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Crystal structure of 4-[(4-methylbenzyl)oxy]-*N*′-(4-nitrobenzylidene)benzohydrazide: a new hydrazone derivative

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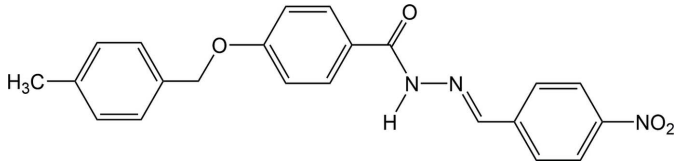
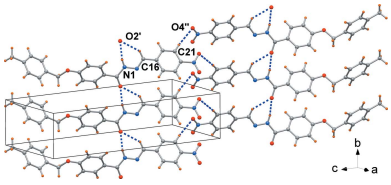
The molecular structure of the title compound, $C_{22}H_{19}N_3O_4$, shows a non-coplanar conformation, with dihedral angles between the phenyl rings of 73.3 (1) and 80.9 (1)°. These deformations are induced by the crystal packing that is mainly governed by N—H···O and C—H···O hydrogen bonds, forming a mono-periodic arrangement parallel to the *b* axis.

1. Chemical context

Hydrazones are a special class of Schiff bases, which can be obtained by condensation between an alkyl or aryl hydrazine and a carbonyl compound (aldehyde or ketone). The active pharmacophore group, —CH═N—NH—C═O—, present in a hydrazone is primarily responsible for its broad spectrum of biological aspects (Taha *et al.*, 2013). The presence of tautomeric forms facilitates their coordination behavior in neutral or anionic species (Banna *et al.*, 2022) with metal ions (Zülfikaroğlu *et al.*, 2020). The chemical diversity and pharmacological accessibility of hydrazone and its derivatives paves the way for research exploring drug design and discovery (Verma *et al.*, 2014).



In this context and in a continuation of our recent work (Banna *et al.*, 2023), we report here on the synthesis and crystal-structure determination of another derivatized aroylhydrazone bearing an ether group.



2. Structural commentary

The molecular structure of the hydrazone compound is shown in Fig. 1. The acyl–hydrazone (—CH═N—NH—C═O—) group connects the *p*-nitrophenyl group and the central phenyl ring, which in turn is bound to the *p*-methylbenzyloxy fragment. An *E*-configuration is observed with respect to the double bond of the hydrazone bridge N2═C16. The N1—N2 bond length of 1.376 (4) Å is slightly shorter than that of

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

D—H···A	D—H	H···A	D···A	D—H···A
C14—H14···N2^{i}	0.95	2.68	3.524 (5)	148
C16—H16···O2^{ii}	0.95	2.45	3.259 (4)	143
C21—H21···O4^{iii}	0.95	2.59	3.532 (5)	171
N1—H1···O2^{ii}	0.90 (4)	2.04 (4)	2.911 (4)	161 (3)

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

1.397 (4) Å determined in the corresponding derivative having a thienyl ring replacing the *p*-nitrophenyl group (Banna *et al.*, 2023). On the other hand, the O2═C15 bond of 1.237 (4) Å is close to that determined in the thienyl derivative [1.236 (4) Å], and typical of a ketonic linkage, while an equilibrium between the keto and enol forms is present in solution. The nitrophenyl group and the benzohydrazone fragment form a dihedral angle of 73.3 (1)° while the terminal 4-methylbenzyl group is rotated by 80.9 (1)° with respect to the central phenyl ring.

Fig. 2 depicts a superimposition of the molecular structure of the title compound with the thienyl derivative (Banna *et al.*, 2023). It is worth noting the different orientations of the carbohydrazide CO—NH—N moiety, likely induced by crystal-packing requirements.

