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N-(4-Ethoxyphenyl)-3-oxobutanamide

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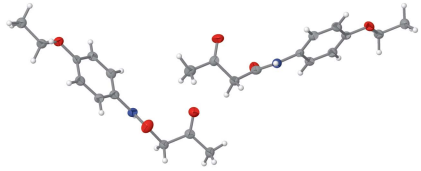
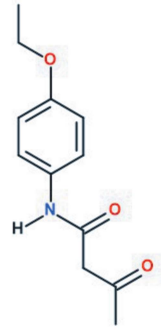
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $C_{12}H_{15}NO_3$, crystallizes with $Z' = 2$ in space group $Pca2_1$ with the two independent molecules having almost the same conformation, differing mostly at the end of the butanamide chain. A local inversion center near 1/8, 3/4, z relates the two molecules, as is common for structures in this space group with $Z' = 2$. The molecule crystallizes as the keto tautomer, and the β-diketone moieties are twisted out of planarity, with O—C···C—O pseudo torsion angles of −74.4 (5) and −83.9 (5)°. The N—H group of each independent molecule donates an intermolecular hydrogen bond to an amide carbonyl oxygen atom by positive or negative translations along the b axis, thus forming antiparallel chains propagating in the [010] direction.

3D view



Chemical scheme



Structure description

N-(4-Ethoxyphenyl)-3-oxobutanamide is a putative intermediate in the biotransformation of bucetin [*N*-(4-ethoxyphenyl)-3-hydroxybutanamide], an analgesic–antipyretic once considered to be a safer alternative for phenacetin (Fujimura & Shinozaki, 1996; Grüssner & Schnider, 1996; Togei *et al.*, 1987). Shibasaki *et al.* (1968) demonstrated that approximately 62% of orally administered bucetin in rabbits is converted to glucuronides of *N*-(4-hydroxyphenyl)-3-oxobutanamide, *N*-(4-hydroxyphenyl)-3-hydroxybutanamide, and *N*-(4-hydroxyphenyl)acetamide. Intravenous administration of bucetin, on the other hand, mainly resulted in the formation of the glucuronide of *N*-(4-hydroxyphenyl)acetamide, with a maximum yield of 98%. These findings indicate that oxidative *O*-de-ethylation, keto conversion, and γ-decarboxylation are involved in the biotransformation of bucetin, leading to the endogenous production of *N*-(4-hydroxyphenyl)acetamide, the relevant analgesic compound. However, the specific order of *O*-de-ethylation and keto conversion remains uncertain (Shibasaki *et al.*, 1968).

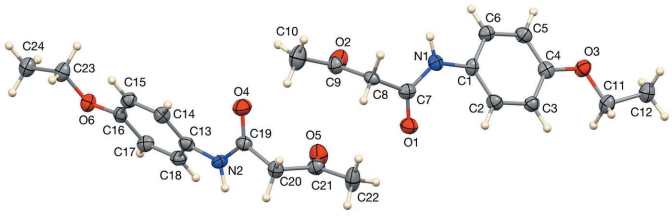


Figure 1
The asymmetric unit of the title compound showing 50% displacement ellipsoids.

The molecular structure of *N*-(4-ethoxyphenyl)-3-oxobutanamide, $C_{12}H_{15}NO_3$, contains a β-diketone functionality that is similar in nature to the one present in linear and cyclic 1,3-diketone compounds (Hansen, 2021; Shokova *et al.*, 2015). Understandably, the diketone functionality also exists in its enol tautomeric form. This structural characteristic makes the amide side chain susceptible to electrophilic substitution reactions, particularly with oxidizing agents in the cellular milieu such as peroxynitrite ($O{=}NOO^-$)-peroxynitrous acid (O=NOOH; p$K_a \simeq 6.8$) and hypochlorite ($^-$OCl)-hypochlorous acid (HOCl; p$K_a \simeq 7.5$) conjugate acid–base systems (Agu *et al.*, 2020; Uppu & Pryor, 1996; Zhang & Banwell, 2011). Furthermore, the keto conversion process of bucetin eliminates the chiral center, potentially facilitating the formation of various types of metal-ion chelates (Basak & Singh, 2015; Karki *et al.*, 2016). To further comprehend the processes and potential implications for the overall toxicity of bucetin and its congeners, in the present study, the crystal structure of the title compound is reported.

