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# Synthesis and structure of a 1:1 1-phenylsemicarbazide–1-phenylpyrazolidin-3-one cocrystal

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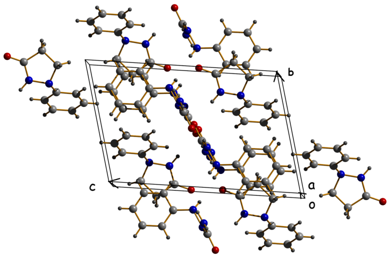
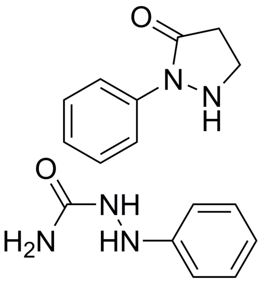
The title cocrystal, $C_7H_9N_3O{\cdot}C_9H_{10}N_2O$, was obtained by the cocrystallization of 1-phenylsemicarbazide ($A$) and 1-phenylpyrazolidin-3-one ($B$) in a 1:1 molar ratio from methanol solution. The structure features a *gauche* arrangement about the N—N bond in the semicarbazide fragment and a twisted conformation of the pyrazolidinone ring. In the extended structure, the molecules are linked by $A \rightarrow A$ and $B \rightarrow A$ N—H$\cdots$O hydrogen bonds, supplemented by C—H$\cdots\pi$ contacts to generate a three-dimensional supramolecular framework.



## 1. Chemical context

Semicarbazide ($CH_5N_3O$) is the diamino derivative of urea and contains three N atoms and a carbonyl group as potential hydrogen-bonding sites and for coordination with metal centers (Asifa *et al.*, 2021). It forms semicarbazones on condensation with aldehydes/ketone (Reena *et al.*, 2008; Reena & Kurup, 2010). Consequently, semicarbazide and its derivatives have found extensive utility in the synthesis of compounds with biological and industrial relevance. Beyond its biological applications, semicarbazide derivatives have also been reported to act as effective corrosion inhibitors in aqueous environments (Olasunkanmi *et al.*, 2020).

In the field of crystal engineering, cocrystals defined as single-phase crystalline materials comprising two or more neutral molecular species have long been exploited to tune physicochemical attributes while preserving the molecular identity of active components (Taylor & Day, 2018). A recent review reaffirms that cocrystallization remains a powerful approach to modulate API properties, with modern design strategies expanding *via* techniques such as spray drying, hot-melt extrusion and supercritical fluid processing (Sakhiya & Borkhataria 2024). Rode and colleagues demonstrated the potential of flavonoid-based cocrystal and coamorphous systems (Rode *et al.*, 2024).



As part of our studies in this area, we now describe the synthesis and structure of the title 1:1 cocrystal formed between 1-phenylsemicarbazide (*A*) and 1-phenylpyrazolidin-3-one (*B*), $C_7H_9N_3O \cdot C_9H_{10}N_2O$, (**I**), Fig. 1.

## 2. Structural commentary

The semicarbazide–aromatic linkage in molecule *A* of (**I**) displays a pronounced deviation from coplanarity, as shown by the C1—N2—N3—C2 torsion angle of −99.2 (2)°, indicating a *gauche* arrangement about the N—N bond. The O1—C1—N2—N3 torsion of 177.2 (1)° confirms an anti-periplanar relationship between the carbonyl oxygen atom and the N—N linkage, while the N1—C1—N2—N3 torsion angle of −1.9 (2)° supports near planarity at C1 and $sp^2$ hybridization at N1. In the side chain, C3—C2—N3—N2 [−167.0 (1)°] is close to anti-periplanar, whereas C7—C2—N3—N2 [17.9 (2)°] indicates a *gauche* disposition of the phenyl substituent.

The pyrazolidinone ring (C8–C10/N4/N5) in molecule *B* adopts a twisted conformation about C10—C9, with Cremer–Pople parameters $Q(2)$ = 0.229 (2) Å and $\Phi(2)$ = 263.7 (5)°. The pseudorotation parameters $P$ = 65.5 (4)° and $\tau_M$ = 23.9 (2)° (Jia *et al.*, 2008) confirm this geometry. The mean absolute torsion angle (17.6°) and atomic deviations in the ring (–0.142 to +0.132 Å) indicate moderate non-planarity, in line with reported pyrazolidinone structures (Domenicano *et al.*, 1975). The pyrazolidinone and phenyl (C11–C16) rings are inclined by 54.42 (12)°, producing a significant out-of-plane arrangement.

