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Crystal structure and Hirshfeld surface analysis of 2-oxo-2-phenylethyl 3-nitroso-2-phenylimidazo-[1,2-*a*]pyridine-8-carboxylate

Fouad El Kalai,[a] Cemile Baydere,[b]* Necmi Dege,[b] Abdulmalik Abudunia,[c]* Noureddine Benchat[a] and Khalid Karrouchi[d]

[a]Laboratory of Applied Chemistry and Environment (LCAE), Faculty of Sciences, Mohammed I University, 60000 Oujda, Morocco, [b]Department of Physics, Faculty of Arts and Sciences, Ondokuz Mayıs University, 55139-Samsun, Turkey, [c]Department of Pharmacology, Faculty of Clinical Pharmacy, University of Medical and Applied Sciences, Yemen, and [d]Laboratory of Analytical Chemistry and Bromatology, Faculty of Medicine and Pharmacy, Mohammed V University in Rabat, Morocco. *Correspondence e-mail: cemle28baydere@hotmail.com, abdulmalikabudunia@gmail.com

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The title compound, $C_{22}H_{15}N_3O_4$, is built up from a central imidazo[1,2-*a*]-pyridine ring system connected to a nitroso group, a phenyl ring and a 2-oxo-2-phenylethyl acetate group. The imidazo[1,2-*a*] pyridine ring system is almost planar (r.m.s. deviation = 0.017 Å) and forms dihedral angles of 22.74 (5) and 45.37 (5)°, respectively, with the phenyl ring and the 2-oxo-2-phenylethyl acetate group. In the crystal, the molecules are linked into chains parallel to the *b* axis by C—H···O hydrogen bonds, generating R_2^1 (5) and R_4^4 (28) graph-set motifs. The chains are further linked into a three-dimensional network by C—H···π and π-stacking interactions. The intermolecular interactions were investigated using Hirshfeld surface analysis and two-dimensional fingerprint plots, revealing that the most important contributions for the crystal packing are from H···H (36.2%), H···C/C···H (20.5%), H···O/O···H (20.0%), C···O/O···C (6.5%), C···N/N···C (6.2%), H···N/N···H (4.5%) and C···C (4.3%) interactions.

1. Chemical context

Numerous drugs contain *N*-heterocycles as the core structure, including imidazo[1,2-*a*]pyridine and its derivatives, which are used in medicinal chemistry (Swainston Harrison & Keating, 2005; Deep *et al.*, 2017) or that exhibit diverse biological properties, such as antibacterial (Mishra *et al.*, 2021), anti-tubercular (Wang *et al.*, 2019), tyrosinase inhibitory (Damghani *et al.*, 2020), HIV inhibitory (Bode *et al.*, 2011), antidiabetic (Saeedi *et al.*, 2021), anti-inflammatory (Gundlewad *et al.*, 2020) or anticancer activities (Yu *et al.*, 2020; Sigalapalli *et al.*, 2021). Encouraged by these features and in a continuation of our exploration of the synthesis, molecular structures and Hirshfeld surface analysis of new *N*-heterocyclic compounds (Daoui *et al.*, 2021, 2022; El Kalai *et al.*, 2021*a*,*b*), we report herein the crystal structure and Hirshfeld surface analysis of 2-oxo-2-phenylethyl 3-nitroso-2-phenylimidazo[1,2-*a*]pyridine-8-carboxylate, $C_{22}H_{15}N_3O_4$ (I).

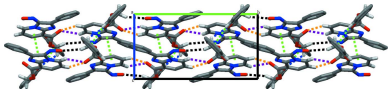

Table 1
Hydrogen-bond geometry (Å, °).

*Cg*4 is the centroid of the C17–C22 phenyl ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C15—H15*A*···O4^{i}	0.97	2.54	3.1257 (19)	119
C15—H15*B*···O1^{ii}	0.97	2.61	3.4841 (18)	150
C9—H9···O2^{iii}	0.93	2.46	3.1176 (16)	128
C10—H10···O2^{iii}	0.93	2.67	3.2243 (17)	119
C9—H9···O1	0.93	2.35	2.8736 (18)	116
C1—H1···N1	0.93	2.51	3.081 (2)	120
C22—H22···*Cg*4^{iv}	0.93	2.80	3.657 (2)	153

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

2. Structural commentary

The molecular structure of (I) is shown in Fig. 1. The imidazo[1,2-*a*] pyridine ring system is planar with an r.m.s deviation of 0.017 Å and a maximum deviation of 0.028 (1) Å for atom C11. The mean plane through the fused ring system makes dihedral angles of 22.74 (5) and 45.37 (5)° with the phenyl ring (C1–C6) and the 2-oxo-2-phenylethyl acetate group (C14–C22), respectively. The dihedral angle between the two aromatic rings (C1–C6 and C17–C22) is 59.63 (5)°. The molecular conformation is stabilized by two weak intramolecular C9—H9···O1 and C1—H1···N1 hydrogen bonds, generating *S*(6) ring motifs (Table 1, Fig. 1).