The title compound, shown in Fig. 1, crystallizes with two independent molecules in the asymmetric unit. The conformations of the two molecules are quite similar, with the largest difference being at the end of the butanamide chain (O2—C9—C10 and O5—C21—C22). An overlay of the two molecules (Fig. 2) shows the small difference, with r.m.s. deviation = 0.10 Å and maximum deviation 0.30 (1) Å for C10···C22. This small difference in conformation can also be seen in torsion angles describing the twist of the β-diketone units, −74.4 (5)° for O1—C7···C9—O2 and −83.9 (5)° for O4—C19···C21—O5.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*···O1^{i}	0.92 (6)	1.98 (6)	2.878 (6)	165 (5)
N2—H2*N*···O4^{ii}	0.89 (7)	1.98 (7)	2.856 (6)	168 (5)

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

The N—H moiety in both molecules donates an intermolecular hydrogen bond (Table 1) to amide carbonyl oxygen atoms as shown in Fig. 3. The N1···O1 (at $x, y-1, z$) distance is 2.878 (6) Å and the N2···O4 (at $x, y+1, z$) distance is 2.856 (6) Å. Thus, the two independent molecules form antiparallel chains in the [010] direction, as shown in Fig. 3.

The unit cell is illustrated in Fig. 4, which shows local approximate inversion centers at 0.123 0.737, 0.750 and 0.623, 0.263, 0.750. Marsh *et al.* (1998) have shown that approximately 75% of structures with $Z' = 2$ in space groups $Pca2_1$ and

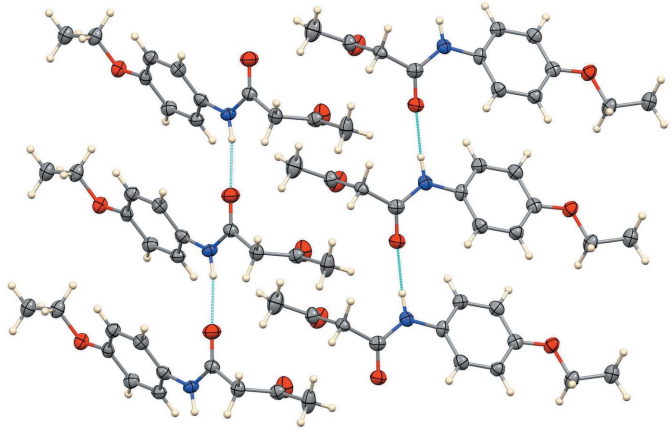


Figure 3
Partial packing diagram with N—H···O hydrogen bonds shown as blue lines.

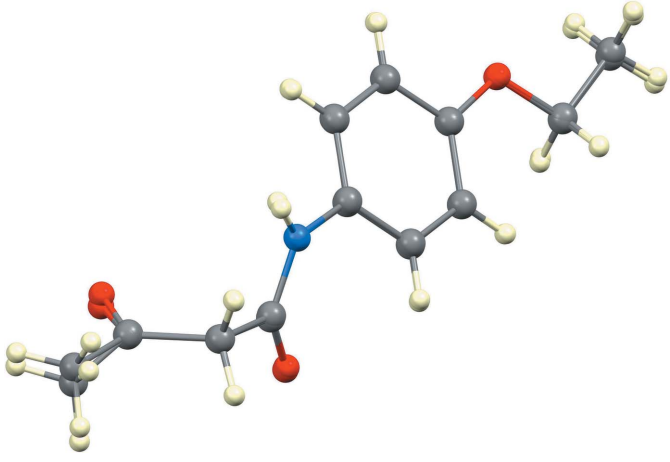


Figure 2
Overlay of the two independent molecules.

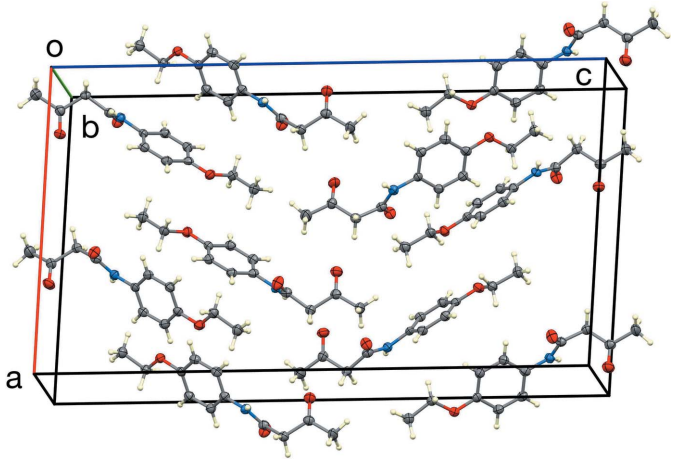


Figure 4
The unit-cell packing, viewed approximately down [010].