## 3. Supramolecular features

The extended structure of (**I**) features an extensive network of intermolecular interactions, including N—H⋯O hydrogen bonds (Table 1) and C—H⋯π contacts, which collectively underpin its efficient packing and structural cohesion.

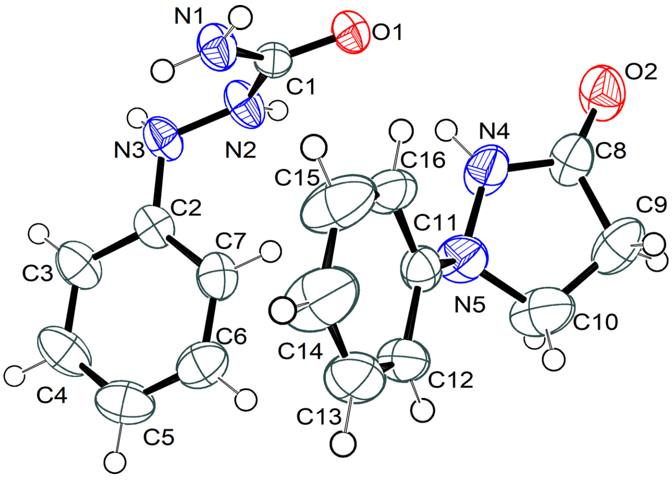


**Figure 1**
The molecular structure of (**I**) with displacement ellipsoids drawn at the 50% probability level.

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

*Cg*2 and *Cg*3 are the centroids of the C11–C16 and C2–C7 rings, respectively

| *D*—H⋯*A* | *D*—H | H⋯*A* | *D*⋯*A* | *D*—H⋯*A* |
|---|---|---|---|---|
| N1—H1*B*⋯O1$^{i}$ | 0.93 (2) | 2.09 (2) | 3.0164 (17) | 178 (2) |
| N1—H1*A*⋯O2$^{ii}$ | 0.87 (2) | 2.12 (2) | 2.9645 (18) | 161 (2) |
| N2—H2*N*⋯O1$^{iii}$ | 0.88 (2) | 2.09 (2) | 2.9486 (17) | 166 (2) |
| N3—H3*N*⋯O2$^{iii}$ | 0.84 (2) | 2.15 (2) | 2.9641 (19) | 161 (2) |
| N4—H4*N*⋯O1 | 0.88 (2) | 2.08 (2) | 2.9471 (19) | 167 (2) |
| C4—H4⋯*Cg*2$^{iv}$ | 0.93 | 2.77 | 3.653 (3) | 158 |
| C9—H9*B*⋯*Cg*3$^{v}$ | 0.97 | 2.64 | 3.510 (2) | 149 |

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

Five significant hydrogen bonds were identified, featuring donor–acceptor (*D*⋯*A*) distances shorter than 3.05 Å. These hydrogen bonds all involve N—H donors and carbonyl oxygen atom acceptors (Fig. 2): the strong, near-linear interactions such as N1—H1*B*⋯O1 and N4—H4*N*⋯O1 are consistent with hydrogen-bonding motifs typical of semicarbazide-based structures, contributing to a well-defined supramolecular framework (Kurup *et al.*, 2011; Kunnath *et al.*, 2026).

Complementing these, C—H⋯π interactions consolidate the structure: these interactions were identified by short hydrogen-to-centroid distances (< 3.0 Å) and favorable angular geometries (Desiraju & Steiner, 1999). Two notable C—H⋯π contacts include C4—H4⋯*Cg*2 with an H⋯*Cg* distance of 2.77 Å and C9—H9*B*⋯*Cg*3 with a shorter H⋯*Cg* distance of 2.64 Å. The latter exhibits a more linear approach, facilitating an effective perpendicular hydrogen-bonding

