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Ethyl 2-(6-nitro-1*H*-indazol-1-yl)acetate

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

[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, and [b]Department of Chemistry, Tulane University, New Orleans, LA 70118, USA. *Correspondence e-mail: mmohamedabdelahi@gmail.com

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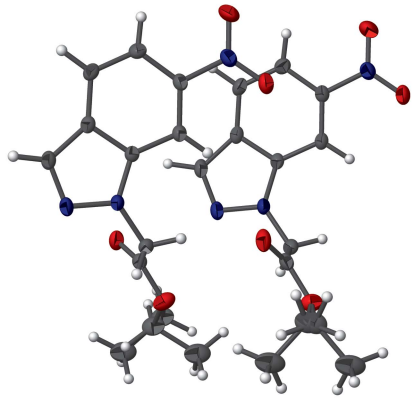
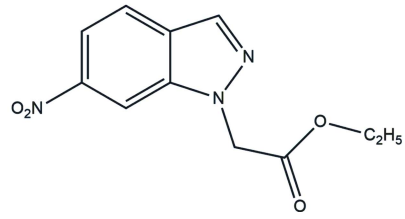
The asymmetric unit of the title compound, $C_{11}H_{11}N_3O_4$, comprises two independent molecules, both of which display positional disorder of their ethyl chains in 0.868 (4):0.132 (4) and 0.839 (4):0.161 (4) ratios. The packing is directed by a combination of C—H···O hydrogen bonds and N—O···π interactions between nitro groups and the aromatic rings.

3D view



Chemical scheme



Structure description

As a continuation of our studies of N-substituted indazole derivatives and their potential pharmacological activities (Boulhaoua *et al.*, 2016; Mohamed Abdelahi *et al.*, 2017), we now describe the synthesis and structure of the title compound.

The asymmetric unit comprises two independent molecules differing primarily in the orientations of the ester groups (Fig. 1). The dihedral angle between the five- and six-membered rings making up the imidazole rings are 1.12 (3)° in the molecule containing N1 and N2 and 1.28 (3)° in the other. In both molecules, the ethyl groups are approximately 15% disordered.

The packing is directed by a combination of C—H···O hydrogen bonds (Table 1) and N—O···π contacts between nitro groups and the six-membered rings of the indazole moieties. Fig. 1 shows the C8—H8*A*···O5 hydrogen bond occurring within the asymmetric unit as well as the N3—O3···π(C12–C17 ring) interaction [O···π = 3.131 (1) Å, N—O···π = 102.81 (9)°] The second N—O···π interaction occurs between N6—O7 and the centroid of the C1–C6 ring at $x, y, z + 1$ [O···π = 3.14 (1) Å, N—O···π = 109.16 (9)°]. The combination of hydrogen bonds and N—O···π interactions leads to a layer structure parallel to (100) (Figs. 2 and 3).

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

D—H···A	D—H	H···A	D···A	D—H···A
C4—H4···O4^{i}	0.93 (2)	2.50 (2)	3.1923 (18)	131.3 (16)
C7—H7···O3^{ii}	0.934 (19)	2.579 (18)	3.1973 (17)	124.0 (14)
C8—H8A···O5	0.978 (19)	2.276 (19)	3.1960 (17)	156.4 (15)
C15—H15···O8^{i}	0.94 (2)	2.55 (2)	3.2616 (18)	132.0 (16)
C18—H18···O7^{ii}	0.975 (19)	2.461 (18)	3.1606 (18)	128.5 (14)
C19—H19B···O1^{iii}	0.95 (2)	2.30 (2)	3.1923 (17)	155.2 (16)
C21—H21B···O3^{iv}	0.99	2.62	3.423 (3)	138
C22—H22A···O4^{iv}	0.98	2.54	3.367 (3)	142

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

Synthesis and crystallization

To a solution of 6-nitro-1*H*-indazole (1 g, 5 mmol) in THF (30 ml) was added ethyl bromoacetate (0.8 g, 5 mmol), potassium carbonate (1.24 g, 9 mmol) and a catalytic quantity of tetra-*n*-butylammonium iodide. The mixture was stirred at room temperature for 48 h. The solution was filtered and the solvent removed under reduced pressure. The residue was recrystallized from ethanol solution to afford the title compound as yellow crystals (yield: 66%).

