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

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The title compound, C22H15N3O4, 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 R21(5) and R44(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), antitubercular (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., 2021a,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, C22H15N3O4 (I).
the two aromatic rings (C1–C6 and C17–C22) is 59.63 (5)°. The dihedral angle between the phenyl ring (C1–C6) and the 2-oxo-2-phenylethyl acetate group (C14–C22), respectively. The mean plane through the fused ring system makes dihedral angles of 22.74 (5)° and 45.37 (5)° for atom C11. The mean plane through the fused ring system is planar with an r.m.s deviation of 0.017 Å and a maximum deviation of 0.028 (1) Å.

The molecular conformation is stabilized by two weak intramolecular hydrogen bonds are indicated by dashed lines. Intramolecular hydrogen bonds are indicated by dashed lines. The molecular conformation is stabilized by two weak intramolecular C9—H9···C110 ring motifs (Table 1, Fig. 1).

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···O1ii and C10—H10···O2iii 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—H15A···O4i and C15—H15B···O1ii hydrogen bonds with $R_2^1(28)$ ring motifs are also present, generating a three-dimensional supramolecular network that also comprises a weak C22—H22···Cg4iv interaction (Cg4 is the centroid of the C17–C22 phenyl ring) as well as π···π stacking interactions involving the centroids (Cg1 and Cg2) of the N2/C13/N3/C7–C8 and N2/C9–C13 rings with a centroid-to-centroid distance Cg1···Cg2 (x, 1/2 − y, −1/2 + z) of 3.5750 (9) Å and a slippage of 0.685 Å (Fig. 2).

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]carbonimidoyl]-phenol (TUQCEP; Elaatiaoui et al., 2015). In MIXZOJ, C15H13N3O, 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, C21H17N3O, the fused ring system is almost planar (r.m.s. deviation = 0.31 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. 3a). The shape-index map of the title molecule was generated in the range −1 to 1 Å (Fig. 3b), 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

Table 1

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|-----|------|-------|---------|
| C15—H15A···O4i | 0.97 | 2.54 | 3.1257 (19) | 119 |
| C15—H15B···O1ii | 0.97 | 2.61 | 3.4841 (18) | 150 |
| C9—H9···O1 | 0.93 | 2.46 | 3.1176 (16) | 128 |
| C10—H10···O2iii | 0.93 | 2.67 | 3.2343 (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···O4iv | 0.93 | 2.80 | 3.657 (2) | 153 |

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

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—H15A···O4i, C15—H15B···O1ii, C9—H9···O2iii and C10—H10···O2iii hydrogen bonds, respectively; π···π and C—H···π interactions are shown as green dashed lines.
was generated in the range $-4.0$ to $4.0$ Å (Fig. 3c) and shows flat surface patches characteristic of planar stacking. The Hirshfeld surface representations with the function $d_{\text{norm}}$ 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. 4a–g, respectively. The overall two-dimensional fingerprint plot is illustrated in Fig. 5a, 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. 5b–h, respectively. The most important intermolecular interaction is H–H, contributing 36.2% to the overall crystal packing (Fig. 5b). H–/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. 5c). 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. 5d). The C–C contacts are a measure of π–π stacking interactions and contribute 4.3% of the Hirshfeld surface (Fig. 5h). 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 3
(a) $d_{\text{norm}}$ 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.

Figure 4
The Hirshfeld surface representations of (I) with the function $d_{\text{norm}}$ 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-α]-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 \([U_{eq}(H) = 1.5U_{eq}(C)]\), C—H = 0.93 Å for aromatic \([U_{eq}(H) = 1.2U_{eq}(C)]\) and C—H = 0.98 Å for methane \([U_{eq}(H) = 1.2U_{eq}(C)]\) H atoms.

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Table 2

| Crystal data                  | Chemical formula | C_{22}H_{15}N_{3}O_{4} |
|------------------------------|------------------|------------------------|
| 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 (Å³)                      | 1812.9 (3)       |
| Z                            | 4                |
| Radiation type               | Mo Kα            |
| 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)

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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

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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 pubICIF (Westrip, 2010).

