_3$
M_r	284.08
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	100
a, *b*, *c* (Å)	13.9863 (5), 7.8783 (3), 18.5549 (7)
β (°)	100.786 (1)
V (Å^3)	2008.41 (13)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	4.09
Crystal size (mm)	0.28 × 0.24 × 0.13
Data collection	
Diffractometer	Bruker SMART APEX CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2016)
T_{min}, T_{max}	0.52, 0.62
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	37783, 5389, 4592
R_{int}	0.032
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.685
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.023, 0.062, 1.09
No. of reflections	5389
No. of parameters	291
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.68, −0.25

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *DIAMOND* (Brandenburg & Putz, 2012) and *SHELXTL* (Sheldrick, 2008).

References

Boulouard, M., Schumann-Bard, P., Butt-Gueulle, S., Lohou, E., Stiebing, S., Collot, V. & Rault, S. (2007). *Bioorg. Med. Chem. Lett.* **17**, 3177–3180.

Brandenburg, K. & Putz, H. (2012). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.

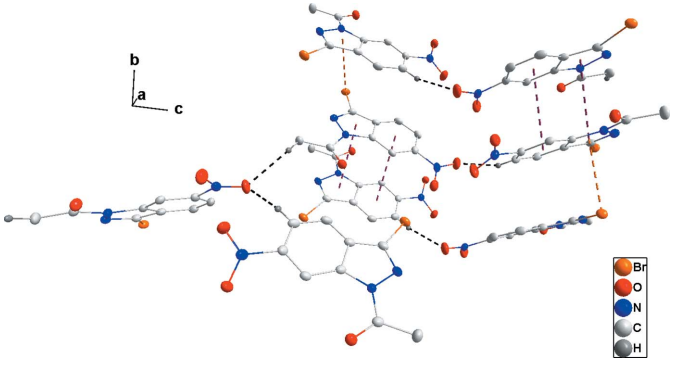


Figure 2
Detail of the intermolecular interactions. C—H···O hydrogen bonds are depicted by black dashed lines, π-stacking interactions by purple dashed lines and C—Br···π(ring) interactions by orange dashed lines.

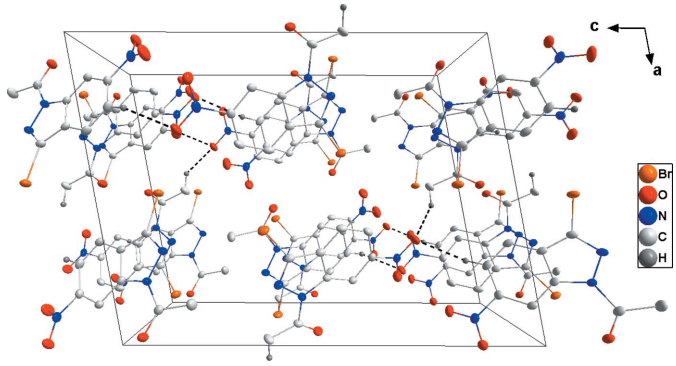


Figure 3
Packing viewed along the *b*-axis direction, with C—H···O hydrogen bonds shown as dashed lines.

Bruker (2016). *APEX3*, *SADABS* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.
Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.
Steffan, R. J., Matelan, E., Ashwell, M. A., Moore, W. J., Solvibile, W. R., Trybulski, E., Chadwick, C. C., Chippari, S., Kenney, T., Eckert, A., Borges-Marcucci, L., Keith, J. C., Xu, Z., Mosyak, L. & Harnish, D. C. (2004). *J. Med. Chem.* **47**, 6435–6438.
Tandon, V. K., Yadav, D. B., Chaturvedi, A. K. & Shukla, P. K. (2005). *Bioorg. Med. Chem. Lett.* **15**, 3288–3291.

full crystallographic data

IUCrData (2017). **2**, x170660 [https://doi.org/10.1107/S2414314617006605]

1-(3-Bromo-6-nitro-1*H*-indazol-1-yl)ethan-1-one

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1-(3-Bromo-6-nitro-1*H*-indazol-1-yl)ethan-1-one

Crystal data

$C_9H_6BrN_3O_3$
M_r = 284.08
Monoclinic, $P2_1/n$
a = 13.9863 (5) Å
b = 7.8783 (3) Å
c = 18.5549 (7) Å
β = 100.786 (1)°
V = 2008.41 (13) Å^3
Z = 8
$F(000)$ = 1120
D_x = 1.879 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9129 reflections
θ = 2.8–29.1°
μ = 4.09 mm^{-1}
T = 100 K
Thick plate, colourless
0.28 × 0.24 × 0.13 mm