3. Supramolecular features

The crystal packing is governed by hydrogen-bonding interactions (Table 1, with corresponding symmetry codes) realized between the imino group N1—H1 with carbonyl oxygen atom O2^{ii} of a symmetry-related molecule. This results in a mono-periodic arrangement parallel to the *b* axis. In addition, non-classical C16—H16···O2^{ii} hydrogen bonds between a methine group and the carbonyl O atom and C21—H21···O4^{iii} between an aromatic C—H group and one of the nitro O atoms are also present, as shown in Fig. 3. The ribbons are further connected by C14—H14···N2^{i} interactions (Table 1). No significant π-stacking interaction is found in the crystal (all centroid-to-centroid distances between phenyl rings are > 5.0 Å).

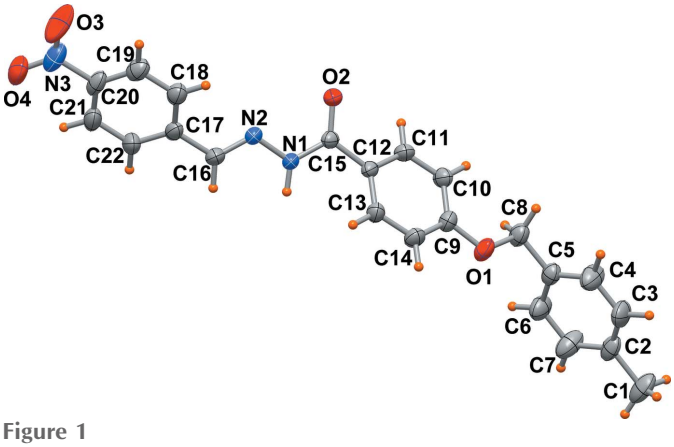


Figure 1
The molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level.

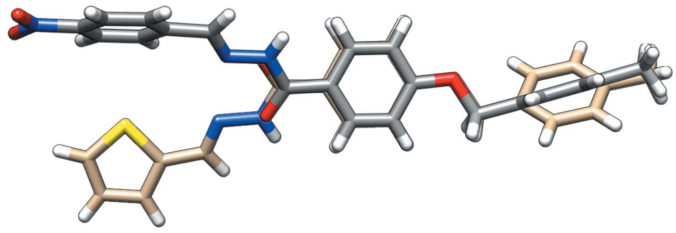


Figure 2
Overlay plot of the molecule of the title compound and the reported thienyl derivative (Banna *et al.*, 2023).

4. Database survey

For a closely related structure with a thienyl moiety, see: Banna *et al.* (2023); for some other aroylhydrazones, see: Ban & Li (2009); Chantrapromma *et al.* (2016); Horkaew *et al.* (2011); Zong & Wu (2013). All these molecules exhibit an *E*-configuration about the double bond of the hydrazone bridge, and they have comparable bond lengths and angles in the C═N—NH—C moiety, in agreement with the present geometrical parameters. For reference bond-length data, see: Allen *et al.* (1987).

5. Synthesis and crystallization

The synthesis of the compound follows a procedure previously described (Banna *et al.*, 2023). To a solution of 4-[(4-methylbenzyl)oxy]benzoylhydrazine (0.25 g, 0.97 mmol in 20 ml of absolute ethanol), a solution of 4-nitrobenzaldehyde (0.14 g, 0.97 mmol) in 5 ml ethanol was added and the mixture was heated and refluxed for 2 h. A colorless precipitate was obtained, filtered off, and washed several times with hot ethanol to eliminate any types of starting materials prior to being dried in a desiccator. The title compound was recrystallized from a mixture of DMF and ethanol. Colorless crystals suitable for X-ray diffraction were obtained after 60 d of keeping the sample solution undisturbed.

Yield: 0.29 g, 79%; melting point (m.p.): 531–533 K; FT–IR: 1636 ν(C═O$_{amide}$), 3315 ν(N—H), 1606 ν(C═N$_{azomethine}$).