3. Supramolecular features

In the crystal, molecules are linked by C9—H9···O2^{iii} and C10—H10···O2^{iii} hydrogen bonds, forming chains that propagate parallel to the *b* axis and enclose $R_2^1(5)$ ring motifs (Table 1, Fig. 2). Additionally, intermolecular C15—H15*A*···O4^{i} and C15—H15*B*···O1^{ii} hydrogen bonds with $R_4^4(28)$ ring motifs are also present, generating a three-dimensional supramolecular network that also comprises a weak C22—H22···*Cg*4^{iv} interaction (*Cg*4 is the centroid of the C17–C22 phenyl ring) as well as π–π stacking interactions involving the centroids (*Cg*1 and *Cg*2) of the N2/C13/N3/C7–C8 and N2/C9–C13 rings with a centroid-to-centroid distance *Cg*1···*Cg*2 (x, 1/2 − y, −1/2 + z) of 3.5750 (9) Å and a slippage of 0.685 Å (Fig. 2).

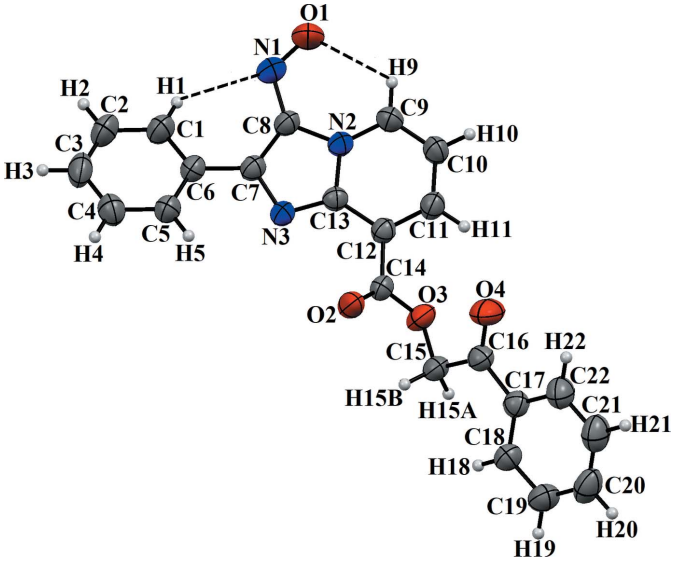

Figure 1
The molecular structure of (I), with atom labelling. Displacement ellipsoids are drawn at the 50% probability level. Intramolecular hydrogen bonds are indicated by dashed lines.

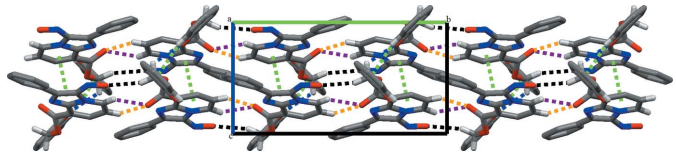

Figure 2
A view along the *a* axis of the crystal structure of (I). Blue, black, purple and orange dashed lines symbolize intermolecular C15—H15*A*···O4^{i}, C15—H15*B*···O1^{ii}, C9—H9···O2^{iii} and C10—H10···O2^{iii} hydrogen bonds, respectively; π–π and C—H···π interactions are shown as green dashed lines.

4. Database survey

A search of the Cambridge Structural Database (CSD, version 5.40, update of August 2019; Groom *et al.*, 2016) using 2-phenylimidazo[1,2-*a*]pyridin-3-amine as the main skeleton revealed the presence of 54 structures with different substituents on the imidazo[1,2-*a*]pyridine ring. The two structures most similar to (I) are *N*-(2-phenylimidazo[1,2-*a*]pyridin-3-yl)acetamide (MIXZOJ; Anaflous *et al.*, 2008) and 4-[(7-methyl-2-phenylimidazo[1,2-*a*]pyridin-3-yl)carbonoimidoyl]-phenol (TUQCEP; Elaatiaoui *et al.*, 2015). In MIXZOJ, $C_{15}H_{13}N_3O$, the crystal structure consists of molecular columns that are interconnected by N—H···N hydrogen bonds along the *b*-axis direction. The torsion angle between the imidazo[1,2-*a*]pyridine ring system and the phenyl ring is 9.04 (5)°. In TUQCEP, $C_{21}H_{17}N_3O$, the fused ring system is almost planar (r.m.s. deviation = 0.031 Å) and forms dihedral angles of 64.97 (7) and 18.52 (6)° with the phenyl ring and the (iminomethyl)phenol group, respectively. In its crystal, molecules are linked by pairs of C—H···π interactions into centrosymmetric dimeric units, which are further connected by O—H···N hydrogen bonds, forming layers parallel to (101).

