IUCrData

ISSN 2414-3146

Ethyl 4-(3,4,6-trimethyl-1-phenyl-1*H*-pyrazolo-[3,4-*b*]pyridin-5-yl)benzoate

Jabrane Jouha,[a]* Mohamed Loubidi,[b] Mohamed El Hafi,[c] Zahira Tber,[b] El Mokhtar Essassi[c] and Joel T. Mague[d]

[a]Laboratoire de Chimie Organique et Analytique, Université Sultan Moulay Slimane, Faculté des Sciences et Techniques, BP 523, 23000, Beni-Mellal, Morocco, [b]Laboratoire de Chimie Bioorganique & Analytique, URAC 22 Université Hassan II, Mohammedia-Casablanca, Faculté des Sciences et Techniques, BP 146, 28800, Mohammedia, Morocco, [c]Laboratoire de Chimie Organique Hétérocyclique, Centre de Recherche Des Sciences des Médicaments, Pôle de Compétence Pharmacochimie, Av Ibn Battouta, BP 1014, Faculté des Sciences, Université Mohammed V, Rabat, Morocco, and [d]Department of Chemistry, Tulane University, New Orleans, LA 70118, USA. *Correspondence e-mail: jabranejouha1@gmail.com

Received 11 October 2018
Accepted 14 October 2018

Edited by W. T. A. Harrison, University of Aberdeen, Scotland

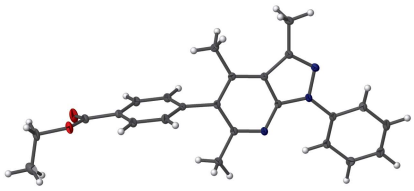
Keywords: crystal structure; hydrogen bond; pyrazolopyridine; C—H$\cdots\pi$ interaction.

CCDC reference: 1873180

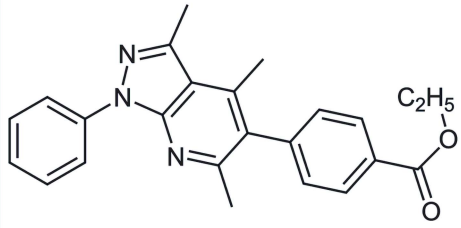
Structural data: full structural data are available from iucrdata.iucr.org

In the title compound, $C_{24}H_{23}N_3O_2$, the dihedral angles between the pyrazolopyridine ring system (r.m.s. deviation = 0.001 Å) and the N-bound and C-bound benzene rings are 15.95 (2) and 83.71 (4)°, respectively. The conformation of the former is influenced by an intramolecular C—H$\cdots$N hydrogen bond, which generates an *S*(6) ring. In the crystal, stepped layers are generated by three sets of C—H$\cdots\pi$ interactions.

3D view



Chemical scheme



Structure description

Pyrazolo[3,4-*b*]pyridine derivatives show various biological properties, for example, anti-proliferative and anti-coagulant activities (Goda *et al.*, 2004; Kundariya *et al.*, 2011). In this work we continue the investigation of pyrazolo[3,4-*b*]pyridine derivatives published by our group (Jouha *et al.*, 2017).

As expected, the pyrazolylpyridine moiety is almost planar (r.m.s. deviation = 0.001). The pendant C10–C15 (attached to N2) and C16–C21 (attached to C2) benzene rings are inclined to the mean plane of the pyrazolylpyridine ring system by 15.95 (2) and 83.71 (4)°, respectively. The orientation of the C10–C15 ring is determined in part by an intramolecular C15—H15$\cdots$N1 hydrogen bond (Fig. 1 and Table 1). In the crystal, inversion-related pairs of C6—H6*A*$\cdots$*Cg*2 and of C18—H18$\cdots$*Cg*3 interactions form dimers (Table 1 and Fig. 2), which are connected by inversion-related pairs of C23—H23*A*$\cdots$*Cg*4 interactions into stepped layers (Fig. 3).