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

Crystal data

| Parameter       | Value                           |
|-----------------|---------------------------------|
| C_{22}H_{15}N_{3}O_{4} | Mr = 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 Kα 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

| Parameter       | Value                           |
|-----------------|---------------------------------|
| Stoe IPDS 2     |                                 |
| Diffraclometer  |                                 |
| Radiation source| sealed X-ray tube, 12 x 0.4 mm  |
| 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 > 2σ(I) |                     |
| R_{int}         | 0.070                          |
| θ_{min}         | 32.9°, θ_{max} = 2.6°          |
| h, k, l         | -24→24, -22→22, -10→11        |

Refinement

| Parameter       | Value                           |
|-----------------|---------------------------------|
| Refinement on F^2 |                                 |
| Least-squares matrix: full |                     |
| R[F^2 > 2σ(F^2)] | 0.046                          |
| wR(F^2)         | 0.118                          |
| S               | 0.92                           |
| 262 parameters  | 0 restraints                   |
| Hydrogen site location: inferred from neighbouring sites |                     |
| H-atom parameters constrained |                     |
\[ w = \frac{1}{\sigma^2(F_o^2) + (0.0506P)^2} \]
where \( P = (F_o^2 + 2F_c^2)/3 \)

\( (\Delta/\sigma)_{\text{max}} < 0.001 \)

\( \Delta \rho_{\text{max}} = 0.15 \text{ eÅ}^{-3} \)

\( \Delta \rho_{\text{min}} = -0.16 \text{ eÅ}^{-3} \)

**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 (Å²)**

|    | x     | y     | z     | \( U_{\text{eq}} \) |
|----|-------|-------|-------|---------------------|
| 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 | 0.85553 (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* |
### Atomic displacement parameters (Å²)

|   | U¹¹ | U¹² | U¹³ | U¹² | U¹³ | U¹³ |
|---|-----|-----|-----|-----|-----|-----|
| 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) | 0.0007 (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, °)

|   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|
| 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 |
| Bond                  | Length  | Angle         | Bond                  | Length  |
|----------------------|---------|---------------|----------------------|---------|
| N3—C13               | 1.3526  | 117.98 (11)   | H15A—C15—H15B       | 108.4   |
| N2—C9                | 1.3729  | 110.88 (10)   | C6—C12—C13           | 119.9   |
| N2—C13               | 1.3918  | 110.15 (11)   | C11—C12—C13          | 119.9   |
| N2—C8                | 1.4092  | 118.33 (11)   | C11—C12—C14          | 119.9   |
| O4—C16               | 1.2157  | 120.15 (11)   | C11—C12—C14          | 119.9   |
| O1—N1                | 1.2446  | 117.93 (11)   | C12—C13—C12         | 120.1   |
| N1—C8                | 1.3732  | 112.44 (10)   | C12—C13—C14         | 120.1   |
| C14—C12              | 1.4951  | 112.44 (10)   | C12—C13—C12      | 120.1   |
| C12—C11              | 1.3783  | 112.44 (10)   | C12—C13—C12      | 120.1   |
| C12—C13              | 1.4166  | 112.44 (10)   | C12—C13—C12      | 120.1   |
| C7—C8                | 1.4115  | 112.44 (10)   | C12—C13—C12      | 120.1   |
| C7—C6                | 1.4803  | 112.44 (10)   | C12—C13—C12      | 120.1   |
| C17—C18              | 1.390   | 112.44 (10)   | C12—C13—C12      | 120.1   |
| C17—C22              | 1.391   | 112.44 (10)   | C12—C13—C12      | 120.1   |
| C17—C16              | 1.4907  | 112.44 (10)   | C12—C13—C12      | 120.1   |
| C6—C5                | 1.387   | 112.44 (10)   | C12—C13—C12      | 120.1   |
| C6—C1                | 1.396   | 112.44 (10)   | C12—C13—C12      | 120.1   |
| C11—C10              | 1.4002  | 112.44 (10)   | C12—C13—C12      | 120.1   |
| C11—H11              | 0.9300  | 112.44 (10)   | C12—C13—C12      | 120.1   |
| C16—C15              | 1.511   | 112.44 (10)   | C12—C13—C12      | 120.1   |
| C14—O3—C15           | 117.98  | 118.33 (11)   | C11—C12—C12     | 120.1   |
| C7—N3—C13            | 105.94  | 118.33 (11)   | C11—C12—C12     | 120.1   |
| C9—N2—C13            | 123.04  | 118.33 (11)   | C11—C12—C12     | 120.1   |
| C9—N2—C8             | 131.29  | 118.33 (11)   | C11—C12—C12     | 120.1   |
| C13—N2—C8            | 105.67  | 118.33 (11)   | C11—C12—C12     | 120.1   |
| O1—N1—C8             | 117.36  | 118.33 (11)   | C11—C12—C12     | 120.1   |
| O2—C14—O3            | 124.53  | 118.33 (11)   | C11—C12—C12     | 120.1   |
| O2—C14—C12           | 125.28  | 118.33 (11)   | C11—C12—C12     | 120.1   |
| O3—C14—C12           | 110.15  | 118.33 (11)   | C11—C12—C12     | 120.1   |
| C11—C12—C13          | 118.33  | 118.33 (11)   | C11—C12—C12     | 120.1   |
| C11—C12—C14          | 120.41  | 118.33 (11)   | C11—C12—C12     | 120.1   |
| C13—C12—C14          | 120.94  | 118.33 (11)   | C11—C12—C12     | 120.1   |
| N3—C13—N2            | 111.88  | 118.33 (11)   | C11—C12—C12     | 120.1   |
| N3—C13—C12           | 130.17  | 118.33 (11)   | C11—C12—C12     | 120.1   |
| N2—C13—C12           | 117.93  | 118.33 (11)   | C11—C12—C12     | 120.1   |
| N3—C7—C8             | 111.24  | 118.33 (11)   | C11—C12—C12     | 120.1   |
| N3—C7—C6             | 121.04  | 118.33 (11)   | C11—C12—C12     | 120.1   |
| C8—C7—C6             | 127.70  | 118.33 (11)   | C11—C12—C12     | 120.1   |
| C18—C17—C22          | 119.06  | 118.33 (11)   | C11—C12—C12     | 120.1   |
| C18—C17—C16          | 122.36  | 118.33 (11)   | C11—C12—C12     | 120.1   |
| C22—C17—C16          | 118.53  | 118.33 (11)   | C11—C12—C12     | 120.1   |
| N1—C8—N2             | 127.33  | 118.33 (11)   | C11—C12—C12     | 120.1   |
| N1—C8—C7             | 127.34  | 118.33 (11)   | C11—C12—C12     | 120.1   |
| N2—C8—C7             | 105.26  | 118.33 (11)   | C11—C12—C12     | 120.1   |
| C5—C6—C1             | 118.72  | 118.33 (11)   | C11—C12—C12     | 120.1   |
| C5—C6—C7             | 119.55  | 118.33 (11)   | C11—C12—C12     | 120.1   |
| C1—C6—C7             | 121.73  | 118.33 (11)   | C11—C12—C12     | 120.1   |
| Bond/Angle | Value (deg) | Bond/Angle | Value (deg) |
|-----------|------------|-----------|------------|
| 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 |  |