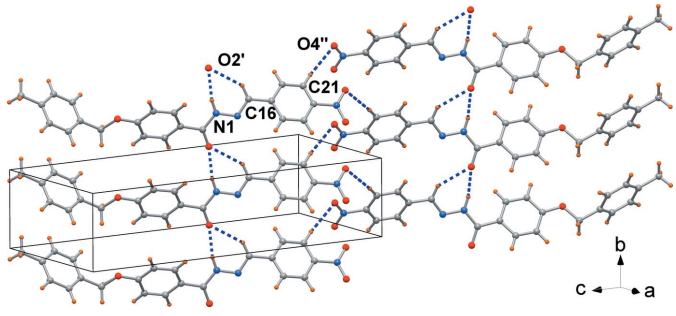


Figure 3
Crystal packing of the title compound showing the mono-periodic arrangement parallel to the *b* axis built by N—H···O and C—H···O hydrogen bonds (dashed lines).

LC–MS (FAB) *m*/*z*: $[M + H]^+$ calculated for $C_{22}H_{19}N_3O_4$; 390.1446; found 390.1448.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Hydrogen atoms were placed at geometrical positions, except for the N—H hydrogen atom, the position of which was located in a difference-Fourier map and freely refined. The Flack parameter of −0.8 (9) indicates that the absolute structure cannot confidently be derived from the data based on Mo radiation.

Acknowledgements

The authors express their gratitude to the Department of Chemistry, University of Rajshahi for laboratory facilities. MCS and RM acknowledge the Center for Environmental Conservation and Research Safety, University of Toyama for providing facilities for single-crystal X-ray analyses.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{22}H_{19}N_3O_4$
M_r	389.40
Crystal system, space group	Monoclinic, $P2_1$
Temperature (K)	173
a, b, c (Å)	8.9485 (8), 5.0612 (5), 20.949 (2)
β (°)	96.585 (7)
V (Å^3)	942.54 (16)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.10
Crystal size (mm)	0.30 × 0.28 × 0.03
Data collection	
Diffractometer	Rigaku R-AXIS RAPID
Absorption correction	Multi-scan (*ABSCOR*; Higashi, 1995)
T_{min}, T_{max}	0.749, 0.997
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	9086, 3799, 2635
R_{int}	0.050
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.053, 0.126, 1.04
No. of reflections	3799
No. of parameters	266
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.19, −0.16
Absolute structure	Unknown: Flack x determined using 741 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter	−0.8 (9)

Computer programs: *RAPID-AUTO* (Rigaku, 2018), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*), *DIAMOND* (Brandenburg, 1999) and *WinGX* (Farrugia, 2012).

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Computing details

Data collection: *RAPID-AUTO* (Rigaku, 2018); cell refinement: *RAPID-AUTO* (Rigaku, 2018); data reduction: *RAPID-AUTO* (Rigaku, 2018); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015b); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

4-[(4-Methylbenzyl)oxy]-*N*′-(4-nitrobenzylidene)benzohydrazide

Crystal data

$C_{22}H_{19}N_3O_4$
M_r = 389.40
Monoclinic, $P2_1$
a = 8.9485 (8) Å
b = 5.0612 (5) Å
c = 20.949 (2) Å
β = 96.585 (7)°
V = 942.54 (16) Å^3
Z = 2
$F(000)$ = 408
D_x = 1.372 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71075 Å
Cell parameters from 5984 reflections
θ = 2.3–27.5°
μ = 0.10 mm^{-1}
T = 173 K
Platel, colorless
0.30 × 0.28 × 0.03 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Detector resolution: 10.000 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.749, T_{max} = 0.997
9086 measured reflections
3799 independent reflections
2635 reflections with $I > 2\sigma(I)$
R_{int} = 0.050
θ_{max} = 27.5°, θ_{min} = 2.0°
h = −11→11
k = −5→6
l = −27→27

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.126
S = 1.03
3799 reflections
266 parameters
1 restraint
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0637P)^2 + 0.0221P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}

Absolute structure: Flack *x* determined using 741 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: −0.8 (9)