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{12}H_{15}NO_3$
M_r	221.25
Crystal system, space group	Orthorhombic, $Pca2_1$
Temperature (K)	100
a, b, c (Å)	16.4113 (8), 4.9076 (3), 28.8889 (15)
V (Å^3)	2326.7 (2)
Z	8
Radiation type	Cu $K\alpha$
μ (mm^{-1})	0.75
Crystal size (mm)	0.31 × 0.09 × 0.03
Data collection	
Diffractometer	Bruker Kappa APEXII CCD DUO
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.732, 0.978
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	16274, 4191, 3503
R_{int}	0.061
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.603
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.058, 0.156, 1.04
No. of reflections	4191
No. of parameters	299
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})	0.20, −0.32
Absolute structure	Flack x determined using 1426 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013).
Absolute structure parameter	0.3 (3)

Computer programs: *APEX2* and *SAINT* (Bruker, 2016), *SHELXT2014/5* (Sheldrick, 2008), *SHELXL2017/1* (Sheldrick, 2015), *Mercury* (Macrae *et al.*, 2020), and *publCIF* (Westrip, 2010).

$Pna2_1$ have such local centers and that in $Pca2_1$, the local centers tend to be near 1/8, 1/4, z. This agrees well with what we observe in the title structure, after an origin shift of x – 1/2 or y – 1/2.

Synthesis and crystallization

N-(4-Ethoxyphenyl)-3-oxobutanamide, $C_{12}H_{15}NO_3$ (CAS No. 122–87-2) was obtained from AmBeed, Arlington Heights, IL, USA and was used without further purification. Crystals in the form of colorless laths were prepared by slow cooling of a nearly saturated solution of the title compound in boiling deionized water.

Refinement

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

Funding information

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full crystallographic data

IUCrData (2023). **8**, x230565 [https://doi.org/10.1107/S2414314623005655]

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Crystal data

$C_{12}H_{15}NO_3$
M_r = 221.25
Orthorhombic, $Pca2_1$
a = 16.4113 (8) Å
b = 4.9076 (3) Å
c = 28.8889 (15) Å
V = 2326.7 (2) Å^3
Z = 8
$F(000)$ = 944
D_x = 1.263 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54184 Å
Cell parameters from 3285 reflections
θ = 3.1–68.1°
μ = 0.75 mm^{-1}
T = 100 K
Lath, colourless
0.31 × 0.09 × 0.03 mm

Data collection

Bruker Kappa APEXII CCD DUO diffractometer
Radiation source: IμS microfocus
QUAZAR multilayer optics monochromator
φ and ω scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
T_{min} = 0.732, T_{max} = 0.978
16274 measured reflections
4191 independent reflections
3503 reflections with $I > 2\sigma(I)$
R_{int} = 0.061
θ_{max} = 68.4°, θ_{min} = 3.1°
h = −19→19
k = −5→5
l = −34→34

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.156
S = 1.04
4191 reflections
299 parameters
1 restraint
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1042P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}
Absolute structure: Flack x determined using 1426 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013).
Absolute structure parameter: 0.3 (3)

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.

Refinement. All H atoms were located in difference maps and those on C were thereafter treated as riding in geometrically idealized positions with C—H distances of 0.95 Å for phenyl, 0.99 Å for CH_2, and 0.98 Å for methyl. The coordinates of the N-bound H atoms were refined. U_{iso}(H) values were assigned as $1.2U_{eq}$ for the attached atom (1.5 for methyl).