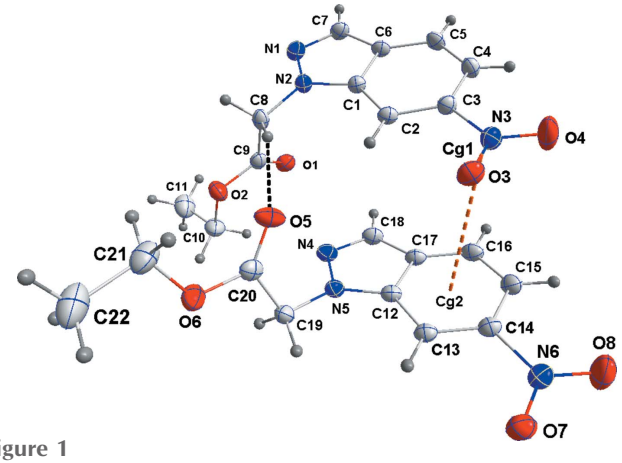


Figure 1
The asymmetric unit with labeling scheme and 50% probability ellipsoids. The intermolecular C—H···O hydrogen bond and the N—O···π interaction are shown, respectively, as black and orange dotted lines.

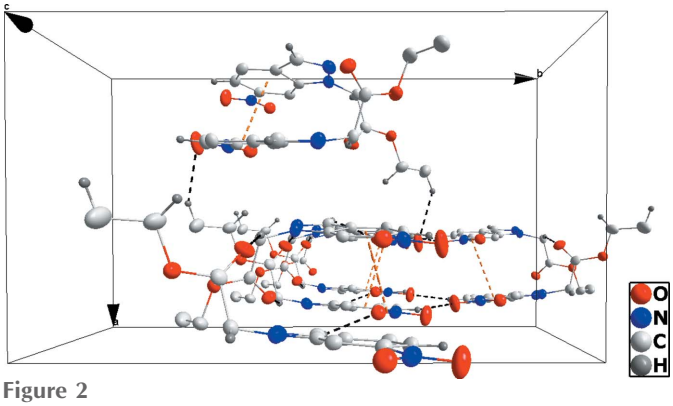


Figure 2
A portion of the packing viewed along the *c*-axis direction giving an elevation view of the layer structure. The key to the intermolecular interactions is given in Fig. 1

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{11}H_{11}N_3O_4$
M_r	249.23
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, b, c (Å)	12.6867 (6), 21.7492 (10), 8.1393 (4)
β (°)	90.772 (1)
V (Å^3)	2245.64 (18)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.12
Crystal size (mm)	0.36 × 0.34 × 0.29
Data collection	
Diffractometer	Bruker SMART APEX CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2016)
T_{min}, T_{max}	0.88, 0.97
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	43057, 6063, 5118
R_{int}	0.029
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.687
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.051, 0.142, 1.04
No. of reflections	6063
No. of parameters	387
No. of restraints	4
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.73, −0.49

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

Refinement

Crystal and refinement details appear in Table 2. The ethyl groups (C10, C11 and C21 C22) are disordered over two sites in 0.868 (4):0.132 (4) and 0.839 (4):0.161 (4) ratios, respectively. The components of the disorder were refined subject to restraints that their geometries be comparable and with the

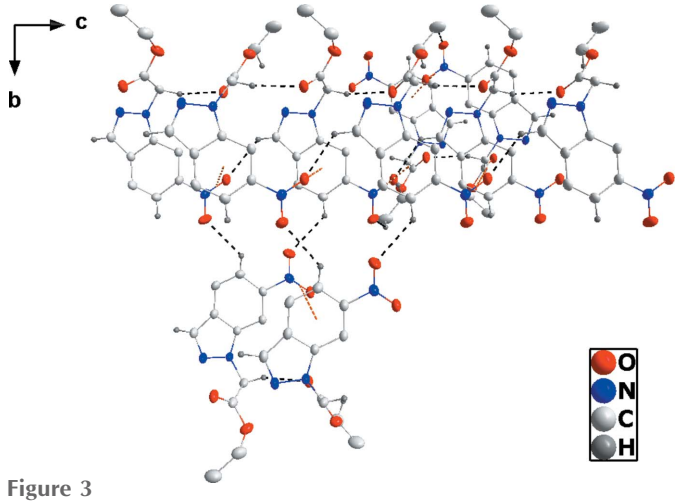


Figure 3
A portion of the packing viewed along the *a*-axis direction giving a plan view of the layer structure. The key to the intermolecular interactions is given in Fig. 1

attached H atoms included as riding contributions in idealized positions. The largest peak in the final difference map (0.73 e-Å^{-3}) is 0.86 Å from O4 and suggests a slight (< 9%) disorder in this nitro group, which is also suggested by the elongation of the displacement ellipsoid towards the residual peak. However, the rest of this group does not show such indications so it was decided to not include disorder here in the final refinement.