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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.1477 (3)	0.5424 (5)	0.66816 (11)	0.0476 (7)
O2	0.3072 (3)	0.1188 (5)	0.39878 (10)	0.0407 (6)
O3	0.7195 (4)	0.3955 (11)	0.04333 (15)	0.0967 (14)
O4	0.5966 (4)	0.7477 (8)	0.00909 (14)	0.0786 (10)
N1	0.3611 (4)	0.5542 (5)	0.38830 (13)	0.0369 (7)
H1	0.354 (4)	0.724 (8)	0.4011 (17)	0.044*
N2	0.4173 (3)	0.5102 (5)	0.33080 (12)	0.0359 (7)
N3	0.6379 (4)	0.5860 (10)	0.05105 (16)	0.0632 (11)
C1	−0.1011 (5)	0.8823 (12)	0.93031 (19)	0.0716 (14)
H1A	−0.136189	1.063016	0.920871	0.086*
H1B	−0.010078	0.886972	0.961152	0.086*
H1C	−0.179652	0.782238	0.948641	0.086*
C2	−0.0660 (4)	0.7506 (9)	0.86904 (16)	0.0472 (10)
C3	0.0290 (5)	0.5425 (10)	0.86983 (18)	0.0648 (13)
H3	0.074131	0.476727	0.909949	0.078*
C4	0.0622 (5)	0.4232 (10)	0.81397 (18)	0.0661 (13)
H4	0.130000	0.278228	0.816291	0.079*
C5	−0.0019 (4)	0.5115 (8)	0.75470 (16)	0.0401 (8)
C6	−0.0974 (5)	0.7189 (9)	0.75353 (18)	0.0554 (11)
H6	−0.143298	0.783136	0.713380	0.067*
C7	−0.1295 (5)	0.8387 (11)	0.80936 (19)	0.0655 (13)
H7	−0.196585	0.984825	0.806939	0.079*
C8	0.0349 (4)	0.3846 (8)	0.69368 (16)	0.0462 (9)
H8A	0.072933	0.203070	0.702463	0.055*
H8B	−0.056490	0.374539	0.662284	0.055*
C9	0.1823 (4)	0.4840 (7)	0.60809 (15)	0.0360 (8)
C10	0.1222 (4)	0.2735 (7)	0.57052 (15)	0.0387 (9)
H10	0.052049	0.156850	0.586470	0.046*
C11	0.1652 (4)	0.2362 (7)	0.51033 (15)	0.0382 (8)
H11	0.123802	0.092481	0.485007	0.046*
C12	0.2679 (4)	0.4034 (6)	0.48530 (15)	0.0311 (8)
C13	0.3289 (4)	0.6103 (7)	0.52395 (15)	0.0388 (8)
H13	0.399403	0.727021	0.508241	0.047*
C14	0.2876 (4)	0.6465 (7)	0.58475 (16)	0.0419 (9)
H14	0.332136	0.785035	0.610979	0.050*

