data reports

Crystal structure of 13-(2-methoxyphenyl)-3,4-dihydro-2H-indazolo[1,2-b]phthalazine-1,6,11(13H)-trione

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In the title compound, $C_{22}H_{18}N_2O_4$, the three fused rings of the pyrazolophthalazine moiety are coplanar (r.m.s. deviation = 0.027 Å). The cyclohexene ring fused to the pyrazolidine ring, so forming the indazolophthalazine unit, has a half-chair conformation. The benzene ring is almost normal to the mean plane of the pyrazolophthalazine moiety, with a dihedral angle of 87.21 (6)° between their planes. In the crystal, molecules are linked by pairs of C—H···O hydrogen bonds forming inversion dimers. The dimers are linked via C—H···π interactions, forming slabs parallel to (100). Between the slabs there are weak π–π interactions [shortest inter-centroid distance = 3.6664 (9) Å], leading to the formation of a three-dimensional structure.

1. Related literature

For the synthesis of phthalazine derivatives, see: Hasaninejed et al., (2012); Keshipour et al., (2012). For applications of this class of compounds, see: Soliman et al. (1981); Nomoto et al. (1990); Abd El-Wahab et al. (2013); Cashman & Ghirmai (2009); Hall et al. (1992, 2001). For the synthesis of the title compound, see: Khurana & Magoo (2009). For similar condensation reactions as used here, see: Atar et al. (2015). For the Cambridge Structural Database, see: Groom & Allen (2014).
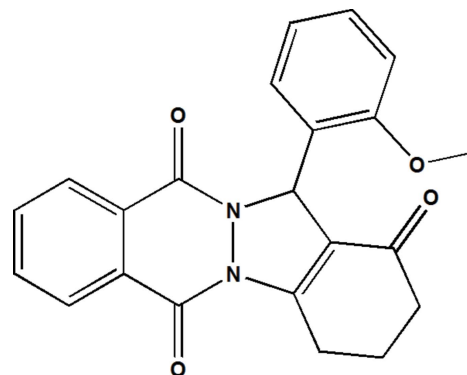
2. Experimental

2.1. Crystal data

$C_{22}H_{18}N_2O_4$
$M_r = 374.38$
Monoclinic, $P2_1/c$
$a = 8.5839$ (2) Å
$b = 11.8474$ (2) Å
$c = 17.5317$ (4) Å
$\beta = 102.199$ (1)°

$V = 1742.66$ (6) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.10$ mm^{-1}
$T = 295$ K
$0.15 \times 0.11 \times 0.08$ mm

2.2. Data collection

Bruker APEXII diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 2011)
$T_{min} = 0.983$, $T_{max} = 0.991$

17655 measured reflections
5142 independent reflections
3865 reflections with $I > 2\sigma(I)$
$R_{int} = 0.02$

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.163$
$S = 1.03$
5142 reflections

254 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.56$ e Å^{-3}
$\Delta\rho_{min} = -0.41$ e Å^{-3}

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

$Cg3$ is the centroid of ring C2–C7.

D—H···A	D—H	H···A	D···A	D—H···A
C22—H22B···O1[i]	0.96	2.43	3.379 (2)	168
C20—H20···$Cg3$[ii]	0.93	2.90	3.726 (2)	149

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

Data collection: APEX2 (Bruker, 2011); cell refinement: SAINT (Bruker, 2011); data reduction: SAINT; program(s) used to solve structure: SIR2002 (Burla et al., 2005); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 2012) and DIAMOND (Brandenburg & Berndt, 2001); software used to prepare material for publication: WinGX (Farrugia, 2012).

Acknowledgements

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References

Atar, A. B., Lee, S. D., Cho, B. G., Cho, D. W. & Jeong, Y. T. (2015). *Res. Chem. Intermed.* doi:10.1007/s11164-015-2113-3.

Brandenburg, K. & Berndt, M. (2001). *DIAMOND*. Crystal Impact, Bonn, Germany.