5. Hirshfeld surface analysis

Hirshfeld surface analysis was used to quantify the intermolecular contacts of the title compound, using *Crystal Explorer* (Turner *et al.*, 2017). The Hirshfeld surface was generated with a standard (high) surface resolution and with the three-dimensional d_{norm} surface plotted over a fixed colour scale of −0.1706 (red) to 1.2371 (blue) a.u. (Fig. 3*a*). The shape-index map of the title molecule was generated in the range −1 to 1 Å (Fig. 3*b*), revealing the presence of red and blue triangles that are indicative of the presence of π–π stacking interactions. The curvedness map of the title complex

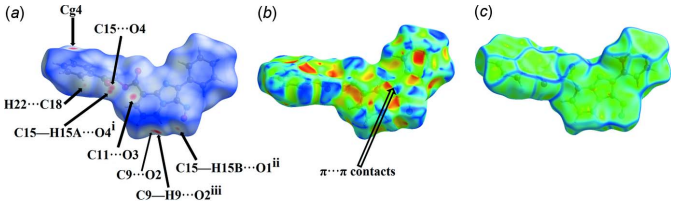

Figure 3
(*a*) d_{norm} mapped on the Hirshfeld surface to visualize the intermolecular interactions, (*b*) shape-index map of the title compound and (*c*) curvedness map of the title compound using a range from −4 to 4 Å.

was generated in the range −4.0 to 4.0 Å (Fig. 3*c*) and shows flat surface patches characteristic of planar stacking. The Hirshfeld surface representations with the function d_{norm} plotted onto the surface are shown for the H···H, H···C/C···H, H···O/O···H, C···O/O···C, C···N/N···C, H···N/N···H and C···C interactions in Fig. 4*a*–*g*, respectively. The overall two-dimensional fingerprint plot is illustrated in Fig. 5*a*, with those delineated into H···H, H···C/C···H, H···O/O···H, C···O/O···C, C···N/N···C, H···N/N···H and C···C contacts associated with their relative contributions to the Hirshfeld surface in Fig. 5*b*–*h*, respectively. The most important intermolecular interaction is H···H, contributing 36.2% to the overall crystal packing (Fig. 5*b*). H···C/C···H contacts, with a 20.5% contribution to the Hirshfeld surface, indicate the presence of the weak C—H···π interaction (Table 1). Two pairs of characteristic wings in the fingerprint plot with pairs of tips at $d_e + d_i$ ∼2.74 Å are present (Fig. 5*c*). H···O/O···H contacts arising from intermolecular C—H···O hydrogen bonding make a 20.0% contribution to the Hirshfeld surface and are represented by a pair of sharp spikes in the region $d_e + d_i$ ∼2.34 Å (Fig. 5*d*). The C···C contacts are a measure of π–π stacking interactions and contribute 4.3% of the Hirshfeld surface (Fig. 5*h*). The contributions of the other contacts to the Hirshfeld surface are C···O/O···C of 6.5%, C···N/N···C of 6.2% and H···N/N···H of 4.5%.