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.4059 (2)	0.8722 (7)	0.59122 (13)	0.0370 (8)
O2	0.3364 (2)	0.5583 (9)	0.49998 (18)	0.0416 (10)
O3	0.1960 (2)	0.5495 (8)	0.77556 (15)	0.0318 (9)
N1	0.3749 (2)	0.4356 (10)	0.61261 (17)	0.0279 (9)
H1N	0.376 (3)	0.257 (13)	0.603 (2)	0.034*
C1	0.3280 (4)	0.4895 (9)	0.6532 (2)	0.0253 (13)
C2	0.3476 (3)	0.6947 (10)	0.68408 (16)	0.0291 (10)
H2	0.390918	0.816564	0.677246	0.035*
C3	0.3040 (3)	0.7231 (10)	0.72522 (17)	0.0284 (9)
H3	0.317128	0.865235	0.746269	0.034*
C4	0.2411 (3)	0.5422 (10)	0.7353 (2)	0.0271 (12)
C5	0.2219 (3)	0.3388 (10)	0.70439 (17)	0.0309 (10)
H5	0.178674	0.216337	0.711170	0.037*
C6	0.2650 (3)	0.3111 (10)	0.66356 (16)	0.0286 (9)
H6	0.251432	0.169414	0.642516	0.034*
C7	0.4104 (2)	0.6254 (10)	0.58497 (18)	0.0295 (10)
C8	0.4576 (4)	0.5086 (9)	0.5444 (3)	0.0255 (12)
H8A	0.507672	0.617418	0.539584	0.031*
H8B	0.474213	0.319620	0.551754	0.031*
C9	0.4082 (4)	0.5078 (10)	0.5000 (3)	0.0323 (13)
C10	0.4544 (4)	0.4355 (16)	0.4575 (3)	0.0487 (15)
H10A	0.416301	0.407453	0.431853	0.073*
H10B	0.485339	0.267644	0.462942	0.073*
H10C	0.492058	0.583596	0.449776	0.073*
C11	0.2132 (3)	0.7601 (11)	0.80814 (18)	0.0326 (10)
H11A	0.198941	0.940344	0.795033	0.039*
H11B	0.271821	0.760281	0.816206	0.039*
C12	0.1621 (3)	0.7016 (11)	0.85056 (17)	0.0370 (11)
H12A	0.104273	0.701628	0.842045	0.055*
H12B	0.171948	0.842421	0.873961	0.055*
H12C	0.176886	0.523000	0.863171	0.055*
O4	0.6561 (2)	0.6038 (8)	0.40666 (14)	0.0420 (8)
O5	0.5875 (2)	0.9503 (9)	0.49781 (19)	0.0435 (10)
O6	0.4501 (2)	0.9546 (7)	0.22415 (15)	0.0301 (8)
N2	0.6290 (3)	1.0406 (9)	0.38715 (18)	0.0264 (10)
H2N	0.641 (3)	1.208 (13)	0.397 (2)	0.032*
C13	0.5832 (4)	0.9997 (9)	0.3459 (3)	0.0276 (14)
C14	0.6010 (3)	0.7971 (10)	0.31464 (16)	0.0288 (10)
H14	0.643442	0.671498	0.321243	0.035*
C15	0.5576 (3)	0.7736 (10)	0.27343 (16)	0.0297 (10)