C15	0.3126 (4)	0.3454 (7)	0.42105 (15)	0.0318 (8)
C16	0.4317 (4)	0.7143 (7)	0.29601 (16)	0.0410 (8)
H16	0.404496	0.884332	0.310034	0.049*
C17	0.4910 (4)	0.6807 (7)	0.23383 (16)	0.0405 (9)
C18	0.5876 (5)	0.4754 (8)	0.22322 (18)	0.0463 (9)
H18	0.620600	0.356662	0.257043	0.056*
C19	0.6358 (5)	0.4437 (9)	0.16319 (18)	0.0509 (10)
H19	0.702781	0.304857	0.155381	0.061*
C20	0.5843 (4)	0.6185 (9)	0.11485 (17)	0.0491 (10)
C21	0.4894 (5)	0.8217 (8)	0.12357 (17)	0.0545 (11)
H21	0.455193	0.937239	0.089234	0.065*
C22	0.4445 (5)	0.8546 (8)	0.18362 (17)	0.0526 (10)
H22	0.380496	0.998273	0.191162	0.063*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0515 (15)	0.0606 (18)	0.0328 (13)	−0.0128 (14)	0.0139 (11)	−0.0079 (12)
O2	0.0605 (16)	0.0307 (12)	0.0321 (12)	0.0011 (13)	0.0101 (11)	−0.0015 (11)
O3	0.076 (2)	0.168 (4)	0.0489 (19)	0.040 (3)	0.0199 (16)	−0.007 (2)
O4	0.113 (3)	0.086 (2)	0.0419 (17)	−0.015 (2)	0.0324 (17)	0.0032 (17)
N1	0.0571 (18)	0.0288 (16)	0.0259 (14)	0.0000 (15)	0.0105 (12)	−0.0017 (12)
N2	0.0492 (17)	0.0322 (15)	0.0274 (15)	0.0007 (14)	0.0087 (12)	−0.0020 (12)
N3	0.059 (2)	0.094 (3)	0.038 (2)	−0.011 (2)	0.0142 (17)	−0.008 (2)
C1	0.065 (3)	0.110 (4)	0.043 (2)	−0.008 (3)	0.023 (2)	−0.018 (2)
C2	0.0412 (19)	0.068 (3)	0.035 (2)	−0.014 (2)	0.0156 (15)	−0.0043 (19)
C3	0.092 (3)	0.069 (3)	0.031 (2)	0.011 (3)	−0.002 (2)	0.0080 (19)
C4	0.083 (3)	0.070 (3)	0.044 (2)	0.034 (3)	−0.001 (2)	0.002 (2)
C5	0.0385 (19)	0.049 (2)	0.0337 (18)	−0.0054 (19)	0.0090 (15)	−0.0003 (16)
C6	0.064 (2)	0.065 (3)	0.035 (2)	0.015 (2)	−0.0024 (18)	0.0006 (19)
C7	0.055 (2)	0.094 (4)	0.046 (2)	0.025 (3)	0.0002 (19)	−0.015 (2)
C8	0.048 (2)	0.056 (2)	0.037 (2)	−0.008 (2)	0.0126 (16)	−0.0022 (18)
C9	0.0385 (19)	0.042 (2)	0.0282 (17)	0.0001 (17)	0.0049 (14)	−0.0003 (15)
C10	0.0410 (19)	0.037 (2)	0.0396 (19)	−0.0052 (17)	0.0121 (16)	−0.0015 (16)
C11	0.0473 (19)	0.0326 (17)	0.0349 (19)	−0.0044 (17)	0.0051 (15)	−0.0069 (15)
C12	0.0395 (19)	0.0279 (17)	0.0259 (16)	0.0045 (16)	0.0035 (14)	−0.0016 (13)
C13	0.0467 (19)	0.039 (2)	0.0311 (17)	−0.0066 (18)	0.0073 (15)	−0.0001 (16)
C14	0.049 (2)	0.043 (2)	0.0333 (19)	−0.0072 (19)	0.0019 (15)	−0.0074 (16)
C15	0.0373 (19)	0.0297 (18)	0.0276 (16)	0.0041 (16)	0.0006 (14)	−0.0006 (14)
C16	0.061 (2)	0.0318 (18)	0.0320 (18)	−0.0014 (18)	0.0108 (16)	−0.0054 (15)
C17	0.056 (2)	0.036 (2)	0.0312 (18)	−0.0137 (18)	0.0114 (16)	−0.0051 (15)
C18	0.054 (2)	0.048 (2)	0.038 (2)	−0.008 (2)	0.0104 (17)	−0.0014 (17)
C19	0.051 (2)	0.057 (2)	0.047 (2)	−0.009 (2)	0.0170 (18)	−0.010 (2)
C20	0.051 (2)	0.068 (3)	0.0306 (19)	−0.019 (2)	0.0144 (16)	−0.007 (2)
C21	0.079 (3)	0.054 (3)	0.032 (2)	−0.018 (2)	0.0133 (19)	0.0022 (18)
C22	0.082 (3)	0.040 (2)	0.039 (2)	−0.006 (2)	0.021 (2)	0.0025 (17)