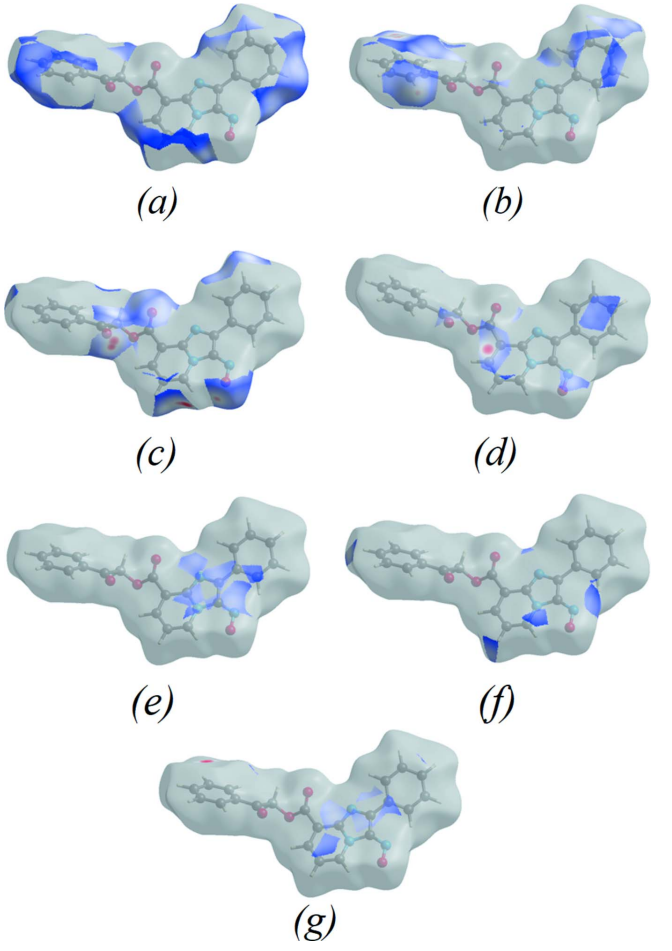

Figure 4
The Hirshfeld surface representations of (**I**) with the function d_{norm} plotted onto the surface for (*a*) H···H, (b) H···C/C···H, (*c*) H···O/O···H, (*d*) C···O/O···C, (*e*) C···N/N···C, (*f*) H···N/N···H and (*g*) C···C interactions.

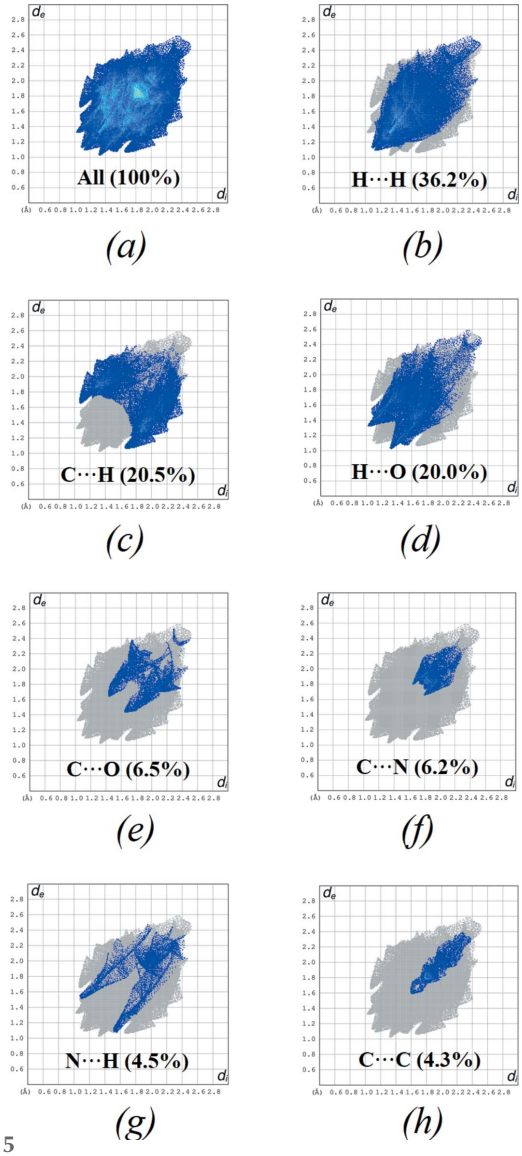

Figure 5
The full two-dimensional fingerprint plots for the title compound, showing (*a*) all interactions, and delineated into (*b*) H···H, (*c*) H···C/C···H, (*d*) H···O/ O···H, (*e*) C···O/O···C, (*f*) C···N/N···C, (*g*) H···N/N···H and (*h*) C···C interactions, together with their relative contributions.

6. Synthesis and crystallization

To a solution of 2-oxo-2-phenylethyl 2-phenylimidazo[1,2-*a*]-pyridine-8-carboxylate (0.71 g, 2 mmol) in acetic acid (50 ml), sodium nitrite (1.4 g, 2 mmol) was added at room temperature. The resulting precipitate was washed with water and extracted with dichloromethane (3 × 20 ml). The combined dichloromethane extracts were dried over anhydrous sodium sulfate and filtered. The remaining solution was concentrated under reduced pressure. The residue was purified chromatographically on a neutral alumina gel column using dichloromethane as eluent. Single crystals were obtained by slow evaporation of a dichloromethane solution at room temperature (yield 80%).

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Hydrogen atoms were fixed geometrically and treated as riding, with C—H = 0.97 Å for methylene [U_{iso}(H) = 1.5U_{eq}(C)], C—H = 0.93 Å for aromatic [U_{iso}(H) = 1.2U_{eq}(C)] and C—H = 0.98 Å for methine [U_{iso}(H) = 1.2U_{eq}(C)] H atoms.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{22}H_{15}N_3O_4$
M_r	385.37
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	296
a, b, c (Å)	15.9256 (14), 14.8256 (14), 7.6787 (6)
β (°)	90.566 (7)
V (Å^3)	1812.9 (3)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.10
Crystal size (mm)	0.56 × 0.38 × 0.15
Data collection	
Diffractometer	Stoe IPDS 2
Absorption correction	Integration (*X-RED32*; Stoe & Cie, 2012)
T_{min}, T_{max}	0.946, 0.969
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	27945, 6703, 3040
R_{int}	0.070
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.765
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.046, 0.118, 0.92
No. of reflections	6703
No. of parameters	262
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.15, −0.16

Computer programs: *X-AREA* and *X-RED* (Stoe & Cie, 2012), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*), *Mercury* (Macrae *et al.*, 2020), *WinGX* (Farrugia, 2012), *PLATON* (Spek, 2020) and *publCIF* (Westrip, 2010).