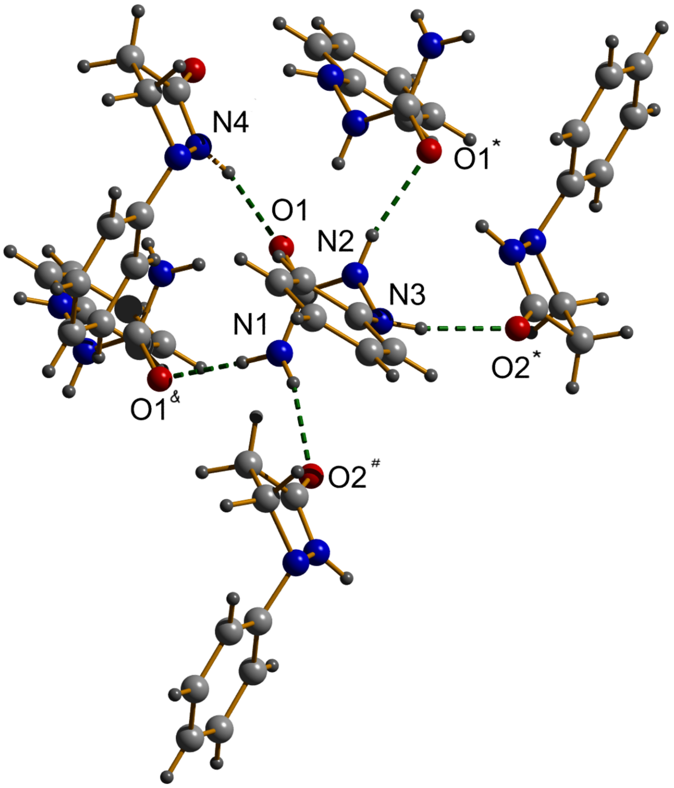


**Figure 2**
Hydrogen bonds in the crystal packing of (**I**) shown as dashed lines.

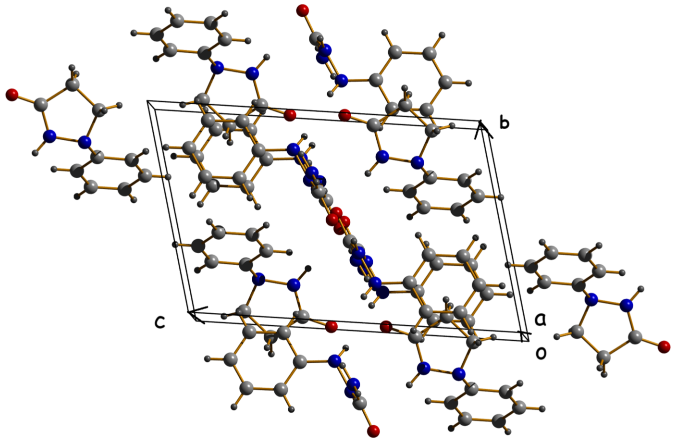


**Figure 3**
The packing of (**I**) viewed down [100].

interaction to the $\pi$-system (Mahadevi & Sastry, 2016). These C—H$\cdots\pi$ contacts further enhance the cohesion of the structure of (**I**) but there are no significant $\pi$–$\pi$ interactions present in the crystal (Fig. 3).

## 4. Hirshfeld surface analysis

Hirshfeld surface analysis and the associated two-dimensional fingerprint plots were generated using *CrystalExplorer* (Spackman *et al.*, 2021). The Hirshfeld surfaces were mapped over the normalized contact distance ($d_{\rm norm}$), shape index, curvedness, and fragment patches for both the 1-phenylsemicarbazide and 1-phenylpyrazolidin-3-one components (see supplementary Figure). The $d_{\rm norm}$ surfaces of both molecules exhibit bright-red spots that signify close intermolecular contacts (shorter than the sum of van der Waals radii). For the 1-phenylsemicarbazide moiety, these red regions are concentrated around the amine donors (N1, N2) and the carbonyl acceptor (O1). Similarly, the 1-phenylpyrazolidin-3-one surface shows deep-red depressions near the N4 donor and O2 acceptor atoms. These features confirm the presence of the strong N—H$\cdots$O hydrogen bonding network identified in the crystal structure analysis.

The two-dimensional fingerprint plots (Fig. 4) provide a quantitative comparison of the intermolecular interactions for the two distinct units. The surface of *A* is dominated by H$\cdots$H contacts (47.6%), followed by C$\cdots$H/H$\cdots$C contacts (24.1%), which correspond to the C—H$\cdots\pi$ interactions. The O$\cdots$H/H$\cdots$O interactions, representing the strong hydrogen bonds, make a significant contribution of 23.5% and appear as sharp, distinct spikes. In *B*, a higher dominance of H$\cdots$H contacts (54.7%) can be seen and a similar contribution from C$\cdots$H/H$\cdots$C interactions (25.7%). However, the O$\cdots$H/H$\cdots$O interactions contribute less (13.3%) compared to the semicarbazide unit.

## 5. Synthesis and crystallization

Compound (**I**) was formed by mixing equimolar quantities of 1-phenylsemicarbazide (0.1512 g, 1 mmol) and 1-phenylpyrazolidin-3-one (0.1621 g, 1 mmol) in methanol (20 ml) and refluxing with stirring until a clear solution was obtained. The hot solution was filtered to remove any insoluble material and allowed to cool slowly to room temperature. Brown block-shaped crystals of (**I**) were obtained after slow evaporation of the solvent over several days.