Data collection

Bruker SMART APEX CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 8.3333 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2016)
T_{min} = 0.52, T_{max} = 0.62
37783 measured reflections
5389 independent reflections
4592 reflections with $I > 2\sigma(I)$
R_{int} = 0.032
θ_{max} = 29.2°, θ_{min} = 1.7°
h = −19→19
k = −10→10
l = −25→25

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.023
$wR(F^2)$ = 0.062
S = 1.09
5389 reflections
291 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
$w = 1/[\sigma^2(F_o^2) + (0.0368P)^2 + 0.0704P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.68 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}

Special details

Experimental. The diffraction data were obtained from 3 sets of 400 frames, each of width 0.5° in ω, collected at φ = 0.00, 90.00 and 180.00° and 2 sets of 800 frames, each of width 0.45° in φ, collected at ω = –30.00 and 210.00°. The scan time was 15 sec/frame.

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 $F^2 > 2\text{sigma}(F^2)$ 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. H-atoms attached to carbon were placed in calculated positions (C—H = 0.95 - 0.98 Å). All were included as riding contributions with isotropic displacement parameters 1.2 - 1.5 times those of the attached atoms.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.87667 (2)	0.69535 (2)	−0.10776 (2)	0.01973 (5)
O1	0.82655 (9)	0.28983 (17)	0.25598 (7)	0.0303 (3)
O2	0.68943 (9)	0.18565 (17)	0.20109 (7)	0.0295 (3)
O3	0.51681 (8)	0.32535 (15)	−0.03442 (6)	0.0206 (2)
N1	0.65058 (9)	0.45981 (16)	−0.05561 (7)	0.0151 (3)
N2	0.69880 (9)	0.54546 (16)	−0.10335 (8)	0.0166 (3)
N3	0.76125 (10)	0.27475 (18)	0.20217 (7)	0.0195 (3)
C1	0.78515 (11)	0.57816 (19)	−0.06524 (9)	0.0162 (3)
C2	0.79925 (11)	0.51742 (19)	0.00842 (9)	0.0154 (3)
C3	0.87569 (11)	0.5216 (2)	0.06909 (10)	0.0189 (3)
H3	0.9356	0.5754	0.0663	0.023*
C4	0.86134 (11)	0.4455 (2)	0.13281 (9)	0.0190 (3)
H4	0.9114	0.4462	0.1752	0.023*
C5	0.77190 (11)	0.3665 (2)	0.13456 (9)	0.0164 (3)
C6	0.69405 (11)	0.36030 (19)	0.07664 (9)	0.0153 (3)
H6	0.6344	0.3058	0.0800	0.018*
C7	0.70969 (10)	0.44003 (18)	0.01304 (9)	0.0140 (3)
C8	0.55482 (11)	0.4010 (2)	−0.07805 (9)	0.0165 (3)
C9	0.50905 (12)	0.4392 (2)	−0.15563 (9)	0.0213 (4)
H9A	0.5111	0.5619	−0.1641	0.032*
H9B	0.4412	0.4008	−0.1649	0.032*
H9C	0.5448	0.3802	−0.1888	0.032*
Br2	0.98495 (2)	0.44610 (2)	0.64437 (2)	0.02026 (5)
O4	0.59044 (10)	0.35663 (17)	0.30282 (7)	0.0320 (3)
O5	0.51604 (8)	0.56878 (15)	0.34207 (7)	0.0240 (3)
O6	0.56802 (8)	0.74041 (15)	0.59182 (6)	0.0216 (2)
N4	0.71797 (9)	0.62900 (16)	0.60559 (7)	0.0149 (3)
N5	0.80800 (9)	0.59760 (17)	0.64970 (7)	0.0168 (3)
N6	0.58318 (10)	0.46593 (17)	0.34829 (8)	0.0197 (3)
C10	0.85715 (11)	0.5139 (2)	0.60782 (9)	0.0167 (3)
C11	0.80361 (11)	0.48477 (19)	0.53549 (9)	0.0153 (3)
C12	0.82254 (11)	0.4017 (2)	0.47287 (9)	0.0182 (3)
H12	0.8841	0.3513	0.4724	0.022*
C13	0.74902 (12)	0.3953 (2)	0.41204 (9)	0.0190 (3)
H13	0.7586	0.3383	0.3688	0.023*