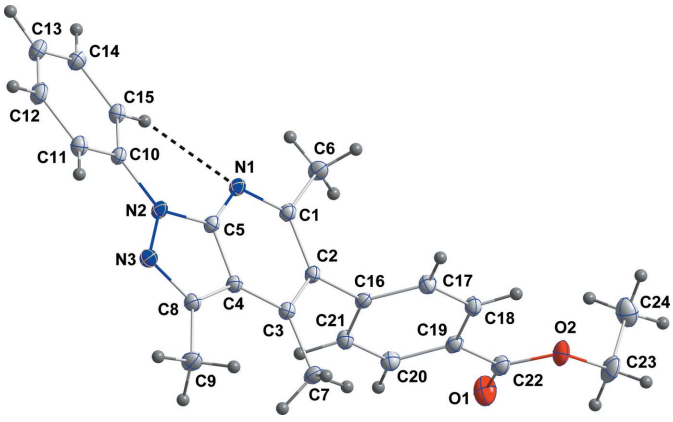


Figure 1
The title molecule showing 50% probability ellipsoids. The intramolecular C—H···N bond is indicated by a dashed line.

Synthesis and crystallization

A flask containing a stirring bar was charged with 5-bromo-3,4,6-trimethyl-1-phenyl-1*H*-pyrazolo[3,4-*b*]pyridine (100 mg, 0.31 mmol), 4-ethoxycarbonylphenyl boronic acid (67 mg, 0.35 mmol) and sodium bicarbonate (1.5 equiv, 0.47 mmol) in a mixture of toluene/ethanol (2/1 *v*/*v*). $Pd(PPh_3)_4$ (0.05 equiv, 0.018 mmol) was added and the mixture was refluxed for 12 h. After cooling, the solvents were removed under reduced pressure and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, *v*/*v* = 90:10). The title compound was recrystallized from ethanol solution at room temperature, giving colourless blocks (yield: 80%; m.p. 422–424 K).

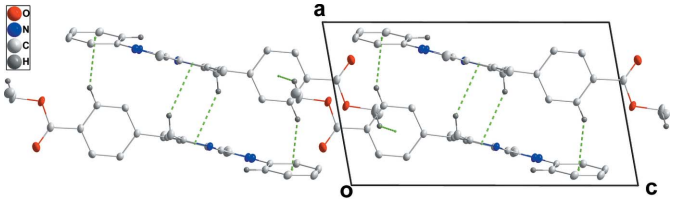


Figure 2
Packing viewed along the *b*-axis direction with C—H···π(ring) interactions shown as dashed lines.

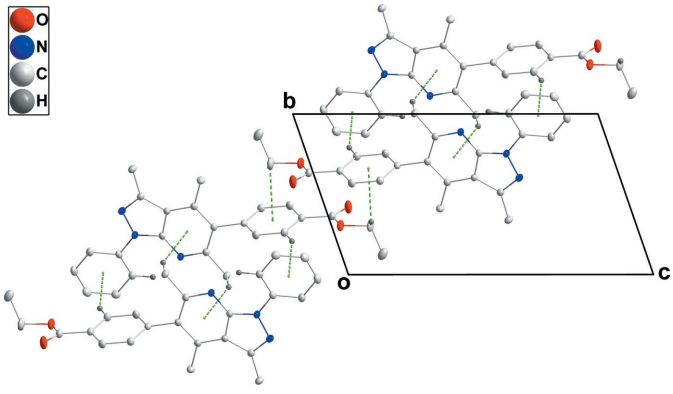


Figure 3
Packing viewed along the *a*-axis direction with C—H···π(ring) interactions shown as dashed lines.