Bruker (2011). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Burla, M. C., Caliandro, R., Camalli, M., Carrozzini, B., Cascarano, G. L., De Caro, L., Giacovazzo, C., Polidori, G. & Spagna, R. (2005). *J. Appl. Cryst.* **38**, 381–388.

Cashman, J. R. & Ghirmai, S. (2009). *Bioorg. Med. Chem.* **17**, 6890–6897.

El-Wahab, A. H. F. A., Mohamed, H. M., El-Agrody, A. M., El-Nassag, M. A. & Bedair, A. H. (2013). *Eur. J. Chem.* **4**, 10–19.

Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.

Groom, C. R. & Allen, F. H. (2014). *Angew. Chem. Int. Ed.* **53**, 662–671.

Hall, I. H., Covington, D. W., Wheaton, J. R., Izydore, R. A. & Zhou, X. (2001). *Pharmazie*, **56**, 168–174.

Hall, I. H., Hall, E. S. & Wong, O. T. (1992). *Anticancer Drugs*, **3**, 55–62.

Hasaninejed, A., Kazerooni, M. R. & Zare, A. (2012). *Catal. Today*, **196**, 148–155.

Keshipour, S., Shojaei, S. & Shaabani, A. (2012). *Tetrahedron*, **68**, 6141–6145.

Khurana, J. M. & Magoo, D. (2009). *Tetrahedron Lett.* **50**, 7300–7303.

Nomoto, Y., Obase, H., Takai, H., Teranishi, M., Nakamura, J. & Kubo, K. (1990). *Chem. Pharm. Bull.* **38**, 2179–2183.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Soliman, R., Gabr, M., Abouzeit-har, M. S. & Sharabi, F. M. (1981). *J. Pharm. Sci.* **70**, 94–96.

supporting information

Crystal structure of 13-(2-methoxyphenyl)-3,4-dihydro-2*H*-indazolo[1,2-*b*]phthalazine-1,6,11(13*H*)-trione

Abdelmalek Bouraiou, Sofiane Bouacida, Hocine Merazig, Aissa Chibani and Zouhair Bouaziz

S1. Comment

Nitrogen heterocycles containing a phthalazine moiety have attracted significant synthetic interest because they show biological and pharmacological activities such as anticonvulsant (Soliman *et al.*, 1981), cardiotonic (Nomoto *et al.*, 1990), and antimicrobial (Abd El-Wahab *et al.*, 2013). In addition, phthalazines have been reported to act as potential inhibitors of serotonin re-uptake (Cashman & Ghirmai, 2009) and as effective anti-proliferative agents against different human and murine tumor cells (Hall *et al.*, 1992;2001). During the last two decades there is a growing interest in the synthesis of several phthalazines as promising drug candidates for the treatment of cancer (Hasaninejed *et al.*, 2012; Keshipour *et al.*, 2012). Herein we report on the synthesis and crystal structure of the title compound, synthesized by condensation of phthalhydrazide, 2-methoxybenzaldehyde and 1,3-cyclohexadione (Atar *et al.*, 2015).

The molecule structure of the title compound is illustrated in Fig. 1. It consists of an indazolone moiety bearing a methoxypenyl group and attached to a phthalazine. The phthalazine ring is quasi-planar with a maximum deviation of 0.0203 (17) Å for atom C3, and forms a dihedral angle of 86.76 (4) ° with the benzene ring. All bond distances and angles are within the ranges of accepted values, CSD, (Groom & Allen, 2014).

In the crystal, molecules are linked by pairs of C—H⋯O hydrogen bonds forming inversion dimers (Table 1). The dimers are linked *via* C—H⋯π interactions forming slabs parallel to (100); Table 1 and Fig. 2. Between the slabs there are weak π–π interactions [shortest inter-centroid distance = 3.6664 (9) ° for Cg1⋯Cg3^i; Cg1 and Cg3 and the centroids of rings N1/N2/C9/C10/C15 and C2—C7, respectively; symmetry code: -x+1, -y, -z+1], leading to the formation of a three-dimensional structure.