C14	0.65985 (11)	0.47404 (19)	0.41478 (9)	0.0162 (3)
C15	0.63782 (11)	0.55937 (18)	0.47456 (9)	0.0149 (3)
H15	0.5766	0.6122	0.4741	0.018*
C16	0.71298 (11)	0.56155 (18)	0.53582 (9)	0.0140 (3)
C17	0.64391 (12)	0.71328 (19)	0.63304 (9)	0.0171 (3)
C18	0.66666 (13)	0.7624 (2)	0.71242 (9)	0.0247 (4)
H18A	0.6780	0.6599	0.7427	0.037*
H18B	0.6117	0.8257	0.7250	0.037*
H18C	0.7251	0.8337	0.7215	0.037*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.01677 (8)	0.01729 (9)	0.02671 (10)	−0.00333 (5)	0.00815 (6)	0.00148 (6)
O1	0.0241 (6)	0.0447 (8)	0.0188 (6)	0.0035 (6)	−0.0042 (5)	0.0037 (6)
O2	0.0290 (7)	0.0402 (8)	0.0199 (7)	−0.0076 (6)	0.0063 (5)	0.0019 (6)
O3	0.0156 (5)	0.0243 (6)	0.0216 (6)	−0.0061 (4)	0.0030 (5)	−0.0001 (5)
N1	0.0130 (6)	0.0174 (6)	0.0147 (7)	−0.0027 (5)	0.0017 (5)	−0.0004 (5)
N2	0.0159 (6)	0.0160 (6)	0.0187 (7)	−0.0019 (5)	0.0050 (5)	0.0005 (5)
N3	0.0209 (7)	0.0229 (7)	0.0148 (7)	0.0062 (5)	0.0035 (5)	−0.0029 (5)
C1	0.0145 (7)	0.0135 (7)	0.0214 (8)	−0.0008 (5)	0.0055 (6)	−0.0009 (6)
C2	0.0140 (7)	0.0115 (7)	0.0211 (8)	−0.0012 (5)	0.0043 (6)	−0.0025 (6)
C3	0.0125 (7)	0.0163 (8)	0.0271 (9)	−0.0020 (6)	0.0018 (6)	−0.0044 (7)
C4	0.0159 (7)	0.0194 (8)	0.0194 (8)	0.0006 (6)	−0.0027 (6)	−0.0050 (6)
C5	0.0172 (7)	0.0177 (7)	0.0146 (8)	0.0026 (6)	0.0035 (6)	−0.0019 (6)
C6	0.0136 (7)	0.0156 (7)	0.0169 (8)	−0.0009 (5)	0.0033 (6)	−0.0043 (6)
C7	0.0113 (7)	0.0141 (7)	0.0162 (8)	0.0001 (5)	0.0013 (5)	−0.0041 (6)
C8	0.0131 (7)	0.0152 (7)	0.0201 (8)	−0.0013 (5)	0.0002 (6)	−0.0034 (6)
C9	0.0185 (8)	0.0225 (9)	0.0200 (9)	−0.0034 (6)	−0.0037 (6)	0.0014 (7)
Br2	0.01229 (8)	0.02216 (9)	0.02581 (10)	0.00376 (5)	0.00225 (6)	0.00464 (6)
O4	0.0401 (8)	0.0345 (7)	0.0196 (7)	0.0146 (6)	0.0012 (6)	−0.0089 (6)
O5	0.0254 (6)	0.0250 (6)	0.0200 (6)	0.0103 (5)	0.0005 (5)	−0.0011 (5)
O6	0.0177 (6)	0.0283 (6)	0.0192 (6)	0.0081 (5)	0.0046 (5)	0.0004 (5)
N4	0.0130 (6)	0.0168 (6)	0.0147 (7)	0.0031 (5)	0.0023 (5)	0.0005 (5)
N5	0.0126 (6)	0.0184 (6)	0.0186 (7)	0.0020 (5)	0.0007 (5)	0.0030 (5)
N6	0.0240 (7)	0.0208 (7)	0.0155 (7)	0.0039 (5)	0.0063 (5)	0.0015 (5)
C10	0.0131 (7)	0.0144 (7)	0.0227 (8)	0.0015 (5)	0.0036 (6)	0.0042 (6)
C11	0.0133 (7)	0.0135 (7)	0.0205 (8)	0.0014 (5)	0.0071 (6)	0.0042 (6)
C12	0.0167 (7)	0.0159 (7)	0.0240 (9)	0.0048 (6)	0.0085 (6)	0.0040 (6)
C13	0.0232 (8)	0.0165 (7)	0.0197 (8)	0.0039 (6)	0.0106 (6)	0.0019 (6)
C14	0.0190 (8)	0.0154 (7)	0.0149 (8)	0.0016 (6)	0.0047 (6)	0.0024 (6)
C15	0.0138 (7)	0.0140 (7)	0.0178 (8)	0.0026 (5)	0.0051 (6)	0.0033 (6)
C16	0.0151 (7)	0.0124 (7)	0.0160 (8)	0.0010 (5)	0.0067 (6)	0.0020 (6)
C17	0.0182 (7)	0.0159 (7)	0.0189 (8)	0.0032 (6)	0.0075 (6)	0.0031 (6)
C18	0.0249 (9)	0.0326 (9)	0.0168 (8)	0.0076 (7)	0.0041 (7)	−0.0025 (7)