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

*Cg*2, *Cg*3 and *Cg*4 are the centroids of the N1/C1–C5, C10–C15 and C16–C21 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C15—H15···N1	0.988 (13)	2.385 (13)	3.0225 (14)	121.6 (10)
C6—H6*A*···*Cg*2^{i}	0.96 (2)	2.79 (3)	3.6483 (15)	149.5 (17)
C18—H18···*Cg*3^{i}	0.948 (15)	2.558 (16)	3.4209 (14)	151.4 (11)
C23—H23*A*···*Cg*4^{ii}	0.975 (17)	2.910 (17)	3.6135 (17)	129.7 (13)

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{24}H_{23}N_3O_2$
M_r	385.45
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	100
a, *b*, *c* (Å)	8.6962 (12), 8.7349 (12), 14.559 (2)
α, β, γ (°)	106.468 (2), 92.949 (2), 111.771 (2)
V (Å^3)	969.5 (2)
Z	2
Radiation type	Mo *Kα*
μ (mm^{-1})	0.09
Crystal size (mm)	0.34 × 0.29 × 0.18
Data collection	
Diffractometer	Bruker SMART APEX CCD
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.97, 0.98
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	18971, 5268, 4248
R_{int}	0.029
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.695
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.046, 0.137, 1.12
No. of reflections	5268
No. of parameters	354
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.48, −0.19

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2018* (Sheldrick, 2015*b*), *Mercury* (Macrae *et al.*, 2008) and *SHELXTL* (Sheldrick, 2008).

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.

References

Bruker (2016). *APEX3*, *SADABS* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Goda, F. E., Abdel-Aziz, A. A. M. & Attef, O. A. (2004). *Bioorg. Med. Chem.* **12**, 1845–1852.

Jouha, J., Loubidi, M., Bouali, J., Hamri, S., Hafid, A., Suzenet, F., Guillaumet, G., Dagcı, T., Khouili, M., Aydın, F., Saso, L. & Armagan, G. (2017). *Eur. J. Med. Chem.* **129**, 41–52.
Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.
Kundariya, D. S., Bheshdadia, B. M., Joshi, N. K. & Patel, P. K. (2011). *Int. J. Chem. Tech. Res*, **3**, 238–243.
Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
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.

full crystallographic data

IUCrData (2018). **3**, x181449 [https://doi.org/10.1107/S2414314618014499]

Ethyl 4-(3,4,6-trimethyl-1-phenyl-1*H*-pyrazolo[3,4-*b*]pyridin-5-yl)benzoate

Jabrane Jouha, Mohamed Loubidi, Mohamed El Hafi, Zahira Tber, El Mokhtar Essassi and Joel T. Mague

Ethyl 4-(3,4,6-trimethyl-1-phenyl-1*H*-pyrazolo[3,4-*b*]pyridin-5-yl)benzoate

Crystal data

$C_{24}H_{23}N_3O_2$
M_r = 385.45
Triclinic, $P\overline{1}$
a = 8.6962 (12) Å
b = 8.7349 (12) Å
c = 14.559 (2) Å
α = 106.468 (2)°
β = 92.949 (2)°
γ = 111.771 (2)°
V = 969.5 (2) Å^3
Z = 2
$F(000)$ = 408
D_x = 1.320 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 8772 reflections
θ = 2.6–29.6°
μ = 0.09 mm^{-1}
T = 100 K
Block, colourless
0.34 × 0.29 × 0.18 mm

Data collection

Bruker SMART APEX CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
T_{min} = 0.97, T_{max} = 0.98
18971 measured reflections
5268 independent reflections
4248 reflections with $I > 2\sigma(I)$
R_{int} = 0.029
θ_{max} = 29.6°, θ_{min} = 2.6°
h = −12→12
k = −12→12
l = −20→20

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.137
S = 1.12
5268 reflections
354 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0918P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.48 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}