Acknowledgements

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full crystallographic data

IUCrData (2017). **2**, x170432 [https://doi.org/10.1107/S2414314617004321]

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Crystal data

$C_{11}H_{11}N_3O_4$
M_r = 249.23
Monoclinic, $P2_1/c$
a = 12.6867 (6) Å
b = 21.7492 (10) Å
c = 8.1393 (4) Å
β = 90.772 (1)°
V = 2245.64 (18) Å^3
Z = 8
$F(000)$ = 1040
D_x = 1.474 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9337 reflections
θ = 2.5–29.1°
μ = 0.12 mm^{-1}
T = 100 K
Block, colourless
0.36 × 0.34 × 0.29 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} = 0.88, T_{max} = 0.97
43057 measured reflections
6063 independent reflections
5118 reflections with $I > 2\sigma(I)$
R_{int} = 0.029
θ_{max} = 29.2°, θ_{min} = 1.6°
h = −17→17
k = −29→29
l = −11→11

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.142
S = 1.04
6063 reflections
387 parameters
4 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0762P)^2 + 1.075P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.73 e Å^{-3}
$\Delta\rho_{min}$ = −0.49 e Å^{-3}

Special details

Experimental. The diffraction data were obtained from 3 sets of 400 frames, each of width 0.5° in ω, colllected 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. The ethyl groups (C10, C11, C21 & C22) are disordered over two sites in 87:13 and 84:16 ratios, respectively. The components of the disorder were refined subject to restraints that their geometries be comparable and with the attached H-atoms included as riding contributions in idealized positions. The largest peak in the final difference map (0.73 e-$Å^{-3}$) is 0.86 Å from O4 and suggests a slight (< 9%) disorder in this nitro group which is also suggested by the elongation of the displacement ellipsoid towards the residual peak. However, the rest of this group does not show such indications so it was decided to not include a disorder here in the final refinement.

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
O1	0.81992 (8)	0.42860 (5)	−0.12528 (12)	0.0269 (2)	
O2	0.77563 (9)	0.35022 (5)	0.04235 (14)	0.0322 (3)	
O3	0.64535 (9)	0.62390 (5)	0.38381 (12)	0.0283 (2)	
O4	0.65775 (14)	0.71177 (5)	0.26110 (16)	0.0495 (4)	
N1	0.60290 (10)	0.47079 (6)	−0.27310 (14)	0.0245 (3)	
N2	0.61891 (9)	0.47588 (5)	−0.10760 (13)	0.0208 (2)	
N3	0.64742 (10)	0.65568 (6)	0.25929 (15)	0.0268 (3)	
C1	0.62452 (10)	0.53588 (6)	−0.05982 (15)	0.0182 (2)	
C2	0.63799 (10)	0.56187 (6)	0.09626 (15)	0.0192 (2)	
H2	0.6457 (15)	0.5377 (8)	0.190 (2)	0.029 (4)*	
C3	0.63737 (11)	0.62513 (6)	0.09891 (16)	0.0208 (3)	
C4	0.62617 (12)	0.66290 (6)	−0.04148 (17)	0.0241 (3)	
H4	0.6349 (16)	0.7053 (9)	−0.030 (2)	0.037 (5)*	
C5	0.61171 (11)	0.63610 (6)	−0.19303 (16)	0.0233 (3)	
H5	0.6059 (16)	0.6620 (9)	−0.289 (3)	0.041 (5)*	
C6	0.60950 (10)	0.57158 (6)	−0.20334 (16)	0.0206 (3)	
C7	0.59634 (11)	0.52741 (6)	−0.33084 (17)	0.0236 (3)	
H7	0.5823 (14)	0.5319 (8)	−0.443 (2)	0.027 (4)*	
C8	0.64448 (11)	0.42197 (6)	−0.01384 (16)	0.0219 (3)	
H8A	0.6341 (15)	0.4315 (8)	0.102 (2)	0.028 (5)*	
H8B	0.5976 (15)	0.3883 (9)	−0.042 (2)	0.031 (5)*	
C9	0.75746 (11)	0.40195 (6)	−0.04133 (16)	0.0224 (3)	
C10	0.88276 (14)	0.32649 (10)	0.0339 (3)	0.0346 (6)	0.868 (4)
H10A	0.9031	0.3064	0.1387	0.041*	0.868 (4)
H10B	0.9330	0.3603	0.0126	0.041*	0.868 (4)
C11	0.88417 (17)	0.28034 (10)	−0.1055 (3)	0.0441 (5)	0.868 (4)
H11A	0.9552	0.2632	−0.1154	0.066*	0.868 (4)
H11B	0.8342	0.2471	−0.0829	0.066*	0.868 (4)
H11C	0.8640	0.3008	−0.2085	0.066*	0.868 (4)
C10A	0.8696 (10)	0.3149 (8)	0.0016 (18)	0.0346 (6)	0.132 (4)
H10C	0.9307	0.3420	−0.0189	0.041*	0.132 (4)