S2. Synthesis and crystallization

Phthalhydrazide (1.0 mmol), 2-methoxybenzaldehyde (1.2 mmol), 1,3-cyclohexanedione (1.0 mmol), H_2SO_4 (0.15 mmol), and 10 ml H_2O-EtOH were mixed under reflux following a published procedure (Khurana & Magoo, 2009). The precipitate formed was collected by filtration, and dried. The crude product was washed well with hot ethanol. The solid obtained, was recrystallized in $CHCl_3$ giving colourless crystals of the title compound on slow evaporation of the solvent.

S3. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The H atoms were localized in difference Fourier maps but introduced in calculated positions and treated as riding atoms: C—H = 0.93 - 0.98 Å with $U_{iso}(H) = 1.5\ U_{eq}(C)$ for methyl H atoms and $1.2U_{eq}(C)$ for other H atoms.
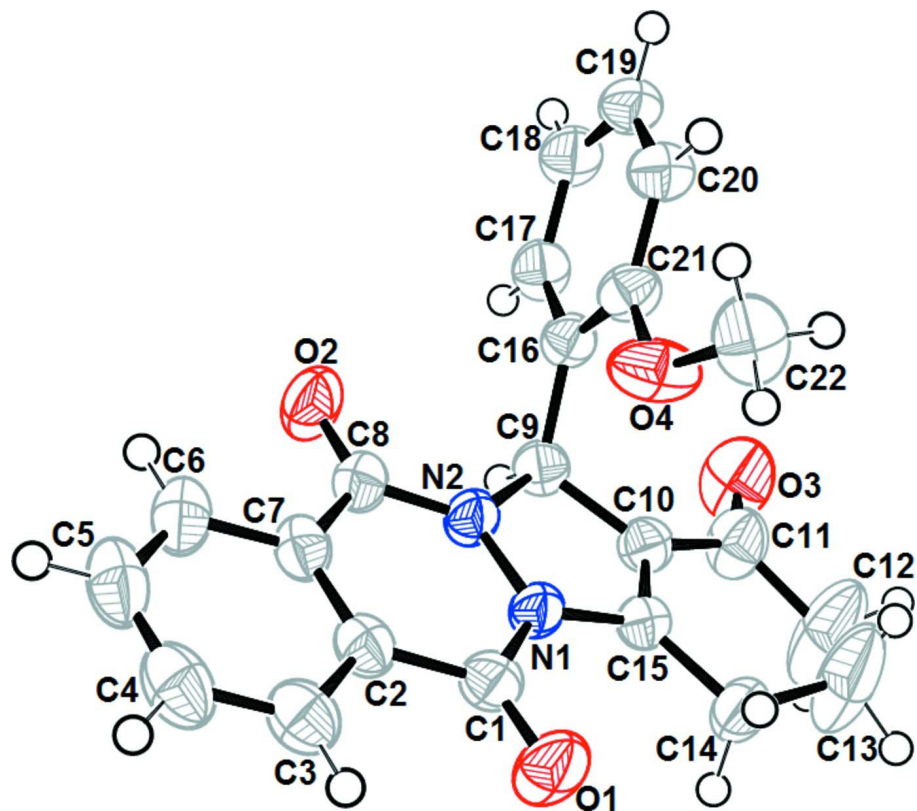
Figure 1