Special details

Experimental. The diffraction data were obtained from 3 sets of 400 frames, each of width 0.5 deg. in omega, colllected at phi = 0.00, 90.00 and 180.00 deg. and 2 sets of 800 frames, each of width 0.45 deg in phi, collected at omega = -30.00 and 210.00 deg. The scan time was 20 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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.23175 (11)	0.57825 (12)	−0.07653 (6)	0.0290 (2)
O2	0.51281 (10)	0.69386 (10)	−0.02991 (5)	0.02180 (19)
N1	0.23651 (11)	0.88745 (11)	0.52975 (6)	0.01411 (19)
N2	0.16953 (11)	0.75274 (11)	0.65507 (6)	0.01468 (19)
N3	0.16485 (11)	0.60229 (11)	0.66993 (6)	0.0164 (2)
C1	0.27729 (12)	0.85912 (12)	0.44097 (7)	0.0138 (2)
C2	0.29302 (13)	0.70350 (12)	0.38726 (7)	0.0133 (2)
C3	0.27667 (13)	0.57422 (12)	0.42865 (7)	0.0136 (2)
C4	0.23587 (12)	0.60380 (12)	0.52264 (7)	0.0134 (2)
C5	0.21382 (12)	0.75768 (12)	0.56641 (7)	0.0132 (2)
C6	0.30824 (15)	1.00548 (14)	0.40044 (8)	0.0186 (2)
H6A	0.425 (3)	1.077 (3)	0.4065 (15)	0.077 (7)*
H6B	0.255 (3)	1.086 (3)	0.4290 (14)	0.069 (6)*
H6C	0.268 (2)	0.968 (2)	0.3306 (13)	0.052 (5)*
C7	0.30068 (15)	0.41217 (14)	0.37623 (8)	0.0185 (2)
H7A	0.201 (2)	0.309 (2)	0.3664 (13)	0.054 (5)*
H7B	0.388 (2)	0.400 (2)	0.4145 (13)	0.053 (5)*
H7C	0.325 (3)	0.409 (3)	0.3160 (15)	0.068 (6)*
C8	0.20401 (13)	0.51302 (13)	0.59214 (7)	0.0150 (2)
C9	0.20687 (16)	0.34153 (14)	0.58796 (8)	0.0202 (2)
H9A	0.1196 (18)	0.2449 (18)	0.5352 (10)	0.025 (4)*
H9B	0.1864 (19)	0.3229 (18)	0.6506 (11)	0.031 (4)*
H9C	0.3194 (19)	0.3413 (17)	0.5768 (10)	0.024 (3)*
C10	0.13290 (13)	0.87315 (13)	0.72905 (7)	0.0140 (2)
C11	0.13272 (13)	0.85723 (14)	0.82151 (8)	0.0168 (2)
H11	0.1558 (18)	0.7698 (18)	0.8352 (9)	0.022 (3)*
C12	0.09668 (14)	0.97454 (14)	0.89422 (8)	0.0201 (2)
H12	0.1010 (18)	0.9640 (18)	0.9589 (10)	0.025 (4)*
C13	0.06252 (14)	1.10730 (15)	0.87670 (8)	0.0209 (2)
H13	0.0429 (18)	1.1944 (17)	0.9304 (10)	0.026 (4)*
C14	0.06191 (14)	1.12117 (14)	0.78412 (8)	0.0188 (2)
H14	0.0400 (18)	1.2165 (18)	0.7725 (10)	0.026 (4)*
C15	0.09546 (13)	1.00400 (13)	0.70950 (7)	0.0159 (2)
H15	0.0939 (17)	1.0137 (16)	0.6435 (10)	0.020 (3)*
C16	0.31614 (13)	0.67883 (12)	0.28381 (7)	0.0135 (2)
C17	0.47296 (13)	0.75326 (13)	0.25873 (7)	0.0160 (2)