H10D	0.8572	0.2881	−0.0950	0.041*	0.132 (4)
C11A	0.8842 (11)	0.2779 (6)	0.1580 (18)	0.0441 (5)	0.132 (4)
H11D	0.9462	0.2513	0.1481	0.066*	0.132 (4)
H11E	0.8943	0.3059	0.2513	0.066*	0.132 (4)
H11F	0.8215	0.2525	0.1759	0.066*	0.132 (4)
O5	0.67001 (8)	0.42925 (5)	0.37686 (12)	0.0295 (2)	
O6	0.71450 (8)	0.35019 (5)	0.54310 (14)	0.0292 (2)	
O7	0.86504 (9)	0.62072 (5)	0.88507 (12)	0.0294 (2)	
O8	0.88491 (12)	0.70869 (5)	0.76740 (15)	0.0436 (3)	
N4	0.88917 (10)	0.46774 (6)	0.22757 (14)	0.0262 (3)	
N5	0.87470 (10)	0.47329 (5)	0.39238 (13)	0.0224 (2)	
N6	0.87448 (10)	0.65280 (6)	0.76228 (15)	0.0263 (3)	
C12	0.87643 (10)	0.53326 (6)	0.44106 (15)	0.0195 (2)	
C13	0.86738 (10)	0.55951 (6)	0.59710 (16)	0.0205 (3)	
H13	0.8557 (15)	0.5355 (9)	0.695 (2)	0.031 (5)*	
C14	0.87669 (11)	0.62260 (6)	0.60066 (16)	0.0217 (3)	
C15	0.89048 (11)	0.66004 (7)	0.46108 (17)	0.0246 (3)	
H15	0.8910 (15)	0.7031 (9)	0.475 (2)	0.034 (5)*	
C16	0.89977 (11)	0.63290 (7)	0.30910 (17)	0.0246 (3)	
H16	0.9084 (15)	0.6583 (9)	0.213 (2)	0.033 (5)*	
C17	0.89463 (10)	0.56863 (6)	0.29821 (16)	0.0218 (3)	
C18	0.90165 (12)	0.52423 (7)	0.17054 (17)	0.0254 (3)	
H18	0.9121 (14)	0.5306 (8)	0.053 (2)	0.028 (4)*	
C19	0.84767 (11)	0.41988 (6)	0.48619 (17)	0.0228 (3)	
H19A	0.8913 (15)	0.3865 (8)	0.454 (2)	0.029 (5)*	
H19B	0.8583 (15)	0.4300 (8)	0.599 (2)	0.031 (5)*	
C20	0.73319 (11)	0.40177 (6)	0.45991 (16)	0.0228 (3)	
C21	0.60636 (16)	0.3281 (2)	0.5411 (7)	0.0356 (9)	0.839 (4)
H21A	0.5859	0.3144	0.4292	0.043*	0.839 (4)
H21B	0.5578	0.3613	0.5747	0.043*	0.839 (4)
C22	0.60087 (18)	0.27658 (10)	0.6565 (3)	0.0471 (6)	0.839 (4)
H22A	0.5287	0.2605	0.6581	0.071*	0.839 (4)
H22B	0.6491	0.2440	0.6218	0.071*	0.839 (4)
H22C	0.6211	0.2907	0.7668	0.071*	0.839 (4)
C21A	0.6069 (5)	0.3291 (13)	0.515 (5)	0.0356 (9)	0.161 (4)
H21C	0.5626	0.3635	0.4748	0.043*	0.161 (4)
H21D	0.5770	0.3140	0.6197	0.043*	0.161 (4)
C22A	0.6082 (10)	0.2795 (5)	0.3940 (17)	0.0471 (6)	0.161 (4)
H22D	0.5362	0.2648	0.3741	0.071*	0.161 (4)
H22E	0.6375	0.2949	0.2911	0.071*	0.161 (4)
H22F	0.6519	0.2456	0.4356	0.071*	0.161 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0284 (5)	0.0334 (5)	0.0190 (5)	−0.0052 (4)	0.0020 (4)	0.0006 (4)
O2	0.0282 (5)	0.0275 (5)	0.0409 (6)	0.0012 (4)	0.0003 (4)	0.0103 (5)
O3	0.0321 (5)	0.0345 (6)	0.0182 (5)	−0.0012 (4)	0.0016 (4)	−0.0021 (4)