The molecule structure of the title compound, showing the atom labelling. Displacement are drawn at the 50% probability level.
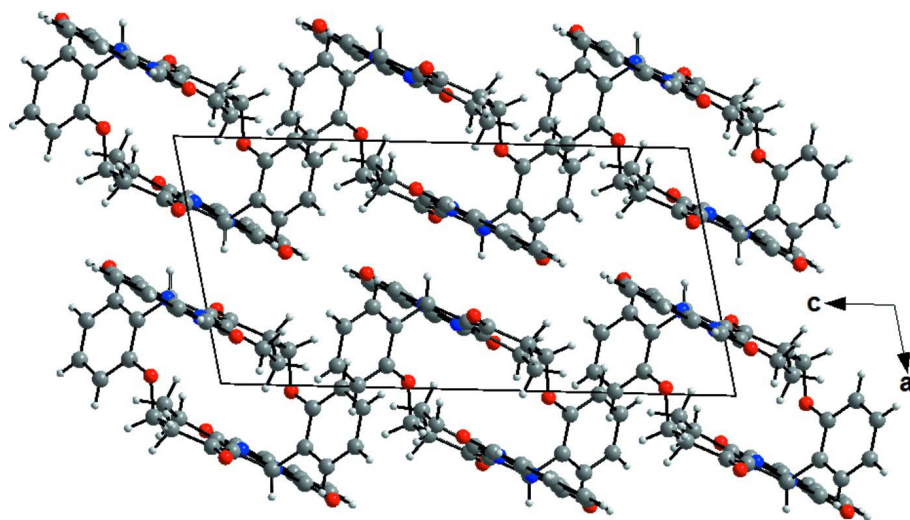
Figure 2

A view along the *b* axis of the crystal packing of the title compound.

13-(2-Methoxyphenyl)-3,4-dihydro-2*H*-indazolo[1,2-*b*]phthalazine-1,6,11(13*H*)-trione

Crystal data

$C_{22}H_{18}N_2O_4$	$F(000) = 784$
$M_r = 374.38$	$D_x = 1.427$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 7478 reflections
$a = 8.5839$ (2) Å	$\theta = 3.0$–30.1°
$b = 11.8474$ (2) Å	$\mu = 0.10$ mm^{-1}
$c = 17.5317$ (4) Å	$T = 295$ K
$\beta = 102.199$ (1)°	Prism, colourless
$V = 1742.66$ (6) Å^3	$0.15 \times 0.11 \times 0.08$ mm
$Z = 4$	

Data collection

Bruker APEXII diffractometer	17655 measured reflections
Radiation source: Enraf Nonius FR590	5142 independent reflections
Graphite monochromator	3865 reflections with $I > 2\sigma(I)$
CCD rotation images, thick slices scans	$R_{int} = 0.02$
Absorption correction: multi-scan (*SADABS*; Bruker, 2011)	$\theta_{max} = 30.2°$, $\theta_{min} = 3.4°$
	$h = -11 \rightarrow 12$
$T_{min} = 0.983$, $T_{max} = 0.991$	$k = -15 \rightarrow 16$
	$l = -24 \rightarrow 24$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.056$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.163$	
$S = 1.03$	H-atom parameters constrained
5142 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0781P)^2 + 0.6856P]$ where $P = (F_o^2 + 2F_c^2)/3$
254 parameters	
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.56$ e Å^{-3}
	$\Delta\rho_{min} = -0.41$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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 (Å²)

	x	y	z	U_{iso}*/U_{eq}
C1	0.74930 (19)	0.02215 (12)	0.50539 (9)	0.0359 (3)
C2	0.68942 (17)	−0.04887 (12)	0.56184 (8)	0.0337 (3)
C3	0.6996 (2)	−0.16641 (14)	0.55560 (10)	0.0430 (4)
H3	0.7435	−0.198	0.5163	0.052*