Acknowledgements

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Computing details

Data collection: *X-AREA* (Stoe & Cie, 2012); cell refinement: *X-AREA* (Stoe & Cie, 2012); data reduction: *X-RED* (Stoe & Cie, 2012); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015b); molecular graphics: *Mercury* (Macrae *et al.*, 2020), *PLATON* (Spek, 2020); software used to prepare material for publication: *WinGX* (Farrugia, 2012), *SHELXL* (Sheldrick, 2015b), *PLATON* (Spek, 2020) and *publCIF* (Westrip, 2010).

2-Oxo-2-phenylethyl 3-nitroso-2-phenylimidazo[1,2-*a*]pyridine-8-carboxylate

Crystal data

$C_{22}H_{15}N_3O_4$
M_r = 385.37
Monoclinic, $P2_1/c$
a = 15.9256 (14) Å
b = 14.8256 (14) Å
c = 7.6787 (6) Å
β = 90.566 (7)°
V = 1812.9 (3) Å^3
Z = 4
$F(000)$ = 800
D_x = 1.412 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 18578 reflections
θ = 1.9–32.8°
μ = 0.10 mm^{-1}
T = 296 K
Rod, green
0.56 × 0.38 × 0.15 mm

Data collection

Stoe IPDS 2 diffractometer
Radiation source: sealed X-ray tube, 12 x 0.4 mm long-fine focus
Plane graphite monochromator
Detector resolution: 6.67 pixels mm^{-1}
rotation method scans
Absorption correction: integration (*X-RED32*; Stoe & Cie, 2012)
T_{min} = 0.946, T_{max} = 0.969
27945 measured reflections
6703 independent reflections
3040 reflections with $I > 2\sigma(I)$
R_{int} = 0.070
θ_{max} = 32.9°, θ_{min} = 2.6°
h = −24→24
k = −22→22
l = −10→11

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.118
S = 0.92
6703 reflections
262 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0506P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.15$ e Å^{-3}
$\Delta\rho_{min} = -0.16$ e Å^{-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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O3	0.63005 (6)	0.31601 (7)	0.48667 (14)	0.0542 (3)
O2	0.58609 (6)	0.39797 (6)	0.25605 (15)	0.0595 (3)
N3	0.40012 (7)	0.34790 (7)	0.20621 (16)	0.0441 (3)
N2	0.39287 (6)	0.19477 (7)	0.20006 (16)	0.0435 (3)
O4	0.75836 (8)	0.26469 (8)	0.30406 (19)	0.0788 (4)
O1	0.25639 (7)	0.09653 (7)	0.0672 (2)	0.0780 (4)
N1	0.25076 (8)	0.18024 (9)	0.06361 (19)	0.0599 (4)
C14	0.58089 (8)	0.33230 (9)	0.34708 (19)	0.0416 (3)
C12	0.52135 (8)	0.25563 (8)	0.31845 (18)	0.0414 (3)
C13	0.44102 (8)	0.27009 (8)	0.24261 (18)	0.0404 (3)
C7	0.32472 (8)	0.32353 (9)	0.13986 (19)	0.0441 (3)
C17	0.86457 (9)	0.34187 (9)	0.46238 (19)	0.0464 (3)
C8	0.31681 (8)	0.22879 (9)	0.1315 (2)	0.0465 (3)
C6	0.26278 (8)	0.39215 (9)	0.08286 (19)	0.0459 (3)
C11	0.54667 (9)	0.16813 (9)	0.3493 (2)	0.0483 (3)
H11	0.598339	0.157821	0.403177	0.058*
C16	0.77582 (9)	0.32058 (9)	0.4145 (2)	0.0495 (3)
C15	0.70537 (8)	0.36842 (9)	0.5070 (2)	0.0498 (3)
H15A	0.719202	0.375040	0.629688	0.060*
H15B	0.697194	0.428055	0.457752	0.060*
C18	0.88553 (9)	0.40814 (10)	0.5833 (2)	0.0524 (4)
H18	0.843669	0.443252	0.632786	0.063*
C9	0.42025 (9)	0.10793 (9)	0.2257 (2)	0.0508 (4)
H9	0.387103	0.059250	0.191712	0.061*
C10	0.49660 (9)	0.09435 (9)	0.3016 (2)	0.0529 (4)
H10	0.515667	0.035964	0.321857	0.063*
C5	0.28989 (9)	0.47829 (10)	0.0411 (2)	0.0537 (4)
H5	0.346539	0.492649	0.052027	0.064*
C4	0.23357 (10)	0.54324 (11)	−0.0168 (2)	0.0618 (4)
H4	0.252468	0.600751	−0.044788	0.074*
C19	0.96856 (10)	0.42184 (11)	0.6299 (3)	0.0645 (4)
H19	0.982383	0.465939	0.711376	0.077*
C3	0.14938 (11)	0.52236 (12)	−0.0328 (2)	0.0669 (5)
H3	0.111528	0.565477	−0.073272	0.080*
C1	0.17725 (9)	0.37247 (11)	0.0689 (3)	0.0633 (4)
H1	0.157736	0.315422	0.098519	0.076*