O4	0.0907 (11)	0.0236 (6)	0.0339 (6)	0.0080 (6)	−0.0098 (7)	−0.0083 (5)
N1	0.0312 (6)	0.0272 (6)	0.0149 (5)	−0.0031 (5)	−0.0008 (4)	−0.0021 (4)
N2	0.0284 (6)	0.0195 (5)	0.0144 (5)	−0.0010 (4)	0.0000 (4)	−0.0002 (4)
N3	0.0322 (6)	0.0256 (6)	0.0224 (6)	0.0041 (5)	−0.0016 (5)	−0.0048 (4)
C1	0.0180 (6)	0.0199 (6)	0.0168 (6)	−0.0002 (4)	0.0009 (4)	0.0002 (4)
C2	0.0192 (6)	0.0222 (6)	0.0162 (5)	0.0015 (5)	0.0006 (4)	0.0001 (5)
C3	0.0226 (6)	0.0225 (6)	0.0174 (6)	0.0021 (5)	−0.0002 (5)	−0.0025 (5)
C4	0.0284 (7)	0.0191 (6)	0.0247 (7)	0.0030 (5)	−0.0001 (5)	0.0015 (5)
C5	0.0269 (7)	0.0229 (6)	0.0201 (6)	0.0032 (5)	−0.0010 (5)	0.0047 (5)
C6	0.0213 (6)	0.0234 (6)	0.0170 (6)	0.0010 (5)	−0.0007 (4)	0.0014 (5)
C7	0.0271 (7)	0.0270 (7)	0.0166 (6)	−0.0014 (5)	−0.0017 (5)	0.0004 (5)
C8	0.0280 (7)	0.0190 (6)	0.0188 (6)	−0.0020 (5)	0.0022 (5)	0.0019 (5)
C9	0.0270 (7)	0.0216 (6)	0.0185 (6)	−0.0030 (5)	−0.0020 (5)	−0.0010 (5)
C10	0.0264 (9)	0.0316 (11)	0.0456 (13)	0.0033 (8)	−0.0056 (8)	0.0035 (8)
C11	0.0350 (10)	0.0347 (10)	0.0628 (14)	0.0049 (8)	0.0066 (9)	0.0013 (9)
C10A	0.0264 (9)	0.0316 (11)	0.0456 (13)	0.0033 (8)	−0.0056 (8)	0.0035 (8)
C11A	0.0350 (10)	0.0347 (10)	0.0628 (14)	0.0049 (8)	0.0066 (9)	0.0013 (9)
O5	0.0282 (5)	0.0416 (6)	0.0187 (5)	0.0091 (4)	−0.0018 (4)	−0.0010 (4)
O6	0.0242 (5)	0.0247 (5)	0.0387 (6)	−0.0009 (4)	−0.0010 (4)	0.0017 (4)
O7	0.0349 (6)	0.0348 (6)	0.0186 (5)	−0.0003 (4)	0.0004 (4)	−0.0011 (4)
O8	0.0711 (9)	0.0262 (6)	0.0336 (6)	−0.0073 (6)	0.0047 (6)	−0.0067 (5)
N4	0.0318 (6)	0.0309 (6)	0.0158 (5)	0.0047 (5)	0.0009 (4)	−0.0017 (4)
N5	0.0287 (6)	0.0236 (6)	0.0150 (5)	0.0018 (4)	0.0004 (4)	−0.0003 (4)
N6	0.0286 (6)	0.0279 (6)	0.0224 (6)	−0.0026 (5)	0.0002 (4)	−0.0031 (5)
C12	0.0181 (6)	0.0236 (6)	0.0167 (6)	0.0010 (5)	−0.0008 (4)	0.0010 (5)
C13	0.0194 (6)	0.0256 (6)	0.0165 (6)	−0.0007 (5)	0.0001 (4)	0.0013 (5)
C14	0.0212 (6)	0.0257 (6)	0.0183 (6)	−0.0007 (5)	−0.0001 (5)	−0.0007 (5)
C15	0.0260 (7)	0.0237 (6)	0.0239 (6)	−0.0037 (5)	−0.0016 (5)	0.0029 (5)
C16	0.0252 (7)	0.0288 (7)	0.0198 (6)	−0.0032 (5)	0.0001 (5)	0.0059 (5)
C17	0.0203 (6)	0.0281 (7)	0.0170 (6)	−0.0001 (5)	0.0002 (4)	0.0022 (5)
C18	0.0279 (7)	0.0318 (7)	0.0167 (6)	0.0022 (5)	0.0019 (5)	0.0005 (5)
C19	0.0260 (7)	0.0220 (6)	0.0205 (6)	0.0018 (5)	−0.0025 (5)	0.0016 (5)
C20	0.0258 (6)	0.0247 (6)	0.0178 (6)	0.0041 (5)	0.0008 (5)	−0.0047 (5)
C21	0.0257 (7)	0.0354 (8)	0.046 (3)	−0.0060 (6)	0.0007 (7)	−0.0052 (12)
C22	0.0375 (11)	0.0325 (10)	0.0713 (16)	−0.0068 (8)	0.0078 (10)	−0.0046 (10)
C21A	0.0257 (7)	0.0354 (8)	0.046 (3)	−0.0060 (6)	0.0007 (7)	−0.0052 (12)
C22A	0.0375 (11)	0.0325 (10)	0.0713 (16)	−0.0068 (8)	0.0078 (10)	−0.0046 (10)