FT IR (cm$^{-1}$) 3291 (N—H stretch); 3190 (aromatic C—H stretch); 1693 (amine N—H stretch); 1663 (C═O stretch); 1427 (pyrazolidinone C═N stretch); 1282 (aromatic C═N stretch); 1024 (semicarbazide N—N stretch). The red shift for the C═O bond from its typical position substantiates the hydrogen bonding in the cocrystal (Siji *et al.*, 2010*a*,*b*). UV/visible (methanol), 245 and 287 nm due to $\pi$–$\pi$* transitions of the aromatic rings. For figures of the IR, UV/visible and $^{1}$H and $^{13}$C NMR spectra of (**I**), see supporting information.

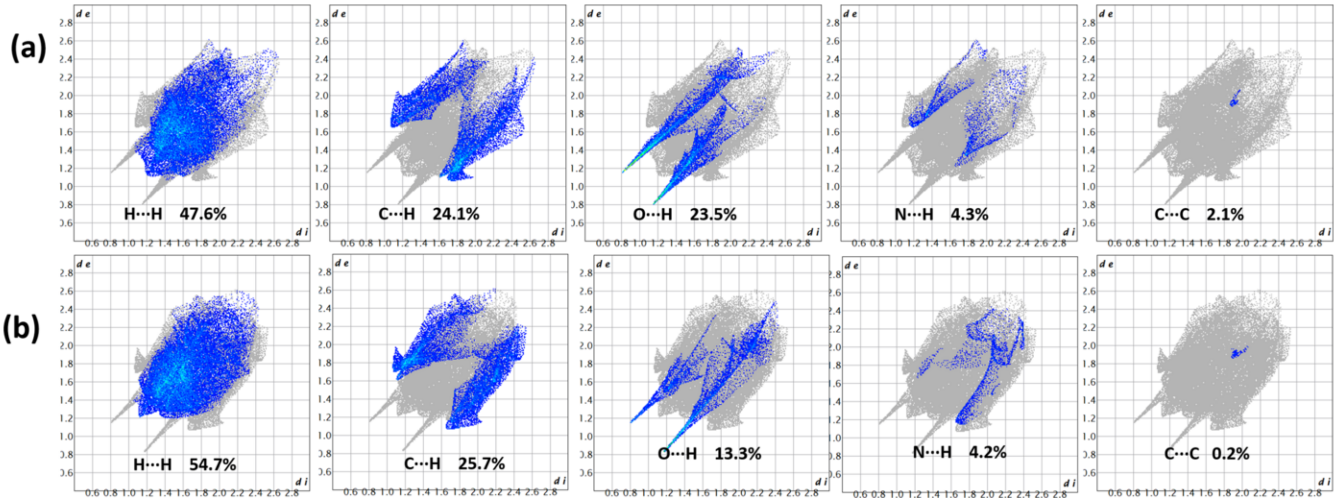


**Figure 4**
Two-dimensional fingerprint plots for (*a*) 1-phenylsemicarbazide and (*b*) 1-phenylpyrazolidin-3-one, delineated into specific intermolecular contacts with their percentage contributions to the Hirshfeld surface area.

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## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The N-bound hydrogen atoms were located in difference maps and freely refined. The C-bound H atoms were placed geometrically and refined using a riding model.

**Table 2**
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $C_7H_9N_3O{\cdot}C_9H_{10}N_2O$ |
| $M_r$ | 313.36 |
| Crystal system, space group | Triclinic, $P\overline{1}$ |
| Temperature (K) | 304 |
| $a$, $b$, $c$ (Å) | 7.3651 (6), 8.8906 (5), 13.3791 (10) |
| $\alpha$, $\beta$, $\gamma$ (°) | 76.121 (2), 88.579 (3), 73.108 (2) |
| $V$ (Å$^3$) | 812.84 (10) |
| $Z$ | 2 |
| Radiation type | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 0.09 |
| Crystal size (mm) | 0.35 × 0.21 × 0.09 |
| | |
| Data collection | |
| Diffractometer | Bruker D8 Venture Diffractometer |
| Absorption correction | Multi-scan (*SADABS*; Krause *et al.*, 2015) |
| $T_{\min}$, $T_{\max}$ | 0.535, 0.745 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 32158, 3069, 2566 |
| $R_{\rm int}$ | 0.063 |
| (sin $\theta/\lambda)_{\max}$ (Å$^{-1}$) | 0.609 |
| | |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.045, 0.123, 1.06 |
| No. of reflections | 3063 |
| No. of parameters | 223 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
| $\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å$^{-3}$) | 0.22, −0.26 |

Computer programs: *APEX4* and *SAINT* (Bruker, 2021), *SHELXT2018/2* (Sheldrick, 2015*a*), *SHELXL2019/3* (Sheldrick, 2015*b*), *ORTEP-3 for Windows* (Farrugia, 2012), *Mercury* (Macrae *et al.*, 2020) and *publCIF* (Westrip, 2010).