C4	0.6449 (2)	−0.23529 (15)	0.60752 (12)	0.0490 (4)
H4	0.6524	−0.3133	0.6034	0.059*
C5	0.5787 (2)	−0.18879 (16)	0.66597 (11)	0.0489 (4)
H5	0.5424	−0.2357	0.701	0.059*
C6	0.5665 (2)	−0.07285 (16)	0.67227 (10)	0.0447 (4)
H6	0.5217	−0.0421	0.7115	0.054*
C7	0.62115 (17)	−0.00193 (13)	0.61993 (9)	0.0341 (3)
C8	0.60256 (17)	0.12191 (13)	0.62625 (9)	0.0352 (3)
C9	0.65657 (17)	0.30813 (12)	0.56789 (8)	0.0320 (3)
H9	0.5459	0.3345	0.5569	0.038*
C10	0.72602 (18)	0.32444 (12)	0.49673 (8)	0.0333 (3)
C11	0.7440 (2)	0.43077 (15)	0.45874 (11)	0.0485 (4)
C12	0.8116 (5)	0.4197 (2)	0.38642 (18)	0.0957 (11)
H12A	0.7232	0.4177	0.3416	0.115*
H12B	0.8726	0.4873	0.3818	0.115*
C13	0.9104 (4)	0.3247 (2)	0.38186 (19)	0.0949 (11)
H13A	1.0142	0.3395	0.4148	0.114*
H13B	0.9251	0.3193	0.3286	0.114*
C14	0.8543 (2)	0.21095 (15)	0.40457 (10)	0.0430 (4)
H14A	0.782	0.1775	0.3603	0.052*
H14B	0.9448	0.1608	0.4201	0.052*
C15	0.77157 (17)	0.22582 (12)	0.47050 (8)	0.0320 (3)
C16	0.74875 (17)	0.36667 (12)	0.64012 (8)	0.0315 (3)
C17	0.67423 (19)	0.44961 (13)	0.67530 (9)	0.0382 (3)
H17	0.5667	0.4645	0.6562	0.046*
C18	0.7569 (2)	0.51077 (14)	0.73840 (10)	0.0435 (4)
H18	0.7055	0.5664	0.7612	0.052*
C19	0.9162 (2)	0.48835 (14)	0.76704 (9)	0.0422 (4)
H19	0.9725	0.5296	0.8091	0.051*
C20	0.9930 (2)	0.40511 (14)	0.73373 (9)	0.0402 (3)
H20	1.1001	0.3898	0.7538	0.048*
C21	0.90965 (19)	0.34405 (13)	0.67001 (9)	0.0350 (3)
C22	1.1419 (2)	0.25375 (17)	0.64403 (14)	0.0562 (5)
H22A	1.1802	0.3224	0.6253	0.084*
H22B	1.17	0.1909	0.6151	0.084*
H22C	1.1893	0.2443	0.6984	0.084*
N1	0.73260 (15)	0.13669 (10)	0.51526 (7)	0.0322 (3)
N2	0.65943 (15)	0.18347 (10)	0.57313 (7)	0.0331 (3)
O1	0.80755 (19)	−0.01451 (11)	0.45288 (8)	0.0575 (4)
O2	0.53946 (16)	0.16813 (11)	0.67456 (8)	0.0511 (3)
O3	0.7009 (2)	0.52090 (11)	0.48121 (10)	0.0660 (4)
O4	0.97523 (15)	0.25908 (12)	0.63425 (8)	0.0533 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0434 (8)	0.0281 (7)	0.0371 (7)	−0.0015 (6)	0.0108 (6)	−0.0034 (5)
C2	0.0333 (7)	0.0295 (7)	0.0368 (7)	−0.0023 (5)	0.0038 (5)	0.0018 (5)