Geometric parameters (Å, º)

O1—C9	1.2023 (17)	O5—C20	1.2007 (17)
O2—C9	1.3335 (17)	O6—C20	1.3333 (18)
O2—C10	1.456 (2)	O6—C21	1.454 (2)
O2—C10A	1.460 (3)	O6—C21A	1.454 (3)
O3—N3	1.2274 (16)	O7—N6	1.2261 (16)
O4—N3	1.2270 (17)	O8—N6	1.2233 (17)
N1—C7	1.3204 (18)	N4—C18	1.3235 (19)
N1—N2	1.3640 (15)	N4—N5	1.3617 (15)

N2—C1	1.3632 (16)	N5—C12	1.3631 (17)
N2—C8	1.4337 (17)	N5—C19	1.4343 (17)
N3—C3	1.4687 (17)	N6—C14	1.4710 (17)
C1—C2	1.3988 (17)	C12—C13	1.3986 (18)
C1—C6	1.4135 (17)	C12—C17	1.4158 (18)
C2—C3	1.3761 (18)	C13—C14	1.3776 (19)
C2—H2	0.930 (19)	C13—H13	0.97 (2)
C3—C4	1.4129 (18)	C14—C15	1.4106 (19)
C4—C5	1.3744 (19)	C15—C16	1.377 (2)
C4—H4	0.93 (2)	C15—H15	0.94 (2)
C5—C6	1.4059 (18)	C16—C17	1.402 (2)
C5—H5	0.96 (2)	C16—H16	0.97 (2)
C6—C7	1.4223 (19)	C17—C18	1.4223 (19)
C7—H7	0.934 (19)	C18—H18	0.975 (19)
C8—C9	1.518 (2)	C19—C20	1.517 (2)
C8—H8A	0.978 (19)	C19—H19A	0.952 (19)
C8—H8B	0.969 (19)	C19—H19B	0.95 (2)
C10—C11	1.515 (3)	C21—C22	1.464 (7)
C10—H10A	0.9900	C21—H21A	0.9900
C10—H10B	0.9900	C21—H21B	0.9900
C11—H11A	0.9800	C22—H22A	0.9800
C11—H11B	0.9800	C22—H22B	0.9800
C11—H11C	0.9800	C22—H22C	0.9800
C10A—C11A	1.517 (4)	C21A—C22A	1.464 (8)
C10A—H10C	0.9900	C21A—H21C	0.9900
C10A—H10D	0.9900	C21A—H21D	0.9900
C11A—H11D	0.9800	C22A—H22D	0.9800
C11A—H11E	0.9800	C22A—H22E	0.9800
C11A—H11F	0.9800	C22A—H22F	0.9800
C9—O2—C10	115.45 (14)	C20—O6—C21	116.5 (3)
C9—O2—C10A	117.6 (6)	C20—O6—C21A	111.1 (18)
C7—N1—N2	106.48 (11)	C18—N4—N5	106.36 (11)
C1—N2—N1	111.47 (11)	N4—N5—C12	111.67 (11)
C1—N2—C8	128.34 (11)	N4—N5—C19	119.28 (11)
N1—N2—C8	119.27 (11)	C12—N5—C19	128.55 (11)
O4—N3—O3	123.60 (12)	O8—N6—O7	123.33 (13)
O4—N3—C3	117.93 (12)	O8—N6—C14	118.08 (12)
O3—N3—C3	118.47 (12)	O7—N6—C14	118.56 (12)
N2—C1—C2	130.63 (12)	N5—C12—C13	130.79 (12)
N2—C1—C6	106.51 (11)	N5—C12—C17	106.46 (11)
C2—C1—C6	122.82 (12)	C13—C12—C17	122.70 (12)
C3—C2—C1	114.69 (12)	C14—C13—C12	114.69 (12)
C3—C2—H2	123.5 (11)	C14—C13—H13	122.3 (11)
C1—C2—H2	121.8 (11)	C12—C13—H13	123.0 (11)
C2—C3—C4	124.69 (12)	C13—C14—C15	124.72 (12)
C2—C3—N3	117.76 (11)	C13—C14—N6	117.45 (12)
C4—C3—N3	117.55 (12)	C15—C14—N6	117.81 (12)