H15	0.570438	0.632640	0.252109	0.036*
C16	0.4955 (3)	0.9561 (10)	0.2636 (2)	0.0261 (11)
C17	0.4762 (3)	1.1597 (11)	0.29542 (17)	0.0294 (10)
H17	0.433225	1.283796	0.289051	0.035*
C18	0.5197 (3)	1.1807 (10)	0.33630 (16)	0.0291 (10)
H18	0.506319	1.319142	0.357984	0.035*
C19	0.6629 (3)	0.8490 (10)	0.41366 (16)	0.0276 (9)
C20	0.7110 (4)	0.9482 (12)	0.4546 (2)	0.0309 (12)
H20A	0.731238	1.134403	0.448221	0.037*
H20B	0.758851	0.828301	0.459146	0.037*
C21	0.6607 (3)	0.9520 (11)	0.4987 (3)	0.0314 (12)
C22	0.7074 (4)	0.9522 (15)	0.5434 (3)	0.0468 (16)
H22A	0.670234	0.993332	0.569083	0.070*
H22B	0.750265	1.090863	0.542116	0.070*
H22C	0.732011	0.772620	0.548316	0.070*
C23	0.4662 (3)	0.7422 (10)	0.19102 (18)	0.0321 (10)
H23A	0.451954	0.562321	0.204233	0.038*
H23B	0.524691	0.740870	0.182612	0.038*
C24	0.4147 (3)	0.8001 (11)	0.14883 (17)	0.0360 (11)
H24A	0.357062	0.805463	0.157740	0.054*
H24B	0.423055	0.656115	0.125810	0.054*
H24C	0.430410	0.976165	0.135568	0.054*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0448 (18)	0.028 (2)	0.0384 (19)	−0.0009 (15)	0.0072 (15)	−0.0003 (16)
O2	0.0267 (19)	0.059 (2)	0.039 (2)	0.0075 (17)	−0.0055 (16)	−0.007 (2)
O3	0.0274 (18)	0.0360 (19)	0.032 (2)	−0.0007 (14)	0.0038 (15)	−0.0065 (17)
N1	0.027 (2)	0.029 (2)	0.028 (2)	0.0025 (16)	−0.0001 (18)	0.003 (2)
C1	0.020 (2)	0.034 (3)	0.022 (3)	0.0030 (16)	−0.003 (2)	0.0009 (16)
C2	0.0237 (19)	0.032 (3)	0.031 (2)	−0.0030 (17)	−0.0004 (17)	0.0022 (19)
C3	0.029 (2)	0.028 (2)	0.029 (2)	−0.0017 (17)	−0.0030 (18)	−0.0004 (19)
C4	0.021 (2)	0.029 (2)	0.031 (3)	0.0067 (17)	−0.001 (2)	0.004 (2)
C5	0.0256 (19)	0.032 (2)	0.035 (2)	−0.0019 (18)	0.0008 (17)	0.002 (2)
C6	0.027 (2)	0.028 (2)	0.030 (2)	0.0009 (18)	−0.0037 (18)	−0.0004 (18)
C7	0.026 (2)	0.029 (3)	0.034 (2)	0.0003 (18)	−0.0044 (18)	−0.001 (2)
C8	0.025 (2)	0.022 (2)	0.030 (3)	0.0018 (15)	0.001 (2)	0.0024 (16)
C9	0.032 (3)	0.036 (3)	0.029 (3)	0.0005 (17)	−0.002 (2)	0.0024 (18)
C10	0.038 (3)	0.073 (4)	0.036 (3)	0.008 (3)	−0.002 (3)	−0.004 (3)
C11	0.027 (2)	0.041 (3)	0.030 (2)	0.002 (2)	0.0008 (18)	−0.005 (2)
C12	0.036 (2)	0.045 (3)	0.029 (2)	0.002 (2)	0.002 (2)	−0.002 (2)
O4	0.057 (2)	0.030 (2)	0.0396 (19)	0.0004 (16)	−0.0100 (17)	−0.0013 (16)
O5	0.031 (2)	0.061 (3)	0.039 (2)	−0.0039 (16)	−0.0005 (17)	0.006 (2)
O6	0.0274 (17)	0.0349 (18)	0.0280 (19)	0.0050 (14)	−0.0025 (15)	−0.0017 (16)
N2	0.026 (2)	0.024 (2)	0.028 (2)	−0.0023 (15)	−0.0042 (17)	−0.0044 (17)
C13	0.024 (3)	0.027 (3)	0.032 (4)	−0.0048 (15)	−0.001 (2)	0.0032 (17)
C14	0.0260 (19)	0.030 (3)	0.030 (2)	0.0006 (18)	−0.0009 (18)	0.0012 (19)

C15	0.028 (2)	0.032 (3)	0.029 (2)	−0.0021 (18)	0.0019 (18)	−0.0038 (18)
C16	0.023 (2)	0.033 (2)	0.023 (3)	−0.0039 (18)	0.003 (2)	0.001 (2)
C17	0.026 (2)	0.029 (2)	0.034 (2)	0.0025 (18)	0.0022 (16)	−0.002 (2)
C18	0.030 (2)	0.024 (2)	0.033 (2)	−0.0001 (18)	0.0034 (18)	−0.0014 (19)
C19	0.027 (2)	0.026 (3)	0.031 (2)	0.0010 (18)	−0.0004 (17)	0.0006 (19)
C20	0.027 (2)	0.037 (3)	0.029 (3)	−0.001 (2)	0.001 (2)	0.000 (2)
C21	0.028 (3)	0.032 (3)	0.035 (3)	−0.0023 (19)	0.000 (2)	−0.001 (2)
C22	0.034 (3)	0.081 (4)	0.025 (3)	−0.005 (3)	−0.002 (2)	0.001 (3)
C23	0.026 (2)	0.041 (3)	0.029 (2)	0.0041 (19)	0.0003 (18)	−0.004 (2)
C24	0.033 (2)	0.044 (3)	0.030 (2)	0.001 (2)	−0.0009 (19)	−0.004 (2)