Geometric parameters (Å, º)

Br1—C1	1.8686 (15)	Br2—C10	1.8673 (15)
O1—N3	1.2264 (18)	O4—N6	1.2230 (18)
O2—N3	1.2226 (19)	O5—N6	1.2293 (17)
O3—C8	1.2060 (19)	O6—C17	1.205 (2)
N1—N2	1.3850 (18)	N4—C16	1.389 (2)
N1—C7	1.3914 (19)	N4—N5	1.3896 (17)
N1—C8	1.4047 (19)	N4—C17	1.4039 (19)
N2—C1	1.306 (2)	N5—C10	1.308 (2)
N3—C5	1.479 (2)	N6—C14	1.477 (2)
C1—C2	1.427 (2)	C10—C11	1.428 (2)
C2—C3	1.400 (2)	C11—C12	1.401 (2)
C2—C7	1.410 (2)	C11—C16	1.405 (2)
C3—C4	1.374 (2)	C12—C13	1.378 (2)
C3—H3	0.9500	C12—H12	0.9500
C4—C5	1.403 (2)	C13—C14	1.402 (2)
C4—H4	0.9500	C13—H13	0.9500
C5—C6	1.380 (2)	C14—C15	1.380 (2)
C6—C7	1.390 (2)	C15—C16	1.396 (2)
C6—H6	0.9500	C15—H15	0.9500
C8—C9	1.492 (2)	C17—C18	1.498 (2)
C9—H9A	0.9800	C18—H18A	0.9800
C9—H9B	0.9800	C18—H18B	0.9800
C9—H9C	0.9800	C18—H18C	0.9800
N2—N1—C7	111.28 (12)	C16—N4—N5	111.27 (12)
N2—N1—C8	121.50 (13)	C16—N4—C17	127.40 (13)
C7—N1—C8	127.21 (13)	N5—N4—C17	121.28 (13)
C1—N2—N1	105.16 (13)	C10—N5—N4	105.00 (13)
O2—N3—O1	123.59 (15)	O4—N6—O5	124.05 (14)
O2—N3—C5	118.66 (13)	O4—N6—C14	117.76 (13)
O1—N3—C5	117.73 (14)	O5—N6—C14	118.19 (13)
N2—C1—C2	113.62 (14)	N5—C10—C11	113.45 (13)
N2—C1—Br1	120.40 (12)	N5—C10—Br2	120.15 (12)
C2—C1—Br1	125.98 (11)	C11—C10—Br2	126.40 (12)
C3—C2—C7	120.97 (15)	C12—C11—C16	121.00 (15)
C3—C2—C1	135.25 (15)	C12—C11—C10	135.01 (14)
C7—C2—C1	103.78 (13)	C16—C11—C10	103.98 (14)
C4—C3—C2	117.98 (15)	C13—C12—C11	117.92 (14)
C4—C3—H3	121.0	C13—C12—H12	121.0
C2—C3—H3	121.0	C11—C12—H12	121.0
C3—C4—C5	119.21 (15)	C12—C13—C14	119.11 (15)
C3—C4—H4	120.4	C12—C13—H13	120.4
C5—C4—H4	120.4	C14—C13—H13	120.4
C6—C5—C4	125.08 (15)	C15—C14—C13	125.34 (15)
C6—C5—N3	116.94 (14)	C15—C14—N6	117.13 (13)
C4—C5—N3	117.91 (14)	C13—C14—N6	117.53 (14)