H17	0.5705 (17)	0.8175 (17)	0.3081 (10)	0.020 (3)*
C18	0.48821 (13)	0.73679 (13)	0.16198 (7)	0.0163 (2)
H18	0.5959 (19)	0.7913 (18)	0.1471 (10)	0.027 (4)*
C19	0.34573 (13)	0.64654 (12)	0.08963 (7)	0.0147 (2)
C20	0.18917 (13)	0.56965 (13)	0.11409 (7)	0.0166 (2)
H20	0.0915 (19)	0.5081 (18)	0.0624 (11)	0.029 (4)*
C21	0.17423 (13)	0.58490 (13)	0.21035 (7)	0.0158 (2)
H21	0.0619 (17)	0.5258 (17)	0.2258 (9)	0.021 (3)*
C22	0.35412 (14)	0.63421 (13)	−0.01422 (7)	0.0174 (2)
C23	0.53668 (18)	0.69586 (17)	−0.12779 (8)	0.0256 (3)
H23A	0.637 (2)	0.671 (2)	−0.1346 (11)	0.035 (4)*
H23B	0.439 (2)	0.6031 (19)	−0.1725 (11)	0.029 (4)*
C24	0.56473 (17)	0.87103 (18)	−0.13631 (10)	0.0291 (3)
H24A	0.661 (2)	0.966 (2)	−0.0887 (12)	0.045 (5)*
H24B	0.463 (2)	0.898 (2)	−0.1262 (11)	0.038 (4)*
H24C	0.588 (2)	0.874 (2)	−0.2032 (12)	0.039 (4)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0264 (4)	0.0428 (5)	0.0154 (4)	0.0095 (4)	0.0018 (3)	0.0124 (4)
O2	0.0248 (4)	0.0301 (4)	0.0152 (4)	0.0121 (4)	0.0103 (3)	0.0117 (3)
N1	0.0175 (4)	0.0149 (4)	0.0118 (4)	0.0074 (3)	0.0050 (3)	0.0056 (3)
N2	0.0199 (4)	0.0154 (4)	0.0124 (4)	0.0089 (3)	0.0070 (3)	0.0067 (3)
N3	0.0202 (4)	0.0150 (4)	0.0162 (4)	0.0076 (3)	0.0061 (4)	0.0074 (3)
C1	0.0150 (5)	0.0146 (4)	0.0128 (4)	0.0066 (4)	0.0037 (4)	0.0052 (4)
C2	0.0140 (4)	0.0144 (4)	0.0115 (4)	0.0052 (4)	0.0040 (4)	0.0044 (4)
C3	0.0139 (4)	0.0134 (4)	0.0133 (5)	0.0053 (4)	0.0035 (4)	0.0041 (4)
C4	0.0150 (5)	0.0130 (4)	0.0127 (4)	0.0058 (4)	0.0038 (4)	0.0046 (3)
C5	0.0144 (4)	0.0143 (4)	0.0111 (4)	0.0058 (4)	0.0032 (4)	0.0042 (4)
C6	0.0273 (6)	0.0171 (5)	0.0167 (5)	0.0115 (4)	0.0077 (4)	0.0092 (4)
C7	0.0265 (6)	0.0155 (5)	0.0172 (5)	0.0115 (4)	0.0085 (5)	0.0058 (4)
C8	0.0169 (5)	0.0145 (4)	0.0146 (5)	0.0063 (4)	0.0045 (4)	0.0058 (4)
C9	0.0290 (6)	0.0168 (5)	0.0205 (5)	0.0121 (4)	0.0094 (5)	0.0098 (4)
C10	0.0139 (4)	0.0151 (4)	0.0121 (4)	0.0050 (4)	0.0050 (4)	0.0034 (4)
C11	0.0176 (5)	0.0190 (5)	0.0153 (5)	0.0075 (4)	0.0049 (4)	0.0070 (4)
C12	0.0220 (5)	0.0244 (5)	0.0144 (5)	0.0093 (4)	0.0084 (4)	0.0064 (4)
C13	0.0223 (5)	0.0220 (5)	0.0184 (5)	0.0099 (4)	0.0097 (4)	0.0041 (4)
C14	0.0196 (5)	0.0184 (5)	0.0207 (5)	0.0097 (4)	0.0078 (4)	0.0064 (4)
C15	0.0165 (5)	0.0174 (5)	0.0144 (5)	0.0068 (4)	0.0050 (4)	0.0058 (4)
C16	0.0175 (5)	0.0128 (4)	0.0122 (4)	0.0076 (4)	0.0051 (4)	0.0046 (3)
C17	0.0155 (5)	0.0180 (5)	0.0128 (5)	0.0050 (4)	0.0021 (4)	0.0049 (4)
C18	0.0160 (5)	0.0182 (5)	0.0152 (5)	0.0061 (4)	0.0056 (4)	0.0067 (4)
C19	0.0194 (5)	0.0151 (4)	0.0122 (4)	0.0088 (4)	0.0047 (4)	0.0055 (4)
C20	0.0166 (5)	0.0186 (5)	0.0135 (5)	0.0064 (4)	0.0013 (4)	0.0049 (4)
C21	0.0162 (5)	0.0171 (5)	0.0147 (5)	0.0068 (4)	0.0049 (4)	0.0060 (4)
C22	0.0228 (5)	0.0182 (5)	0.0143 (5)	0.0095 (4)	0.0062 (4)	0.0074 (4)
C23	0.0357 (7)	0.0340 (6)	0.0169 (5)	0.0190 (6)	0.0153 (5)	0.0141 (5)