## Acknowledgements

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# supporting information

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## Synthesis and structure of a 1:1 1-phenylsemicarbazide–1-phenylpyrazolidin-3-one cocrystal

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### Computing details

### 1-Phenylsemicarbazide–1-phenylpyrazolidin-3-one (1/1)

*Crystal data*

$C_7H_9N_3O{\cdot}C_9H_{10}N_2O$
$M_r = 313.36$
Triclinic, $P\overline{1}$
$a = 7.3651$ (6) Å
$b = 8.8906$ (5) Å
$c = 13.3791$ (10) Å
$\alpha = 76.121$ (2)°
$\beta = 88.579$ (3)°
$\gamma = 73.108$ (2)°
$V = 812.84$ (10) Å$^3$
$Z = 2$
$F(000) = 332$
$D_x = 1.280$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9264 reflections
$\theta = 2.6$–25.6°
$\mu = 0.09$ mm$^{-1}$
$T = 304$ K
Block, brown
0.35 × 0.21 × 0.09 mm

*Data collection*

Bruker D8 Venture Diffractometer
Radiation source: fine focus sealed tube
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan
(SADABS; Krause *et al.*, 2015)
$T_{\min} = 0.535$, $T_{\max} = 0.745$
32158 measured reflections
3069 independent reflections
2566 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.063$
$\theta_{\max} = 25.7°$, $\theta_{\min} = 2.9°$
$h = -8 \rightarrow 8$
$k = -10 \rightarrow 10$
$l = -16 \rightarrow 16$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.123$
$S = 1.06$
3063 reflections
223 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0602P)^2 + 0.2037P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.22$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.26$ 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 (Å²)*

| | *x* | *y* | *z* | $U_{\text{iso}}$*/$U_{\text{eq}}$ |
|---|---|---|---|---|
| C1 | 0.2118 (2) | 0.60592 (16) | 0.52900 (10) | 0.0311 (3) |
| C2 | −0.0439 (2) | 0.79617 (18) | 0.69126 (12) | 0.0372 (3) |
| C3 | −0.1379 (2) | 0.9337 (2) | 0.72492 (14) | 0.0498 (4) |
| H3 | −0.197869 | 1.029765 | 0.677228 | 0.060* |
| C4 | −0.1425 (2) | 0.9279 (3) | 0.82926 (16) | 0.0589 (5) |
| H4 | −0.206428 | 1.020272 | 0.851105 | 0.071* |
| C5 | −0.0538 (3) | 0.7872 (3) | 0.90105 (15) | 0.0577 (5) |
| H5 | −0.056367 | 0.784348 | 0.971004 | 0.069* |
| C6 | 0.0385 (3) | 0.6513 (2) | 0.86799 (15) | 0.0544 (5) |
| H6 | 0.098617 | 0.555851 | 0.916145 | 0.065* |
| C7 | 0.0435 (2) | 0.6540 (2) | 0.76410 (14) | 0.0455 (4) |
| H7 | 0.105433 | 0.560428 | 0.743041 | 0.055* |
| C8 | 0.3195 (2) | 0.0381 (2) | 0.66850 (14) | 0.0480 (4) |
| C9 | 0.3529 (3) | −0.0688 (2) | 0.77620 (15) | 0.0605 (5) |
| H9A | 0.486672 | −0.126278 | 0.791363 | 0.073* |
| H9B | 0.281541 | −0.146969 | 0.785807 | 0.073* |
| C10 | 0.2827 (4) | 0.0488 (3) | 0.84304 (16) | 0.0755 (7) |
| H10A | 0.152873 | 0.054819 | 0.861230 | 0.091* |
| H10B | 0.362110 | 0.016182 | 0.905826 | 0.091* |
| C11 | 0.4384 (2) | 0.26709 (17) | 0.80707 (12) | 0.0382 (4) |
| C12 | 0.4607 (3) | 0.2703 (2) | 0.90964 (13) | 0.0470 (4) |
| H12 | 0.385872 | 0.227717 | 0.958919 | 0.056* |
| C13 | 0.5924 (3) | 0.3359 (2) | 0.93827 (15) | 0.0617 (5) |
| H13 | 0.608361 | 0.335093 | 1.007139 | 0.074* |
| C14 | 0.7001 (4) | 0.4023 (3) | 0.86646 (17) | 0.0829 (8) |
| H14 | 0.788846 | 0.446994 | 0.886201 | 0.100* |
| C15 | 0.6767 (3) | 0.4026 (3) | 0.76518 (17) | 0.0762 (7) |
| H15 | 0.748700 | 0.449360 | 0.716113 | 0.091* |
| C16 | 0.5478 (3) | 0.3346 (2) | 0.73500 (13) | 0.0502 (4) |
| H16 | 0.534571 | 0.334117 | 0.666125 | 0.060* |
| N1 | 0.3338 (2) | 0.68854 (16) | 0.53556 (11) | 0.0399 (3) |
| N2 | 0.02993 (19) | 0.66632 (17) | 0.55207 (11) | 0.0439 (3) |
| N3 | −0.02852 (19) | 0.80919 (16) | 0.58501 (11) | 0.0420 (3) |
| N4 | 0.2967 (3) | 0.18810 (18) | 0.67682 (12) | 0.0585 (5) |
| N5 | 0.2939 (2) | 0.20624 (18) | 0.77994 (11) | 0.0529 (4) |
| O1 | 0.25943 (14) | 0.47328 (12) | 0.50354 (8) | 0.0368 (3) |
| O2 | 0.3102 (2) | −0.00009 (15) | 0.58679 (10) | 0.0601 (4) |
| H1B | 0.460 (3) | 0.641 (3) | 0.5246 (17) | 0.072* |
| H1A | 0.303 (3) | 0.777 (3) | 0.5578 (17) | 0.072* |