Geometric parameters (Å, º)

O1—C9	1.363 (4)	C8—H8A	0.9900
O1—C8	1.437 (4)	C8—H8B	0.9900
O2—C15	1.237 (4)	C9—C14	1.382 (5)
O3—N3	1.231 (6)	C9—C10	1.395 (5)
O4—N3	1.227 (5)	C10—C11	1.373 (4)
N1—C15	1.358 (4)	C10—H10	0.9500
N1—N2	1.376 (4)	C11—C12	1.395 (5)
N1—H1	0.90 (4)	C11—H11	0.9500
N2—C16	1.279 (4)	C12—C13	1.396 (5)
N3—C20	1.480 (5)	C12—C15	1.477 (4)
C1—C2	1.511 (5)	C13—C14	1.379 (5)
C1—H1A	0.9800	C13—H13	0.9500
C1—H1B	0.9800	C14—H14	0.9500
C1—H1C	0.9800	C16—C17	1.472 (5)
C2—C3	1.353 (6)	C16—H16	0.9500
C2—C7	1.386 (5)	C17—C18	1.385 (5)
C3—C4	1.379 (6)	C17—C22	1.398 (5)
C3—H3	0.9500	C18—C19	1.385 (5)
C4—C5	1.381 (5)	C18—H18	0.9500
C4—H4	0.9500	C19—C20	1.383 (6)
C5—C6	1.352 (6)	C19—H19	0.9500
C5—C8	1.500 (5)	C20—C21	1.360 (6)
C6—C7	1.377 (5)	C21—C22	1.374 (5)
C6—H6	0.9500	C21—H21	0.9500
C7—H7	0.9500	C22—H22	0.9500
C9—O1—C8	117.8 (3)	C14—C9—C10	119.3 (3)
C15—N1—N2	119.1 (3)	C11—C10—C9	119.5 (3)
C15—N1—H1	124 (2)	C11—C10—H10	120.2
N2—N1—H1	117 (2)	C9—C10—H10	120.2
C16—N2—N1	116.0 (3)	C10—C11—C12	121.9 (3)
O4—N3—O3	124.3 (4)	C10—C11—H11	119.1
O4—N3—C20	118.1 (4)	C12—C11—H11	119.1
O3—N3—C20	117.7 (4)	C11—C12—C13	117.9 (3)
C2—C1—H1A	109.5	C11—C12—C15	118.8 (3)
C2—C1—H1B	109.5	C13—C12—C15	123.3 (3)
H1A—C1—H1B	109.5	C14—C13—C12	120.4 (3)
C2—C1—H1C	109.5	C14—C13—H13	119.8
H1A—C1—H1C	109.5	C12—C13—H13	119.8
H1B—C1—H1C	109.5	C13—C14—C9	120.9 (3)
C3—C2—C7	117.0 (4)	C13—C14—H14	119.5
C3—C2—C1	121.6 (4)	C9—C14—H14	119.5
C7—C2—C1	121.4 (4)	O2—C15—N1	122.1 (3)
C2—C3—C4	121.8 (4)	O2—C15—C12	121.7 (3)
C2—C3—H3	119.1	N1—C15—C12	116.2 (3)
C4—C3—H3	119.1	N2—C16—C17	118.7 (3)