C3	0.0455 (9)	0.0316 (8)	0.0503 (9)	0.0000 (6)	0.0063 (7)	0.0012 (7)
C4	0.0474 (9)	0.0334 (8)	0.0614 (11)	−0.0041 (7)	0.0008 (8)	0.0097 (7)
C5	0.0398 (8)	0.0467 (10)	0.0576 (10)	−0.0079 (7)	0.0041 (7)	0.0190 (8)
C6	0.0393 (8)	0.0485 (10)	0.0479 (9)	−0.0041 (7)	0.0129 (7)	0.0096 (7)
C7	0.0293 (6)	0.0348 (7)	0.0378 (7)	−0.0027 (5)	0.0058 (5)	0.0040 (6)
C8	0.0335 (7)	0.0375 (8)	0.0365 (7)	−0.0027 (6)	0.0118 (5)	−0.0010 (6)
C9	0.0334 (7)	0.0283 (7)	0.0354 (7)	0.0020 (5)	0.0094 (5)	−0.0025 (5)
C10	0.0368 (7)	0.0303 (7)	0.0328 (6)	−0.0014 (6)	0.0075 (5)	0.0002 (5)
C11	0.0612 (11)	0.0334 (8)	0.0553 (10)	0.0031 (7)	0.0225 (8)	0.0080 (7)
C12	0.162 (3)	0.0495 (13)	0.105 (2)	0.0176 (16)	0.095 (2)	0.0275 (13)
C13	0.151 (3)	0.0484 (12)	0.118 (2)	0.0047 (15)	0.104 (2)	0.0130 (13)
C14	0.0528 (9)	0.0401 (8)	0.0422 (8)	−0.0032 (7)	0.0242 (7)	−0.0027 (7)
C15	0.0349 (7)	0.0310 (7)	0.0309 (6)	−0.0036 (5)	0.0087 (5)	−0.0010 (5)
C16	0.0368 (7)	0.0270 (6)	0.0323 (6)	0.0008 (5)	0.0107 (5)	−0.0015 (5)
C17	0.0401 (8)	0.0325 (7)	0.0451 (8)	0.0028 (6)	0.0161 (6)	−0.0045 (6)
C18	0.0539 (10)	0.0345 (8)	0.0467 (8)	0.0000 (7)	0.0210 (7)	−0.0113 (7)
C19	0.0536 (9)	0.0381 (8)	0.0366 (7)	−0.0072 (7)	0.0132 (7)	−0.0092 (6)
C20	0.0416 (8)	0.0416 (8)	0.0366 (7)	0.0011 (7)	0.0065 (6)	−0.0040 (6)
C21	0.0408 (8)	0.0312 (7)	0.0342 (7)	0.0049 (6)	0.0104 (6)	−0.0027 (5)
C22	0.0522 (10)	0.0382 (9)	0.0834 (14)	0.0091 (8)	0.0259 (10)	−0.0052 (9)
N1	0.0396 (6)	0.0275 (6)	0.0326 (6)	−0.0021 (5)	0.0145 (5)	−0.0036 (5)
N2	0.0398 (6)	0.0286 (6)	0.0346 (6)	−0.0010 (5)	0.0161 (5)	−0.0038 (5)
O1	0.0913 (10)	0.0349 (6)	0.0579 (8)	0.0002 (6)	0.0419 (7)	−0.0080 (6)
O2	0.0617 (8)	0.0472 (7)	0.0543 (7)	−0.0017 (6)	0.0349 (6)	−0.0038 (6)
O3	0.0920 (11)	0.0336 (7)	0.0801 (10)	0.0118 (7)	0.0353 (9)	0.0094 (6)
O4	0.0429 (6)	0.0565 (8)	0.0566 (7)	0.0165 (6)	0.0016 (5)	−0.0248 (6)

Geometric parameters (Å, º)

C1—O1	1.2168 (19)	C12—H12A	0.97
C1—N1	1.3794 (19)	C12—H12B	0.97
C1—C2	1.472 (2)	C13—C14	1.512 (3)
C2—C7	1.394 (2)	C13—H13A	0.97
C2—C3	1.401 (2)	C13—H13B	0.97
C3—C4	1.377 (2)	C14—C15	1.490 (2)
C3—H3	0.93	C14—H14A	0.97
C4—C5	1.387 (3)	C14—H14B	0.97
C4—H4	0.93	C15—N1	1.3977 (18)
C5—C6	1.384 (3)	C16—C17	1.386 (2)
C5—H5	0.93	C16—C21	1.396 (2)
C6—C7	1.396 (2)	C17—C18	1.386 (2)
C6—H6	0.93	C17—H17	0.93
C7—C8	1.483 (2)	C18—C19	1.379 (3)
C8—O2	1.2266 (18)	C18—H18	0.93
C8—N2	1.3526 (19)	C19—C20	1.382 (2)
C9—N2	1.4797 (19)	C19—H19	0.93
C9—C10	1.504 (2)	C20—C21	1.395 (2)
C9—C16	1.512 (2)	C20—H20	0.93