C22	0.92826 (10)	0.29109 (11)	0.3880 (2)	0.0639 (4)
H22	0.914895	0.247016	0.306093	0.077*
C20	1.03132 (10)	0.37028 (13)	0.5559 (3)	0.0719 (5)
H20	1.087105	0.379435	0.588214	0.086*
C2	0.12162 (10)	0.43762 (13)	0.0113 (3)	0.0727 (5)
H2	0.064726	0.424057	0.002223	0.087*
C21	1.01088 (11)	0.30541 (13)	0.4343 (3)	0.0736 (5)
H21	1.053005	0.271212	0.383457	0.088*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O3	0.0450 (5)	0.0615 (6)	0.0559 (7)	−0.0123 (4)	−0.0143 (5)	0.0119 (5)
O2	0.0558 (6)	0.0431 (5)	0.0792 (8)	−0.0076 (4)	−0.0223 (5)	0.0138 (5)
N3	0.0351 (5)	0.0412 (5)	0.0558 (7)	−0.0003 (4)	−0.0046 (5)	0.0017 (5)
N2	0.0354 (5)	0.0418 (6)	0.0534 (7)	−0.0037 (4)	−0.0030 (5)	0.0028 (5)
O4	0.0687 (7)	0.0791 (8)	0.0882 (9)	0.0000 (6)	−0.0168 (7)	−0.0363 (7)
O1	0.0631 (7)	0.0515 (6)	0.1188 (11)	−0.0111 (5)	−0.0220 (7)	−0.0053 (6)
N1	0.0451 (7)	0.0562 (7)	0.0783 (10)	−0.0071 (6)	−0.0122 (6)	−0.0018 (7)
C14	0.0327 (6)	0.0428 (7)	0.0492 (8)	0.0027 (5)	−0.0041 (6)	0.0002 (6)
C12	0.0360 (6)	0.0430 (7)	0.0451 (8)	−0.0008 (5)	−0.0008 (6)	0.0031 (6)
C13	0.0362 (6)	0.0389 (6)	0.0461 (8)	−0.0031 (5)	0.0003 (6)	0.0024 (6)
C7	0.0348 (6)	0.0467 (7)	0.0508 (8)	−0.0018 (5)	−0.0025 (6)	0.0013 (6)
C17	0.0450 (7)	0.0460 (7)	0.0481 (8)	−0.0002 (5)	−0.0044 (6)	0.0044 (6)
C8	0.0352 (6)	0.0478 (7)	0.0565 (9)	−0.0034 (5)	−0.0068 (6)	0.0020 (6)
C6	0.0382 (7)	0.0485 (7)	0.0511 (9)	0.0024 (5)	−0.0056 (6)	−0.0015 (6)
C11	0.0391 (7)	0.0487 (7)	0.0569 (9)	0.0006 (6)	−0.0046 (6)	0.0084 (6)
C16	0.0525 (8)	0.0448 (7)	0.0511 (9)	−0.0020 (6)	−0.0115 (7)	0.0009 (6)
C15	0.0424 (7)	0.0488 (7)	0.0579 (9)	−0.0040 (6)	−0.0137 (6)	0.0008 (7)
C18	0.0424 (7)	0.0526 (8)	0.0621 (10)	−0.0019 (6)	−0.0039 (7)	−0.0011 (7)
C9	0.0479 (8)	0.0384 (7)	0.0659 (10)	−0.0038 (6)	−0.0058 (7)	0.0021 (6)
C10	0.0482 (8)	0.0385 (7)	0.0719 (11)	0.0012 (6)	−0.0054 (7)	0.0077 (7)
C5	0.0432 (7)	0.0497 (8)	0.0680 (11)	0.0025 (6)	−0.0064 (7)	0.0001 (7)
C4	0.0622 (10)	0.0507 (8)	0.0727 (12)	0.0089 (7)	−0.0027 (8)	0.0057 (8)
C19	0.0520 (9)	0.0631 (9)	0.0780 (12)	−0.0102 (7)	−0.0117 (8)	−0.0004 (9)
C3	0.0594 (10)	0.0706 (10)	0.0704 (12)	0.0231 (8)	−0.0138 (8)	0.0037 (9)
C1	0.0421 (8)	0.0605 (9)	0.0871 (13)	−0.0009 (7)	−0.0118 (8)	0.0028 (8)
C22	0.0569 (9)	0.0647 (10)	0.0702 (12)	0.0109 (7)	−0.0026 (8)	−0.0061 (8)
C20	0.0408 (8)	0.0788 (11)	0.0959 (15)	−0.0031 (8)	−0.0076 (8)	0.0195 (11)
C2	0.0422 (8)	0.0765 (11)	0.0990 (15)	0.0076 (8)	−0.0172 (8)	−0.0003 (10)
C21	0.0534 (9)	0.0793 (12)	0.0880 (15)	0.0150 (9)	0.0052 (9)	0.0043 (10)