C5—C4—C3	119.35 (12)	C16—C15—C14	119.28 (13)
C5—C4—H4	121.6 (13)	C16—C15—H15	122.0 (12)
C3—C4—H4	118.8 (13)	C14—C15—H15	118.7 (12)
C4—C5—C6	118.63 (12)	C15—C16—C17	118.66 (12)
C4—C5—H5	119.1 (12)	C15—C16—H16	119.7 (11)
C6—C5—H5	122.2 (12)	C17—C16—H16	121.6 (11)
C5—C6—C1	119.77 (12)	C16—C17—C12	119.86 (12)
C5—C6—C7	136.03 (12)	C16—C17—C18	136.04 (12)
C1—C6—C7	104.19 (11)	C12—C17—C18	104.10 (12)
N1—C7—C6	111.35 (12)	N4—C18—C17	111.41 (12)
N1—C7—H7	117.2 (11)	N4—C18—H18	119.5 (10)
C6—C7—H7	131.5 (11)	C17—C18—H18	129.1 (10)
N2—C8—C9	111.32 (11)	N5—C19—C20	111.74 (11)
N2—C8—H8A	108.0 (11)	N5—C19—H19A	109.1 (11)
C9—C8—H8A	110.1 (11)	C20—C19—H19A	108.9 (11)
N2—C8—H8B	111.0 (11)	N5—C19—H19B	107.1 (11)
C9—C8—H8B	109.0 (11)	C20—C19—H19B	108.6 (12)
H8A—C8—H8B	107.4 (15)	H19A—C19—H19B	111.4 (16)
O1—C9—O2	125.89 (13)	O5—C20—O6	125.64 (14)
O1—C9—C8	125.21 (13)	O5—C20—C19	125.50 (13)
O2—C9—C8	108.90 (11)	O6—C20—C19	108.86 (11)
O2—C10—C11	106.90 (16)	O6—C21—C22	107.4 (4)
O2—C10—H10A	110.3	O6—C21—H21A	110.2
C11—C10—H10A	110.3	C22—C21—H21A	110.2
O2—C10—H10B	110.3	O6—C21—H21B	110.2
C11—C10—H10B	110.3	C22—C21—H21B	110.2
H10A—C10—H10B	108.6	H21A—C21—H21B	108.5
C10—C11—H11A	109.5	C21—C22—H22A	109.5
C10—C11—H11B	109.5	C21—C22—H22B	109.5
H11A—C11—H11B	109.5	H22A—C22—H22B	109.5
C10—C11—H11C	109.5	C21—C22—H22C	109.5
H11A—C11—H11C	109.5	H22A—C22—H22C	109.5
H11B—C11—H11C	109.5	H22B—C22—H22C	109.5
O2—C10A—C11A	100.4 (8)	O6—C21A—C22A	108.5 (9)
O2—C10A—H10C	111.7	O6—C21A—H21C	110.0
C11A—C10A—H10C	111.7	C22A—C21A—H21C	110.0
O2—C10A—H10D	111.7	O6—C21A—H21D	110.0
C11A—C10A—H10D	111.7	C22A—C21A—H21D	110.0
H10C—C10A—H10D	109.5	H21C—C21A—H21D	108.4
C10A—C11A—H11D	109.5	C21A—C22A—H22D	109.5
C10A—C11A—H11E	109.5	C21A—C22A—H22E	109.5
H11D—C11A—H11E	109.5	H22D—C22A—H22E	109.5
C10A—C11A—H11F	109.5	C21A—C22A—H22F	109.5
H11D—C11A—H11F	109.5	H22D—C22A—H22F	109.5
H11E—C11A—H11F	109.5	H22E—C22A—H22F	109.5
C7—N1—N2—C1	−1.11 (16)	C18—N4—N5—C12	0.83 (16)
C7—N1—N2—C8	−171.01 (12)	C18—N4—N5—C19	173.37 (12)