C9—H9	0.98	C21—O4	1.3684 (18)
C10—C15	1.344 (2)	C22—O4	1.406 (2)
C10—C11	1.448 (2)	C22—H22A	0.96
C11—O3	1.222 (2)	C22—H22B	0.96
C11—C12	1.507 (3)	C22—H22C	0.96
C12—C13	1.422 (4)	N1—N2	1.4143 (16)
O1—C1—N1	121.07 (14)	C14—C13—H13A	107.9
O1—C1—C2	124.22 (14)	C12—C13—H13B	107.9
N1—C1—C2	114.70 (13)	C14—C13—H13B	107.9
C7—C2—C3	119.78 (15)	H13A—C13—H13B	107.2
C7—C2—C1	121.59 (14)	C15—C14—C13	109.23 (15)
C3—C2—C1	118.63 (14)	C15—C14—H14A	109.8
C4—C3—C2	120.11 (17)	C13—C14—H14A	109.8
C4—C3—H3	119.9	C15—C14—H14B	109.8
C2—C3—H3	119.9	C13—C14—H14B	109.8
C3—C4—C5	120.23 (17)	H14A—C14—H14B	108.3
C3—C4—H4	119.9	C10—C15—N1	110.08 (12)
C5—C4—H4	119.9	C10—C15—C14	126.12 (14)
C6—C5—C4	120.21 (16)	N1—C15—C14	123.79 (13)
C6—C5—H5	119.9	C17—C16—C21	118.82 (14)
C4—C5—H5	119.9	C17—C16—C9	119.25 (13)
C5—C6—C7	120.20 (17)	C21—C16—C9	121.84 (12)
C5—C6—H6	119.9	C18—C17—C16	121.27 (15)
C7—C6—H6	119.9	C18—C17—H17	119.4
C2—C7—C6	119.45 (15)	C16—C17—H17	119.4
C2—C7—C8	121.20 (13)	C19—C18—C17	119.40 (14)
C6—C7—C8	119.34 (14)	C19—C18—H18	120.3
O2—C8—N2	120.73 (15)	C17—C18—H18	120.3
O2—C8—C7	124.31 (14)	C18—C19—C20	120.55 (15)
N2—C8—C7	114.96 (13)	C18—C19—H19	119.7
N2—C9—C10	100.10 (11)	C20—C19—H19	119.7
N2—C9—C16	114.01 (12)	C19—C20—C21	119.91 (15)
C10—C9—C16	113.99 (12)	C19—C20—H20	120
N2—C9—H9	109.5	C21—C20—H20	120
C10—C9—H9	109.5	O4—C21—C20	123.87 (14)
C16—C9—H9	109.5	O4—C21—C16	116.07 (13)
C15—C10—C11	122.13 (14)	C20—C21—C16	120.04 (14)
C15—C10—C9	111.54 (13)	O4—C22—H22A	109.5
C11—C10—C9	126.33 (14)	O4—C22—H22B	109.5
O3—C11—C10	122.89 (17)	H22A—C22—H22B	109.5
O3—C11—C12	122.94 (17)	O4—C22—H22C	109.5
C10—C11—C12	114.09 (16)	H22A—C22—H22C	109.5
C13—C12—C11	117.2 (2)	H22B—C22—H22C	109.5
C13—C12—H12A	108	C1—N1—C15	129.00 (12)
C11—C12—H12A	108	C1—N1—N2	123.30 (12)
C13—C12—H12B	108	C15—N1—N2	107.58 (11)
C11—C12—H12B	108	C8—N2—N1	124.21 (12)