Geometric parameters (Å, º)

O3—C14	1.3431 (16)	C15—H15A	0.9700
O3—C15	1.4365 (16)	C15—H15B	0.9700
O2—C14	1.2018 (16)	C18—C19	1.381 (2)
N3—C7	1.3491 (16)	C18—H18	0.9300

N3—C13	1.3526 (16)	C9—C10	1.3581 (19)
N2—C9	1.3729 (17)	C9—H9	0.9300
N2—C13	1.3918 (16)	C10—H10	0.9300
N2—C8	1.4092 (16)	C5—C4	1.386 (2)
O4—C16	1.2157 (17)	C5—H5	0.9300
O1—N1	1.2446 (16)	C4—C3	1.380 (2)
N1—C8	1.3732 (17)	C4—H4	0.9300
C14—C12	1.4951 (18)	C19—C20	1.385 (3)
C12—C11	1.3783 (18)	C19—H19	0.9300
C12—C13	1.4166 (18)	C3—C2	1.375 (3)
C7—C8	1.4115 (19)	C3—H3	0.9300
C7—C6	1.4803 (18)	C1—C2	1.381 (2)
C17—C18	1.390 (2)	C1—H1	0.9300
C17—C22	1.391 (2)	C22—C21	1.376 (2)
C17—C16	1.4907 (19)	C22—H22	0.9300
C6—C5	1.387 (2)	C20—C21	1.377 (3)
C6—C1	1.396 (2)	C20—H20	0.9300
C11—C10	1.4002 (19)	C2—H2	0.9300
C11—H11	0.9300	C21—H21	0.9300
C16—C15	1.511 (2)		

C14—O3—C15	117.98 (11)	H15A—C15—H15B	108.4
C7—N3—C13	105.94 (10)	C19—C18—C17	119.98 (15)
C9—N2—C13	123.04 (11)	C19—C18—H18	120.0
C9—N2—C8	131.29 (11)	C17—C18—H18	120.0
C13—N2—C8	105.67 (10)	C10—C9—N2	118.84 (12)
O1—N1—C8	117.36 (12)	C10—C9—H9	120.6
O2—C14—O3	124.53 (12)	N2—C9—H9	120.6
O2—C14—C12	125.28 (12)	C9—C10—C11	120.11 (13)
O3—C14—C12	110.15 (11)	C9—C10—H10	119.9
C11—C12—C13	118.33 (11)	C11—C10—H10	119.9
C11—C12—C14	120.41 (11)	C4—C5—C6	120.80 (14)
C13—C12—C14	120.94 (11)	C4—C5—H5	119.6
N3—C13—N2	111.88 (10)	C6—C5—H5	119.6
N3—C13—C12	130.17 (11)	C3—C4—C5	119.83 (15)
N2—C13—C12	117.93 (11)	C3—C4—H4	120.1
N3—C7—C8	111.24 (11)	C5—C4—H4	120.1
N3—C7—C6	121.04 (11)	C18—C19—C20	120.37 (16)
C8—C7—C6	127.70 (11)	C18—C19—H19	119.8
C18—C17—C22	119.06 (13)	C20—C19—H19	119.8
C18—C17—C16	122.36 (13)	C2—C3—C4	119.82 (14)
C22—C17—C16	118.53 (13)	C2—C3—H3	120.1
N1—C8—N2	127.33 (12)	C4—C3—H3	120.1
N1—C8—C7	127.34 (12)	C2—C1—C6	120.06 (16)
N2—C8—C7	105.26 (10)	C2—C1—H1	120.0
C5—C6—C1	118.72 (13)	C6—C1—H1	120.0
C5—C6—C7	119.55 (12)	C21—C22—C17	120.64 (16)
C1—C6—C7	121.73 (13)	C21—C22—H22	119.7