| | | | | |
|---|---|---|---|---|
| H2N | −0.052 (3) | 0.614 (3) | 0.5465 (17) | 0.072* |
| H3N | −0.115 (3) | 0.879 (3) | 0.5449 (18) | 0.072* |
| H4N | 0.267 (3) | 0.273 (3) | 0.6235 (18) | 0.072* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0351 (8) | 0.0324 (7) | 0.0255 (7) | −0.0095 (6) | −0.0015 (5) | −0.0065 (5) |
| C2 | 0.0246 (7) | 0.0426 (8) | 0.0471 (9) | −0.0090 (6) | 0.0004 (6) | −0.0171 (7) |
| C3 | 0.0372 (9) | 0.0512 (10) | 0.0570 (11) | 0.0018 (7) | −0.0051 (7) | −0.0229 (8) |
| C4 | 0.0397 (9) | 0.0741 (13) | 0.0656 (12) | −0.0020 (9) | 0.0045 (8) | −0.0403 (10) |
| C5 | 0.0451 (10) | 0.0854 (14) | 0.0469 (10) | −0.0208 (9) | 0.0080 (8) | −0.0224 (10) |
| C6 | 0.0515 (10) | 0.0601 (11) | 0.0512 (11) | −0.0231 (9) | 0.0024 (8) | −0.0044 (8) |
| C7 | 0.0422 (9) | 0.0412 (9) | 0.0555 (10) | −0.0134 (7) | 0.0038 (7) | −0.0148 (7) |
| C8 | 0.0496 (10) | 0.0431 (9) | 0.0544 (10) | −0.0201 (7) | −0.0144 (8) | −0.0077 (7) |
| C9 | 0.0653 (12) | 0.0539 (11) | 0.0631 (12) | −0.0344 (9) | −0.0157 (9) | 0.0068 (9) |
| C10 | 0.1078 (18) | 0.0908 (16) | 0.0520 (12) | −0.0705 (15) | 0.0022 (11) | −0.0117 (11) |
| C11 | 0.0393 (8) | 0.0336 (7) | 0.0391 (8) | −0.0066 (6) | −0.0051 (6) | −0.0085 (6) |
| C12 | 0.0520 (10) | 0.0540 (10) | 0.0369 (9) | −0.0181 (8) | 0.0031 (7) | −0.0119 (7) |
| C13 | 0.0833 (14) | 0.0691 (12) | 0.0412 (10) | −0.0337 (11) | −0.0108 (9) | −0.0142 (9) |
| C14 | 0.1059 (19) | 0.1016 (18) | 0.0610 (13) | −0.0729 (16) | −0.0196 (12) | −0.0022 (12) |
| C15 | 0.0874 (16) | 0.0977 (17) | 0.0542 (12) | −0.0617 (14) | −0.0031 (11) | 0.0043 (11) |
| C16 | 0.0622 (11) | 0.0532 (10) | 0.0330 (8) | −0.0192 (8) | −0.0039 (8) | −0.0027 (7) |
| N1 | 0.0368 (7) | 0.0382 (7) | 0.0507 (8) | −0.0140 (6) | 0.0053 (6) | −0.0184 (6) |
| N2 | 0.0330 (7) | 0.0478 (8) | 0.0601 (9) | −0.0121 (6) | 0.0026 (6) | −0.0299 (7) |
| N3 | 0.0386 (7) | 0.0398 (7) | 0.0458 (8) | −0.0013 (6) | −0.0046 (6) | −0.0188 (6) |
| N4 | 0.0910 (12) | 0.0433 (8) | 0.0427 (8) | −0.0255 (8) | −0.0237 (8) | −0.0035 (6) |
| N5 | 0.0604 (9) | 0.0597 (9) | 0.0448 (8) | −0.0272 (7) | −0.0093 (7) | −0.0117 (7) |
| O1 | 0.0369 (6) | 0.0357 (5) | 0.0416 (6) | −0.0114 (4) | 0.0025 (4) | −0.0157 (4) |
| O2 | 0.0730 (9) | 0.0490 (7) | 0.0625 (8) | −0.0192 (6) | −0.0141 (7) | −0.0182 (6) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| C1—O1 | 1.2554 (16) | C10—H10A | 0.9700 |
| C1—N1 | 1.3311 (19) | C10—H10B | 0.9700 |
| C1—N2 | 1.3489 (19) | C11—C16 | 1.380 (2) |
| C2—C7 | 1.389 (2) | C11—C12 | 1.394 (2) |
| C2—C3 | 1.391 (2) | C11—N5 | 1.416 (2) |
| C2—N3 | 1.403 (2) | C12—C13 | 1.372 (3) |
| C3—C4 | 1.384 (3) | C12—H12 | 0.9300 |
| C3—H3 | 0.9300 | C13—C14 | 1.365 (3) |
| C4—C5 | 1.376 (3) | C13—H13 | 0.9300 |
| C4—H4 | 0.9300 | C14—C15 | 1.369 (3) |
| C5—C6 | 1.372 (3) | C14—H14 | 0.9300 |
| C5—H5 | 0.9300 | C15—C16 | 1.379 (3) |
| C6—C7 | 1.384 (3) | C15—H15 | 0.9300 |
| C6—H6 | 0.9300 | C16—H16 | 0.9300 |
| C7—H7 | 0.9300 | N1—H1B | 0.93 (2) |