C24	0.0291 (6)	0.0348 (7)	0.0315 (7)	0.0137 (6)	0.0100 (6)	0.0206 (6)

Geometric parameters (Å, º)

O1—C22	1.2073 (13)	C10—C15	1.3943 (14)
O2—C22	1.3396 (14)	C11—C12	1.3879 (15)
O2—C23	1.4547 (13)	C11—H11	0.927 (15)
N1—C1	1.3373 (13)	C12—C13	1.3833 (16)
N1—C5	1.3405 (13)	C12—H12	0.972 (14)
N2—C5	1.3736 (13)	C13—C14	1.3869 (16)
N2—N3	1.3776 (12)	C13—H13	0.996 (14)
N2—C10	1.4174 (13)	C14—C15	1.3916 (14)
N3—C8	1.3200 (13)	C14—H14	0.976 (14)
C1—C2	1.4228 (13)	C15—H15	0.988 (13)
C1—C6	1.4979 (14)	C16—C17	1.3943 (14)
C2—C3	1.3907 (14)	C16—C21	1.3984 (14)
C2—C16	1.4948 (13)	C17—C18	1.3930 (14)
C3—C4	1.4080 (13)	C17—H17	0.953 (13)
C3—C7	1.5009 (14)	C18—C19	1.3916 (14)
C4—C5	1.4027 (13)	C18—H18	0.948 (15)
C4—C8	1.4319 (14)	C19—C20	1.3923 (15)
C6—H6A	0.96 (2)	C19—C22	1.4925 (14)
C6—H6B	0.99 (2)	C20—C21	1.3871 (14)
C6—H6C	0.975 (18)	C20—H20	0.971 (15)
C7—H7A	0.961 (19)	C21—H21	0.993 (14)
C7—H7B	0.97 (2)	C23—C24	1.4999 (18)
C7—H7C	0.91 (2)	C23—H23A	0.975 (17)
C8—C9	1.4913 (15)	C23—H23B	0.965 (15)
C9—H9A	0.988 (14)	C24—H24A	0.983 (17)
C9—H9B	0.984 (15)	C24—H24B	1.006 (17)
C9—H9C	1.001 (15)	C24—H24C	1.008 (16)
C10—C11	1.3919 (14)		
C22—O2—C23	117.09 (9)	C10—C11—H11	121.3 (8)
C1—N1—C5	114.70 (8)	C13—C12—C11	121.29 (10)
C5—N2—N3	110.21 (8)	C13—C12—H12	120.7 (8)
C5—N2—C10	131.24 (9)	C11—C12—H12	118.0 (8)
N3—N2—C10	118.55 (8)	C12—C13—C14	119.08 (10)
C8—N3—N2	107.28 (8)	C12—C13—H13	120.5 (8)
N1—C1—C2	123.76 (9)	C14—C13—H13	120.4 (8)
N1—C1—C6	115.23 (9)	C13—C14—C15	120.85 (10)
C2—C1—C6	121.00 (9)	C13—C14—H14	118.7 (8)
C3—C2—C1	120.42 (9)	C15—C14—H14	120.4 (8)
C3—C2—C16	121.38 (9)	C14—C15—C10	119.23 (10)
C1—C2—C16	118.08 (9)	C14—C15—H15	120.6 (8)
C2—C3—C4	116.16 (9)	C10—C15—H15	120.2 (8)
C2—C3—C7	122.03 (9)	C17—C16—C21	119.14 (9)
C4—C3—C7	121.81 (9)	C17—C16—C2	122.16 (9)