| Bond/Angle | Value (deg) | Bond/Angle | Value (deg) |
|-----------|------------|-----------|------------|
| 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—C13 | 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) | C2—C3—C4—C5 | 0.2 (3) |
| C14—C12—C13—N2 | 172.27 (13) | N2—C9—C10—C11 | −1.2 (2) |
| C13—N3—C7—C8 | −0.56 (17) | C12—C11—C10—C9 | −1.2 (3) |
| C13—N3—C7—C6 | −179.33 (13) | C1—C6—C5—C4 | −1.3 (2) |
| O1—N1—C8—N2 | 2.6 (2) | C7—C6—C5—C4 | 178.39 (15) |
| O1—N1—C8—C7 | 179.29 (16) | C6—C5—C4—C3 | 0.2 (3) |
| C9—N2—C8—N1 | −3.5 (3) | C17—C18—C19—C20 | 0.4 (2) |
| C13—N2—C8—N1 | 176.62 (15) | C5—C4—C3—C2 | 1.0 (3) |
| C9—N2—C8—C7 | 179.26 (15) | C5—C6—C1—C2 | 1.2 (3) |
| C13—N2—C8—C7 | −0.61 (15) | C7—C6—C1—C2 | −178.44 (16) |
| N3—C7—C8—N1 | −176.49 (15) | C18—C17—C22—C21 | 0.7 (2) |
| C6—C7—C8—N1 | 2.2 (3) | C16—C17—C22—C21 | −176.95 (16) |
| N3—C7—C8—N2 | 0.74 (17) | C18—C19—C20—C21 | 0.4 (3) |
| C6—C7—C8—N2 | 179.42 (14) | C4—C3—C2—C1 | −1.0 (3) |
| N3—C7—C6—C5 | 21.9 (2) | C6—C1—C2—C3 | −0.1 (3) |
| C8—C7—C6—C5 | −156.69 (16) | C17—C22—C21—C20 | 0.2 (3) |
| N3—C7—C6—C1 | −158.46 (15) | C19—C20—C21—C22 | −0.8 (3) |
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—H15A···O4i   | 0.97  | 2.54   | 3.1257 (19) | 119     |
| C15—H15B···O1ii  | 0.97  | 2.61   | 3.4841 (18) | 150     |
| C9—H9···O2iii    | 0.93  | 2.46   | 3.1176 (16) | 128     |
| C10—H10···O2iii  | 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···Cg4iv | 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) $x$, $-y+1/2$, $z-1/2$. 

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