| | | | |
|---|---|---|---|
| C8—O2 | 1.229 (2) | N1—H1A | 0.87 (2) |
| C8—N4 | 1.326 (2) | N2—N3 | 1.3909 (18) |
| C8—C9 | 1.505 (3) | N2—H2N | 0.88 (2) |
| C9—C10 | 1.508 (3) | N3—H3N | 0.84 (2) |
| C9—H9A | 0.9700 | N4—N5 | 1.426 (2) |
| C9—H9B | 0.9700 | N4—H4N | 0.88 (2) |
| C10—N5 | 1.475 (2) | | |

| | | | |
|---|---|---|---|
| O1—C1—N1 | 122.83 (13) | H10A—C10—H10B | 108.8 |
| O1—C1—N2 | 118.62 (13) | C16—C11—C12 | 118.72 (15) |
| N1—C1—N2 | 118.54 (13) | C16—C11—N5 | 122.61 (15) |
| C7—C2—C3 | 118.78 (15) | C12—C11—N5 | 118.47 (15) |
| C7—C2—N3 | 122.29 (14) | C13—C12—C11 | 120.35 (17) |
| C3—C2—N3 | 118.76 (15) | C13—C12—H12 | 119.8 |
| C4—C3—C2 | 120.15 (17) | C11—C12—H12 | 119.8 |
| C4—C3—H3 | 119.9 | C14—C13—C12 | 120.53 (18) |
| C2—C3—H3 | 119.9 | C14—C13—H13 | 119.7 |
| C5—C4—C3 | 120.84 (17) | C12—C13—H13 | 119.7 |
| C5—C4—H4 | 119.6 | C13—C14—C15 | 119.57 (19) |
| C3—C4—H4 | 119.6 | C13—C14—H14 | 120.2 |
| C6—C5—C4 | 119.08 (17) | C15—C14—H14 | 120.2 |
| C6—C5—H5 | 120.5 | C14—C15—C16 | 120.87 (19) |
| C4—C5—H5 | 120.5 | C14—C15—H15 | 119.6 |
| C5—C6—C7 | 121.05 (17) | C16—C15—H15 | 119.6 |
| C5—C6—H6 | 119.5 | C15—C16—C11 | 119.93 (17) |
| C7—C6—H6 | 119.5 | C15—C16—H16 | 120.0 |
| C6—C7—C2 | 120.10 (16) | C11—C16—H16 | 120.0 |
| C6—C7—H7 | 119.9 | C1—N1—H1B | 117.0 (13) |
| C2—C7—H7 | 119.9 | C1—N1—H1A | 122.8 (14) |
| O2—C8—N4 | 124.66 (16) | H1B—N1—H1A | 120 (2) |
| O2—C8—C9 | 128.52 (16) | C1—N2—N3 | 120.99 (13) |
| N4—C8—C9 | 106.80 (16) | C1—N2—H2N | 119.1 (14) |
| C8—C9—C10 | 103.49 (16) | N3—N2—H2N | 119.9 (15) |
| C8—C9—H9A | 111.1 | N2—N3—C2 | 117.65 (13) |
| C10—C9—H9A | 111.1 | N2—N3—H3N | 110.9 (15) |
| C8—C9—H9B | 111.1 | C2—N3—H3N | 118.1 (15) |
| C10—C9—H9B | 111.1 | C8—N4—N5 | 114.89 (15) |
| H9A—C9—H9B | 109.0 | C8—N4—H4N | 122.9 (14) |
| N5—C10—C9 | 105.18 (16) | N5—N4—H4N | 121.5 (14) |
| N5—C10—H10A | 110.7 | C11—N5—N4 | 114.65 (14) |
| C9—C10—H10A | 110.7 | C11—N5—C10 | 117.83 (15) |
| N5—C10—H10B | 110.7 | N4—N5—C10 | 104.08 (14) |
| C9—C10—H10B | 110.7 | | |