H12A—C12—H12B	107.2	C8—N2—C9	125.25 (12)
C12—C13—C14	117.6 (2)	N1—N2—C9	110.53 (11)
C12—C13—H13A	107.9	C21—O4—C22	118.93 (14)
O1—C1—C2—C7	−178.79 (16)	N2—C9—C16—C17	−127.42 (14)
N1—C1—C2—C7	0.2 (2)	C10—C9—C16—C17	118.48 (15)
O1—C1—C2—C3	0.2 (2)	N2—C9—C16—C21	56.20 (18)
N1—C1—C2—C3	179.20 (14)	C10—C9—C16—C21	−57.90 (18)
C7—C2—C3—C4	−1.1 (2)	C21—C16—C17—C18	0.9 (2)
C1—C2—C3—C4	179.91 (15)	C9—C16—C17—C18	−175.63 (15)
C2—C3—C4—C5	0.3 (3)	C16—C17—C18—C19	−0.3 (3)
C3—C4—C5—C6	0.3 (3)	C17—C18—C19—C20	−0.5 (3)
C4—C5—C6—C7	−0.2 (3)	C18—C19—C20—C21	0.8 (3)
C3—C2—C7—C6	1.2 (2)	C19—C20—C21—O4	−178.87 (16)
C1—C2—C7—C6	−179.82 (14)	C19—C20—C21—C16	−0.2 (2)
C3—C2—C7—C8	−177.54 (14)	C17—C16—C21—O4	178.16 (14)
C1—C2—C7—C8	1.4 (2)	C9—C16—C21—O4	−5.4 (2)
C5—C6—C7—C2	−0.6 (2)	C17—C16—C21—C20	−0.6 (2)
C5—C6—C7—C8	178.20 (15)	C9—C16—C21—C20	175.82 (14)
C2—C7—C8—O2	177.83 (15)	O1—C1—N1—C15	1.5 (3)
C6—C7—C8—O2	−1.0 (2)	C2—C1—N1—C15	−177.53 (13)
C2—C7—C8—N2	−1.4 (2)	O1—C1—N1—N2	177.13 (15)
C6—C7—C8—N2	179.86 (14)	C2—C1—N1—N2	−1.9 (2)
N2—C9—C10—C15	−4.23 (16)	C10—C15—N1—C1	175.69 (15)
C16—C9—C10—C15	117.89 (14)	C14—C15—N1—C1	−5.3 (2)
N2—C9—C10—C11	175.59 (16)	C10—C15—N1—N2	−0.45 (16)
C16—C9—C10—C11	−62.3 (2)	C14—C15—N1—N2	178.51 (14)
C15—C10—C11—O3	178.88 (18)	O2—C8—N2—N1	−179.53 (14)
C9—C10—C11—O3	−0.9 (3)	C7—C8—N2—N1	−0.3 (2)
C15—C10—C11—C12	2.2 (3)	O2—C8—N2—C9	1.5 (2)
C9—C10—C11—C12	−177.6 (2)	C7—C8—N2—C9	−179.30 (13)
O3—C11—C12—C13	156.7 (3)	C1—N1—N2—C8	2.1 (2)
C10—C11—C12—C13	−26.6 (4)	C15—N1—N2—C8	178.49 (13)
C11—C12—C13—C14	45.2 (5)	C1—N1—N2—C9	−178.81 (13)
C12—C13—C14—C15	−35.9 (4)	C15—N1—N2—C9	−2.40 (15)
C11—C10—C15—N1	−176.72 (15)	C10—C9—N2—C8	−177.02 (14)
C9—C10—C15—N1	3.11 (17)	C16—C9—N2—C8	60.88 (19)
C11—C10—C15—C14	4.3 (3)	C10—C9—N2—N1	3.88 (14)
C9—C10—C15—C14	−175.83 (14)	C16—C9—N2—N1	−118.22 (13)
C13—C14—C15—C10	11.7 (3)	C20—C21—O4—C22	−20.5 (3)
C13—C14—C15—N1	−167.1 (2)	C16—C21—O4—C22	160.83 (16)

Hydrogen-bond geometry (Å, º)

Cg3 is the centroid of ring C2-C7.

D—H···A	D—H	H···A	D···A	D—H···A
C22—H22B···O1[i]	0.96	2.43	3.379 (2)	168

C20—H20···Cg3[ii]	0.93	2.90	3.726 (2)	149

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