C3—C4—C5	120.9 (4)	N2—C16—H16	120.6
C3—C4—H4	119.5	C17—C16—H16	120.6
C5—C4—H4	119.5	C18—C17—C22	119.3 (3)
C6—C5—C4	117.6 (4)	C18—C17—C16	121.6 (3)
C6—C5—C8	121.1 (3)	C22—C17—C16	119.1 (3)
C4—C5—C8	121.2 (4)	C19—C18—C17	119.8 (4)
C5—C6—C7	121.3 (4)	C19—C18—H18	120.1
C5—C6—H6	119.3	C17—C18—H18	120.1
C7—C6—H6	119.3	C20—C19—C18	118.6 (4)
C6—C7—C2	121.4 (4)	C20—C19—H19	120.7
C6—C7—H7	119.3	C18—C19—H19	120.7
C2—C7—H7	119.3	C21—C20—C19	123.1 (3)
O1—C8—C5	108.1 (3)	C21—C20—N3	118.5 (4)
O1—C8—H8A	110.1	C19—C20—N3	118.4 (4)
C5—C8—H8A	110.1	C20—C21—C22	117.9 (4)
O1—C8—H8B	110.1	C20—C21—H21	121.1
C5—C8—H8B	110.1	C22—C21—H21	121.1
H8A—C8—H8B	108.4	C21—C22—C17	121.3 (4)
O1—C9—C14	115.7 (3)	C21—C22—H22	119.3
O1—C9—C10	125.0 (3)	C17—C22—H22	119.3

C15—N1—N2—C16	166.0 (3)	C10—C9—C14—C13	2.9 (5)
C7—C2—C3—C4	0.3 (7)	N2—N1—C15—O2	−5.3 (5)
C1—C2—C3—C4	−179.5 (5)	N2—N1—C15—C12	174.1 (3)
C2—C3—C4—C5	−0.5 (8)	C11—C12—C15—O2	−25.7 (5)
C3—C4—C5—C6	0.2 (7)	C13—C12—C15—O2	151.0 (3)
C3—C4—C5—C8	179.3 (4)	C11—C12—C15—N1	154.8 (3)
C4—C5—C6—C7	0.2 (6)	C13—C12—C15—N1	−28.5 (5)
C8—C5—C6—C7	−178.9 (4)	N1—N2—C16—C17	−179.9 (3)
C5—C6—C7—C2	−0.4 (7)	N2—C16—C17—C18	−27.8 (5)
C3—C2—C7—C6	0.2 (7)	N2—C16—C17—C22	149.9 (4)
C1—C2—C7—C6	179.9 (4)	C22—C17—C18—C19	−0.4 (5)
C9—O1—C8—C5	−170.9 (3)	C16—C17—C18—C19	177.2 (4)
C6—C5—C8—O1	80.9 (4)	C17—C18—C19—C20	−0.6 (5)
C4—C5—C8—O1	−98.2 (5)	C18—C19—C20—C21	0.5 (6)
C8—O1—C9—C14	177.9 (3)	C18—C19—C20—N3	179.1 (4)
C8—O1—C9—C10	−3.5 (5)	O4—N3—C20—C21	1.5 (5)
O1—C9—C10—C11	179.5 (3)	O3—N3—C20—C21	−177.5 (4)
C14—C9—C10—C11	−2.0 (5)	O4—N3—C20—C19	−177.2 (4)
C9—C10—C11—C12	0.0 (5)	O3—N3—C20—C19	3.9 (5)
C10—C11—C12—C13	1.1 (5)	C19—C20—C21—C22	0.7 (6)
C10—C11—C12—C15	177.9 (3)	N3—C20—C21—C22	−177.9 (3)
C11—C12—C13—C14	−0.2 (5)	C20—C21—C22—C17	−1.8 (6)
C15—C12—C13—C14	−176.9 (3)	C18—C17—C22—C21	1.7 (6)
C12—C13—C14—C9	−1.8 (5)	C16—C17—C22—C21	−176.0 (3)
O1—C9—C14—C13	−178.5 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C14—H14···N2^{i}	0.95	2.68	3.524 (5)	148
C16—H16···O2^{ii}	0.95	2.45	3.259 (4)	143
C21—H21···O4^{iii}	0.95	2.59	3.532 (5)	171
N1—H1···O2^{ii}	0.90 (4)	2.04 (4)	2.911 (4)	161 (3)

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