Geometric parameters (Å, º)

O1—C7	1.227 (6)	O4—C19	1.226 (6)
O2—C9	1.205 (7)	O5—C21	1.201 (7)
O3—C4	1.379 (8)	O6—C16	1.361 (8)
O3—C11	1.426 (6)	O6—C23	1.440 (6)
N1—C7	1.358 (7)	N2—C19	1.334 (7)
N1—C1	1.427 (8)	N2—C13	1.424 (9)
N1—H1N	0.92 (6)	N2—H2N	0.89 (7)
C1—C2	1.383 (8)	C13—C14	1.375 (8)
C1—C6	1.388 (8)	C13—C18	1.396 (7)
C2—C3	1.394 (7)	C14—C15	1.392 (7)
C2—H2	0.9500	C14—H14	0.9500
C3—C4	1.393 (7)	C15—C16	1.386 (8)
C3—H3	0.9500	C15—H15	0.9500
C4—C5	1.376 (8)	C16—C17	1.394 (7)
C5—C6	1.382 (7)	C17—C18	1.384 (7)
C5—H5	0.9500	C17—H17	0.9500
C6—H6	0.9500	C18—H18	0.9500
C7—C8	1.518 (8)	C19—C20	1.503 (8)
C8—C9	1.516 (10)	C20—C21	1.518 (9)
C8—H8A	0.9900	C20—H20A	0.9900
C8—H8B	0.9900	C20—H20B	0.9900
C9—C10	1.485 (11)	C21—C22	1.502 (10)
C10—H10A	0.9800	C22—H22A	0.9800
C10—H10B	0.9800	C22—H22B	0.9800
C10—H10C	0.9800	C22—H22C	0.9800
C11—C12	1.513 (7)	C23—C24	1.511 (7)
C11—H11A	0.9900	C23—H23A	0.9900
C11—H11B	0.9900	C23—H23B	0.9900
C12—H12A	0.9800	C24—H24A	0.9800
C12—H12B	0.9800	C24—H24B	0.9800
C12—H12C	0.9800	C24—H24C	0.9800
C4—O3—C11	118.0 (4)	C16—O6—C23	117.4 (4)
C7—N1—C1	125.9 (5)	C19—N2—C13	127.0 (4)
C7—N1—H1N	118 (4)	C19—N2—H2N	112 (4)