C12—C11—C10	121.69 (12)	C17—C22—H22	119.7
C12—C11—H11	119.2	C21—C20—C19	119.80 (15)
C10—C11—H11	119.2	C21—C20—H20	120.1
O4—C16—C17	121.74 (14)	C19—C20—H20	120.1
O4—C16—C15	118.84 (13)	C3—C2—C1	120.74 (15)
C17—C16—C15	119.41 (12)	C3—C2—H2	119.6
O3—C15—C16	108.54 (11)	C1—C2—H2	119.6
O3—C15—H15A	110.0	C22—C21—C20	120.14 (17)
C16—C15—H15A	110.0	C22—C21—H21	119.9
O3—C15—H15B	110.0	C20—C21—H21	119.9
C16—C15—H15B	110.0		

C15—O3—C14—O2	−14.9 (2)	C8—C7—C6—C1	23.0 (3)
C15—O3—C14—C12	163.13 (11)	C13—C12—C11—C10	2.5 (2)
O2—C14—C12—C11	141.14 (16)	C14—C12—C11—C10	−171.16 (15)
O3—C14—C12—C11	−36.82 (19)	C18—C17—C16—O4	177.35 (15)
O2—C14—C12—C13	−32.3 (2)	C22—C17—C16—O4	−5.1 (2)
O3—C14—C12—C13	149.69 (13)	C18—C17—C16—C15	−3.6 (2)
C7—N3—C13—N2	0.14 (16)	C22—C17—C16—C15	173.89 (14)
C7—N3—C13—C12	−178.13 (15)	C14—O3—C15—C16	−89.28 (14)
C9—N2—C13—N3	−179.58 (13)	O4—C16—C15—O3	19.49 (19)
C8—N2—C13—N3	0.31 (16)	C17—C16—C15—O3	−159.56 (12)
C9—N2—C13—C12	−1.1 (2)	C22—C17—C18—C19	−1.0 (2)
C8—N2—C13—C12	178.82 (12)	C16—C17—C18—C19	176.52 (14)
C11—C12—C13—N3	176.84 (15)	C13—N2—C9—C10	2.4 (2)
C14—C12—C13—N3	−9.5 (2)	C8—N2—C9—C10	−177.50 (15)
C11—C12—C13—N2	−1.3 (2)	N2—C9—C10—C11	−1.2 (2)
C14—C12—C13—N2	172.27 (13)	C12—C11—C10—C9	−1.2 (3)
C13—N3—C7—C8	−0.56 (17)	C1—C6—C5—C4	−1.3 (2)
C13—N3—C7—C6	−179.33 (13)	C7—C6—C5—C4	178.39 (15)
O1—N1—C8—N2	2.6 (2)	C6—C5—C4—C3	0.2 (3)
O1—N1—C8—C7	179.29 (16)	C17—C18—C19—C20	0.4 (2)
C9—N2—C8—N1	−3.5 (3)	C5—C4—C3—C2	1.0 (3)
C13—N2—C8—N1	176.62 (15)	C5—C6—C1—C2	1.2 (3)
C9—N2—C8—C7	179.26 (15)	C7—C6—C1—C2	−178.44 (16)
C13—N2—C8—C7	−0.61 (15)	C18—C17—C22—C21	0.7 (2)
N3—C7—C8—N1	−176.49 (15)	C16—C17—C22—C21	−176.95 (16)
C6—C7—C8—N1	2.2 (3)	C18—C19—C20—C21	0.4 (3)
N3—C7—C8—N2	0.74 (17)	C4—C3—C2—C1	−1.0 (3)
C6—C7—C8—N2	179.42 (14)	C6—C1—C2—C3	−0.1 (3)
N3—C7—C6—C5	21.9 (2)	C17—C22—C21—C20	0.2 (3)
C8—C7—C6—C5	−156.69 (16)	C19—C20—C21—C22	−0.8 (3)
N3—C7—C6—C1	−158.46 (15)		

Hydrogen-bond geometry (Å, º)

*Cg*4 is the centroid of the C17–C22 phenyl ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C15—H15*A*···O4^{i}	0.97	2.54	3.1257 (19)	119
C15—H15*B*···O1^{ii}	0.97	2.61	3.4841 (18)	150
C9—H9···O2^{iii}	0.93	2.46	3.1176 (16)	128
C10—H10···O2^{iii}	0.93	2.67	3.2243 (17)	119
C9—H9···O1	0.93	2.35	2.8736 (18)	116
C1—H1···N1	0.93	2.51	3.081 (2)	120
C22—H22···*Cg*4^{iv}	0.93	2.80	3.657 (2)	153

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