C5—C4—C3	118.41 (9)	C21—C16—C2	118.63 (9)
C5—C4—C8	104.69 (9)	C18—C17—C16	120.59 (9)
C3—C4—C8	136.89 (9)	C18—C17—H17	119.5 (8)
N1—C5—N2	126.44 (9)	C16—C17—H17	119.9 (8)
N1—C5—C4	126.36 (9)	C19—C18—C17	119.86 (10)
N2—C5—C4	107.17 (9)	C19—C18—H18	121.3 (8)
C1—C6—H6A	113.6 (14)	C17—C18—H18	118.9 (8)
C1—C6—H6B	114.9 (12)	C18—C19—C20	119.79 (9)
H6A—C6—H6B	106.3 (17)	C18—C19—C22	121.86 (10)
C1—C6—H6C	114.1 (11)	C20—C19—C22	118.32 (9)
H6A—C6—H6C	102.5 (16)	C21—C20—C19	120.33 (9)
H6B—C6—H6C	104.2 (16)	C21—C20—H20	121.4 (9)
C3—C7—H7A	111.7 (11)	C19—C20—H20	118.3 (9)
C3—C7—H7B	110.7 (10)	C20—C21—C16	120.28 (10)
H7A—C7—H7B	105.6 (15)	C20—C21—H21	118.9 (7)
C3—C7—H7C	112.7 (13)	C16—C21—H21	120.8 (7)
H7A—C7—H7C	105.6 (16)	O1—C22—O2	124.06 (10)
H7B—C7—H7C	110.3 (17)	O1—C22—C19	123.73 (10)
N3—C8—C4	110.65 (9)	O2—C22—C19	112.20 (9)
N3—C8—C9	118.86 (9)	O2—C23—C24	110.74 (10)
C4—C8—C9	130.48 (9)	O2—C23—H23A	102.5 (9)
C8—C9—H9A	111.3 (8)	C24—C23—H23A	111.7 (9)
C8—C9—H9B	108.6 (8)	O2—C23—H23B	107.7 (9)
H9A—C9—H9B	109.1 (11)	C24—C23—H23B	112.6 (9)
C8—C9—H9C	110.2 (8)	H23A—C23—H23B	111.1 (13)
H9A—C9—H9C	108.8 (11)	C23—C24—H24A	112.3 (10)
H9B—C9—H9C	108.8 (11)	C23—C24—H24B	111.2 (9)
C11—C10—C15	120.41 (10)	H24A—C24—H24B	107.8 (14)
C11—C10—N2	118.83 (9)	C23—C24—H24C	110.3 (9)
C15—C10—N2	120.76 (9)	H24A—C24—H24C	107.5 (13)
C12—C11—C10	119.11 (10)	H24B—C24—H24C	107.6 (13)
C12—C11—H11	119.6 (8)		