C5—C6—C7	114.74 (14)	C14—C15—C16	114.38 (14)
C5—C6—H6	122.6	C14—C15—H15	122.8
C7—C6—H6	122.6	C16—C15—H15	122.8
C6—C7—N1	131.83 (13)	N4—C16—C15	131.46 (14)
C6—C7—C2	121.99 (14)	N4—C16—C11	106.29 (13)
N1—C7—C2	106.16 (13)	C15—C16—C11	122.23 (14)
O3—C8—N1	118.65 (14)	O6—C17—N4	118.39 (15)
O3—C8—C9	125.73 (14)	O6—C17—C18	125.29 (15)
N1—C8—C9	115.62 (14)	N4—C17—C18	116.33 (14)
C8—C9—H9A	109.5	C17—C18—H18A	109.5
C8—C9—H9B	109.5	C17—C18—H18B	109.5
H9A—C9—H9B	109.5	H18A—C18—H18B	109.5
C8—C9—H9C	109.5	C17—C18—H18C	109.5
H9A—C9—H9C	109.5	H18A—C18—H18C	109.5
H9B—C9—H9C	109.5	H18B—C18—H18C	109.5

C7—N1—N2—C1	−0.18 (16)	C16—N4—N5—C10	0.38 (17)
C8—N1—N2—C1	−178.96 (13)	C17—N4—N5—C10	178.10 (14)
N1—N2—C1—C2	0.07 (17)	N4—N5—C10—C11	−0.39 (18)
N1—N2—C1—Br1	−179.62 (10)	N4—N5—C10—Br2	179.26 (10)
N2—C1—C2—C3	−179.36 (17)	N5—C10—C11—C12	−178.64 (17)
Br1—C1—C2—C3	0.3 (3)	Br2—C10—C11—C12	1.7 (3)
N2—C1—C2—C7	0.06 (18)	N5—C10—C11—C16	0.26 (18)
Br1—C1—C2—C7	179.73 (11)	Br2—C10—C11—C16	−179.37 (11)
C7—C2—C3—C4	1.1 (2)	C16—C11—C12—C13	−1.0 (2)
C1—C2—C3—C4	−179.55 (17)	C10—C11—C12—C13	177.75 (17)
C2—C3—C4—C5	0.3 (2)	C11—C12—C13—C14	1.2 (2)
C3—C4—C5—C6	−1.0 (2)	C12—C13—C14—C15	−0.3 (3)
C3—C4—C5—N3	175.56 (14)	C12—C13—C14—N6	179.42 (14)
O2—N3—C5—C6	7.1 (2)	O4—N6—C14—C15	−161.03 (15)
O1—N3—C5—C6	−174.45 (14)	O5—N6—C14—C15	18.8 (2)
O2—N3—C5—C4	−169.81 (14)	O4—N6—C14—C13	19.2 (2)
O1—N3—C5—C4	8.7 (2)	O5—N6—C14—C13	−160.94 (15)
C4—C5—C6—C7	0.2 (2)	C13—C14—C15—C16	−0.7 (2)
N3—C5—C6—C7	−176.44 (13)	N6—C14—C15—C16	179.57 (13)
C5—C6—C7—N1	179.54 (15)	N5—N4—C16—C15	178.78 (15)
C5—C6—C7—C2	1.3 (2)	C17—N4—C16—C15	1.2 (3)
N2—N1—C7—C6	−178.20 (15)	N5—N4—C16—C11	−0.23 (16)
C8—N1—C7—C6	0.5 (3)	C17—N4—C16—C11	−177.78 (14)
N2—N1—C7—C2	0.22 (16)	C14—C15—C16—N4	−178.02 (15)
C8—N1—C7—C2	178.91 (14)	C14—C15—C16—C11	0.8 (2)
C3—C2—C7—C6	−2.0 (2)	C12—C11—C16—N4	179.09 (14)
C1—C2—C7—C6	178.45 (14)	C10—C11—C16—N4	−0.01 (16)
C3—C2—C7—N1	179.36 (13)	C12—C11—C16—C15	0.0 (2)
C1—C2—C7—N1	−0.17 (16)	C10—C11—C16—C15	−179.13 (14)
N2—N1—C8—O3	179.09 (14)	C16—N4—C17—O6	−4.3 (2)
C7—N1—C8—O3	0.5 (2)	N5—N4—C17—O6	178.37 (14)
N2—N1—C8—C9	−0.8 (2)	C16—N4—C17—C18	175.71 (15)

C7—N1—C8—C9	−179.40 (14)	N5—N4—C17—C18	−1.6 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C9—H9*B*···O1^{i}	0.98	2.47	3.301 (2)	142
C13—H13···O1	0.95	2.49	3.380 (2)	157

Symmetry code: (i) $x-1/2, -y+1/2, z-1/2$.