N1—N2—C1—C2	178.65 (13)	N4—N5—C12—C13	−178.31 (13)
C8—N2—C1—C2	−12.6 (2)	C19—N5—C12—C13	10.0 (2)
N1—N2—C1—C6	0.96 (15)	N4—N5—C12—C17	−0.81 (15)
C8—N2—C1—C6	169.71 (13)	C19—N5—C12—C17	−172.49 (13)
N2—C1—C2—C3	−178.47 (13)	N5—C12—C13—C14	177.68 (13)
C6—C1—C2—C3	−1.11 (19)	C17—C12—C13—C14	0.53 (19)
C1—C2—C3—C4	−1.1 (2)	C12—C13—C14—C15	2.2 (2)
C1—C2—C3—N3	177.93 (11)	C12—C13—C14—N6	−176.32 (11)
O4—N3—C3—C2	172.69 (14)	O8—N6—C14—C13	178.48 (14)
O3—N3—C3—C2	−7.12 (19)	O7—N6—C14—C13	0.33 (19)
O4—N3—C3—C4	−8.2 (2)	O8—N6—C14—C15	−0.2 (2)
O3—N3—C3—C4	171.97 (13)	O7—N6—C14—C15	−178.31 (13)
C2—C3—C4—C5	2.0 (2)	C13—C14—C15—C16	−2.7 (2)
N3—C3—C4—C5	−177.05 (13)	N6—C14—C15—C16	175.82 (13)
C3—C4—C5—C6	−0.6 (2)	C14—C15—C16—C17	0.3 (2)
C4—C5—C6—C1	−1.5 (2)	C15—C16—C17—C12	2.2 (2)
C4—C5—C6—C7	179.59 (15)	C15—C16—C17—C18	−179.10 (15)
N2—C1—C6—C5	−179.67 (12)	N5—C12—C17—C16	179.50 (12)
C2—C1—C6—C5	2.4 (2)	C13—C12—C17—C16	−2.7 (2)
N2—C1—C6—C7	−0.43 (14)	N5—C12—C17—C18	0.46 (14)
C2—C1—C6—C7	−178.35 (12)	C13—C12—C17—C18	178.21 (12)
N2—N1—C7—C6	0.81 (16)	N5—N4—C18—C17	−0.51 (16)
C5—C6—C7—N1	178.80 (15)	C16—C17—C18—N4	−178.77 (16)
C1—C6—C7—N1	−0.24 (16)	C12—C17—C18—N4	0.04 (16)
C1—N2—C8—C9	−93.57 (16)	N4—N5—C19—C20	−75.60 (15)
N1—N2—C8—C9	74.42 (15)	C12—N5—C19—C20	95.53 (16)
C10—O2—C9—O1	2.6 (2)	C21—O6—C20—O5	−4.4 (2)
C10A—O2—C9—O1	−14.8 (9)	C21A—O6—C20—O5	2.4 (8)
C10—O2—C9—C8	−177.49 (14)	C21—O6—C20—C19	176.02 (17)
C10A—O2—C9—C8	165.1 (9)	C21A—O6—C20—C19	−177.2 (8)
N2—C8—C9—O1	2.76 (19)	N5—C19—C20—O5	−2.82 (19)
N2—C8—C9—O2	−177.16 (11)	N5—C19—C20—O6	176.73 (11)
C9—O2—C10—C11	−93.65 (18)	C20—O6—C21—C22	−172.46 (17)
C9—O2—C10A—C11A	158.7 (8)	C20—O6—C21A—C22A	100 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4···O4^{i}	0.93 (2)	2.50 (2)	3.1923 (18)	131.3 (16)
C7—H7···O3^{ii}	0.934 (19)	2.579 (18)	3.1973 (17)	124.0 (14)
C8—H8*A*···O5	0.978 (19)	2.276 (19)	3.1960 (17)	156.4 (15)
C15—H15···O8^{i}	0.94 (2)	2.55 (2)	3.2616 (18)	132.0 (16)
C18—H18···O7^{ii}	0.975 (19)	2.461 (18)	3.1606 (18)	128.5 (14)
C19—H19*B*···O1^{iii}	0.95 (2)	2.30 (2)	3.1923 (17)	155.2 (16)
C21—H21*B*···O3^{iv}	0.99	2.62	3.423 (3)	138
C22—H22*A*···O4^{iv}	0.98	2.54	3.367 (3)	142

Symmetry codes: (i) *x*, −*y*+3/2, *z*−1/2; (ii) *x*, *y*, *z*−1; (iii) *x*, *y*, *z*+1; (iv) −*x*+1, −*y*+1, −*z*+1.