C5—N2—N3—C8	−0.46 (11)	N3—N2—C10—C11	14.94 (14)
C10—N2—N3—C8	−179.60 (9)	C5—N2—C10—C15	16.86 (17)
C5—N1—C1—C2	1.16 (15)	N3—N2—C10—C15	−164.22 (9)
C5—N1—C1—C6	−178.18 (9)	C15—C10—C11—C12	−0.73 (16)
N1—C1—C2—C3	−4.27 (16)	N2—C10—C11—C12	−179.90 (9)
C6—C1—C2—C3	175.04 (10)	C10—C11—C12—C13	−0.57 (17)
N1—C1—C2—C16	171.81 (9)	C11—C12—C13—C14	1.01 (17)
C6—C1—C2—C16	−8.88 (14)	C12—C13—C14—C15	−0.16 (17)
C1—C2—C3—C4	3.15 (14)	C13—C14—C15—C10	−1.11 (16)
C16—C2—C3—C4	−172.79 (9)	C11—C10—C15—C14	1.55 (16)
C1—C2—C3—C7	−176.98 (10)	N2—C10—C15—C14	−179.30 (9)
C16—C2—C3—C7	7.08 (15)	C3—C2—C16—C17	−101.45 (12)
C2—C3—C4—C5	0.50 (14)	C1—C2—C16—C17	82.51 (13)
C7—C3—C4—C5	−179.37 (10)	C3—C2—C16—C21	81.68 (13)
C2—C3—C4—C8	178.72 (11)	C1—C2—C16—C21	−94.36 (11)

C7—C3—C4—C8	−1.15 (18)	C21—C16—C17—C18	0.96 (15)
C1—N1—C5—N2	−179.15 (9)	C2—C16—C17—C18	−175.89 (9)
C1—N1—C5—C4	2.93 (15)	C16—C17—C18—C19	0.53 (16)
N3—N2—C5—N1	−177.42 (9)	C17—C18—C19—C20	−1.52 (15)
C10—N2—C5—N1	1.58 (18)	C17—C18—C19—C22	176.35 (9)
N3—N2—C5—C4	0.83 (11)	C18—C19—C20—C21	1.01 (16)
C10—N2—C5—C4	179.82 (10)	C22—C19—C20—C21	−176.93 (9)
C3—C4—C5—N1	−3.85 (16)	C19—C20—C21—C16	0.50 (15)
C8—C4—C5—N1	177.41 (10)	C17—C16—C21—C20	−1.47 (15)
C3—C4—C5—N2	177.91 (9)	C2—C16—C21—C20	175.49 (9)
C8—C4—C5—N2	−0.83 (11)	C23—O2—C22—O1	2.20 (16)
N2—N3—C8—C4	−0.09 (11)	C23—O2—C22—C19	−177.20 (8)
N2—N3—C8—C9	−179.35 (9)	C18—C19—C22—O1	−169.52 (11)
C5—C4—C8—N3	0.58 (11)	C20—C19—C22—O1	8.38 (16)
C3—C4—C8—N3	−177.80 (11)	C18—C19—C22—O2	9.89 (14)
C5—C4—C8—C9	179.73 (11)	C20—C19—C22—O2	−172.21 (9)
C3—C4—C8—C9	1.3 (2)	C22—O2—C23—C24	94.70 (12)
C5—N2—C10—C11	−163.98 (10)		

Hydrogen-bond geometry (Å, º)

Cg2, Cg3 and Cg4 are the centroids of the N1/C1–C5, C10–C15 and C16–C21 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C15—H15···N1	0.988 (13)	2.385 (13)	3.0225 (14)	121.6 (10)
C6—H6*A*···*Cg*2^{i}	0.96 (2)	2.79 (3)	3.6483 (15)	149.5 (17)
C18—H18···*Cg*3^{i}	0.948 (15)	2.558 (16)	3.4209 (14)	151.4 (11)
C23—H23*A*···*Cg*4^{ii}	0.975 (17)	2.910 (17)	3.6135 (17)	129.7 (13)

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