| | | | |
|---|---|---|---|
| C7—C2—C3—C4 | 0.4 (2) | C12—C11—C16—C15 | 0.3 (3) |
| N3—C2—C3—C4 | −174.90 (16) | N5—C11—C16—C15 | 175.19 (18) |
| C2—C3—C4—C5 | 0.4 (3) | O1—C1—N2—N3 | 177.20 (13) |
| C3—C4—C5—C6 | −0.6 (3) | N1—C1—N2—N3 | −1.9 (2) |

| | | | |
|---|---|---|---|
| C4—C5—C6—C7 | 0.1 (3) | C1—N2—N3—C2 | −99.21 (17) |
| C5—C6—C7—C2 | 0.7 (3) | C7—C2—N3—N2 | 17.9 (2) |
| C3—C2—C7—C6 | −0.9 (2) | C3—C2—N3—N2 | −166.97 (14) |
| N3—C2—C7—C6 | 174.18 (14) | O2—C8—N4—N5 | 173.73 (17) |
| O2—C8—C9—C10 | −160.94 (19) | C9—C8—N4—N5 | −4.9 (2) |
| N4—C8—C9—C10 | 17.7 (2) | C16—C11—N5—N4 | 12.7 (2) |
| C8—C9—C10—N5 | −23.4 (2) | C12—C11—N5—N4 | −172.37 (14) |
| C16—C11—C12—C13 | −1.6 (3) | C16—C11—N5—C10 | 135.77 (19) |
| N5—C11—C12—C13 | −176.65 (16) | C12—C11—N5—C10 | −49.3 (2) |
| C11—C12—C13—C14 | 1.6 (3) | C8—N4—N5—C11 | 119.86 (17) |
| C12—C13—C14—C15 | −0.3 (4) | C8—N4—N5—C10 | −10.3 (2) |
| C13—C14—C15—C16 | −1.0 (4) | C9—C10—N5—C11 | −107.49 (18) |
| C14—C15—C16—C11 | 1.0 (4) | C9—C10—N5—N4 | 20.7 (2) |

### *Hydrogen-bond geometry (Å, °)*

*Cg*2 and *Cg*3 are the centroids of the C11–C16 and C2–C7 rings, respectively

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1*B*···O1$^{i}$ | 0.93 (2) | 2.09 (2) | 3.0164 (17) | 178 (2) |
| N1—H1*A*···O2$^{ii}$ | 0.87 (2) | 2.12 (2) | 2.9645 (18) | 161 (2) |
| N2—H2*N*···O1$^{iii}$ | 0.88 (2) | 2.09 (2) | 2.9486 (17) | 166 (2) |
| N3—H3*N*···O2$^{iii}$ | 0.84 (2) | 2.15 (2) | 2.9641 (19) | 161 (2) |
| N4—H4*N*···O1 | 0.88 (2) | 2.08 (2) | 2.9471 (19) | 167 (2) |
| C4—H4···*Cg*2$^{iv}$ | 0.93 | 2.77 | 3.653 (3) | 158 |
| C9—H9*B*···*Cg*3$^{v}$ | 0.97 | 2.64 | 3.510 (2) | 149 |

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