C1—N1—H1N	116 (4)	C13—N2—H2N	121 (4)
C2—C1—C6	119.6 (6)	C14—C13—C18	119.2 (6)
C2—C1—N1	122.6 (5)	C14—C13—N2	122.6 (5)
C6—C1—N1	117.5 (5)	C18—C13—N2	118.1 (5)
C1—C2—C3	120.2 (5)	C13—C14—C15	120.9 (5)
C1—C2—H2	119.9	C13—C14—H14	119.6
C3—C2—H2	119.9	C15—C14—H14	119.6
C4—C3—C2	119.7 (5)	C16—C15—C14	119.9 (5)
C4—C3—H3	120.2	C16—C15—H15	120.1
C2—C3—H3	120.2	C14—C15—H15	120.1
C5—C4—O3	116.3 (5)	O6—C16—C15	124.8 (5)
C5—C4—C3	119.8 (5)	O6—C16—C17	115.6 (5)
O3—C4—C3	123.9 (5)	C15—C16—C17	119.6 (5)
C4—C5—C6	120.6 (5)	C18—C17—C16	119.9 (5)
C4—C5—H5	119.7	C18—C17—H17	120.0
C6—C5—H5	119.7	C16—C17—H17	120.0
C5—C6—C1	120.2 (5)	C17—C18—C13	120.4 (5)
C5—C6—H6	119.9	C17—C18—H18	119.8
C1—C6—H6	119.9	C13—C18—H18	119.8
O1—C7—N1	124.4 (5)	O4—C19—N2	124.0 (4)
O1—C7—C8	121.1 (4)	O4—C19—C20	119.7 (4)
N1—C7—C8	114.5 (4)	N2—C19—C20	116.3 (4)
C9—C8—C7	112.4 (5)	C19—C20—C21	112.3 (5)
C9—C8—H8A	109.1	C19—C20—H20A	109.1
C7—C8—H8A	109.1	C21—C20—H20A	109.1
C9—C8—H8B	109.1	C19—C20—H20B	109.1
C7—C8—H8B	109.1	C21—C20—H20B	109.1
H8A—C8—H8B	107.8	H20A—C20—H20B	107.9
O2—C9—C10	123.2 (7)	O5—C21—C22	121.9 (7)
O2—C9—C8	121.5 (7)	O5—C21—C20	121.7 (7)
C10—C9—C8	115.2 (5)	C22—C21—C20	116.4 (5)
C9—C10—H10A	109.5	C21—C22—H22A	109.5
C9—C10—H10B	109.5	C21—C22—H22B	109.5
H10A—C10—H10B	109.5	H22A—C22—H22B	109.5
C9—C10—H10C	109.5	C21—C22—H22C	109.5
H10A—C10—H10C	109.5	H22A—C22—H22C	109.5
H10B—C10—H10C	109.5	H22B—C22—H22C	109.5
O3—C11—C12	106.7 (4)	O6—C23—C24	107.3 (4)
O3—C11—H11A	110.4	O6—C23—H23A	110.3
C12—C11—H11A	110.4	C24—C23—H23A	110.3
O3—C11—H11B	110.4	O6—C23—H23B	110.3
C12—C11—H11B	110.4	C24—C23—H23B	110.3
H11A—C11—H11B	108.6	H23A—C23—H23B	108.5
C11—C12—H12A	109.5	C23—C24—H24A	109.5
C11—C12—H12B	109.5	C23—C24—H24B	109.5
H12A—C12—H12B	109.5	H24A—C24—H24B	109.5
C11—C12—H12C	109.5	C23—C24—H24C	109.5
H12A—C12—H12C	109.5	H24A—C24—H24C	109.5

H12B—C12—H12C	109.5	H24B—C24—H24C	109.5
C7—N1—C1—C2	−38.1 (8)	C19—N2—C13—C14	−35.7 (9)
C7—N1—C1—C6	147.9 (5)	C19—N2—C13—C18	146.8 (5)
C6—C1—C2—C3	−0.4 (7)	C18—C13—C14—C15	1.1 (8)
N1—C1—C2—C3	−174.3 (5)	N2—C13—C14—C15	−176.3 (5)
C1—C2—C3—C4	0.6 (7)	C13—C14—C15—C16	0.0 (7)
C11—O3—C4—C5	−179.0 (4)	C23—O6—C16—C15	2.1 (7)
C11—O3—C4—C3	2.0 (7)	C23—O6—C16—C17	−178.0 (4)
C2—C3—C4—C5	−0.7 (7)	C14—C15—C16—O6	178.9 (5)
C2—C3—C4—O3	178.2 (4)	C14—C15—C16—C17	−1.0 (7)
O3—C4—C5—C6	−178.5 (4)	O6—C16—C17—C18	−179.1 (4)
C3—C4—C5—C6	0.5 (7)	C15—C16—C17—C18	0.9 (7)
C4—C5—C6—C1	−0.3 (7)	C16—C17—C18—C13	0.2 (7)
C2—C1—C6—C5	0.3 (7)	C14—C13—C18—C17	−1.2 (8)
N1—C1—C6—C5	174.5 (5)	N2—C13—C18—C17	176.3 (5)
C1—N1—C7—O1	−0.7 (8)	C13—N2—C19—O4	−3.0 (9)
C1—N1—C7—C8	179.3 (5)	C13—N2—C19—C20	177.8 (5)
O1—C7—C8—C9	−82.6 (6)	O4—C19—C20—C21	−83.8 (6)
N1—C7—C8—C9	97.4 (5)	N2—C19—C20—C21	95.4 (5)
C7—C8—C9—O2	−10.0 (7)	C19—C20—C21—O5	−19.3 (8)
C7—C8—C9—C10	171.2 (5)	C19—C20—C21—C22	159.5 (5)
C4—O3—C11—C12	−174.0 (4)	C16—O6—C23—C24	−174.6 (4)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*···O1^{i}	0.92 (6)	1.98 (6)	2.878 (6)	165 (5)
N2—H2*N*···O4^{ii}	0.89 (7)	1.98 (7)	2.856 (6)	168 (5)

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