



Structural characterization and comparative analysis of polymorphic forms of psilocin (4-hydroxy-*N,N*-dimethyltryptamine)

Matthias Zeller,^a Stephan Parent^{b†} and Nate Schultheiss^{c*}

^aPurdue University, Department of Chemistry, 560 Oval Drive, West Lafayette, IN 47907-2084, USA, ^bSolsta Consulting LLC, 1200 Fawn Ridge Drive, West Lafayette, IN 47906, USA, and ^cCanna-Chemistries LLC, 400 Main Street, Vincennes IN 47906, USA. *Correspondence e-mail: ns@canna-chemistries.com

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† Current affiliation: Improved Pharma LLC, West Lafayette, IN 47906, USA.

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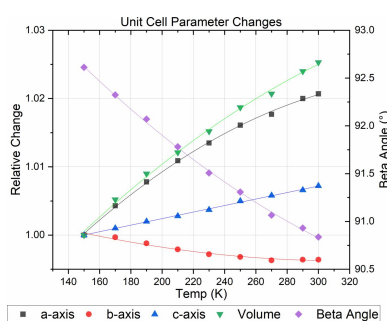
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The title compound, $C_{12}H_{16}N_2O$, is a hydroxy-substituted monoamine alkaloid, and the primary metabolite of the naturally occurring psychedelic compound psilocybin. Crystalline forms of psilocin are known, but their characterization by single-crystal structure analysis is limited. Herein, two anhydrous polymorphic forms (I and II) of psilocin are described. The crystal structure of polymorphic Form I, in space group $P2_1/c$, was first reported in 1974. Along with the redetermination to modern standards and unambiguous location of the acidic H atom and variable-temperature single-crystal unit-cell determinations for Form I, the Form II polymorph of the title compound, which crystallizes in the monoclinic space group $P2_1/n$, is described for the first time. The psilocin molecules are present in both forms in their phenol–amine tautomeric forms (not resolved in the 1974 report). The molecules in Forms I and II, however, feature different conformations of their *N,N*-dimethyl ethylene substituent, with the N–C–C link in Form I being *trans* and in Form II being *gauche*, allowing the latter to bend back to the hydroxyl group of the same molecule, leading to the formation of a strong intramolecular O–H···N hydrogen bond between the hydroxyl moiety and ethylamino-nitrogen group. In the extended structure of Form II, the molecules form one-dimensional strands through N–H···O hydrogen bonds from the indole group to the oxygen atom of the hydroxyl moiety of an adjacent molecule. Form II exhibits whole-molecule disorder due to a pseudo-mirror operation, with an occupancy ratio of 0.689 (5):0.311 (5) for the two components. In contrast, Form I does not feature intramolecular hydrogen bonds but forms a layered structure through intermolecular N–H···O and O–H···N hydrogen bonds.

1. Chemical context

Psychedelic-based therapies have garnered significant interest due to their potential for treating addiction, anxiety, depression, and post-traumatic stress disorder (PTSD) (Nichols, 2016). Currently, psilocybin {3-[2-(dimethylamino)ethyl]-1*H*-indol-4-yl dihydrogen phosphate, $C_{12}H_{17}N_2O_4P$ } is the most widely studied psychedelic compound for mental health conditions (Mitchell *et al.*, 2024). Upon entering the body, the prodrug psilocybin is dephosphorylated by the enzyme alkaline phosphatase, resulting in the active metabolite psilocin (4-hydroxy-*N,N*-dimethyltryptamine, $C_{12}H_{16}N_2O$). Psilocin is classified as a high-affinity agonist at serotonin 5-HT_{2A} receptors, which are responsible for producing the psychoactive effects within the body.

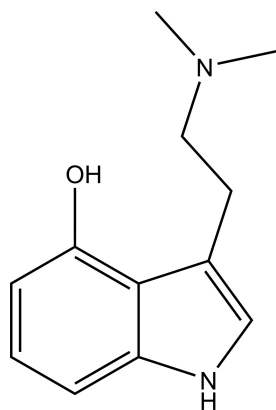
Crystalline materials derive their fundamental properties from the arrangement of individual molecules within the solid. Consequently, polymorphic compounds often exhibit distinct physicochemical properties such as solubility, dissolution,



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stability, and melting point (Bernstein, 2002). Single-crystal structure analysis facilitates inspection of the molecular connectivity and packing, which can lead to a more precise understanding of their structure–property relationships.

Psilocin was first chemically characterized by Albert Hofmann (Hofmann *et al.*, 1958), while a single-crystal structure of the title compound was later solved by Petcher *et al.* (1974) at room temperature in the space group $P2_1/c$. The quality and resolution of the 1974 structure are, by modern standards, relatively poor. For example, the position of the acidic hydrogen atom was not resolved, leading to a questionable interpretation of the data, such as the possibility that the compound exists as a mixture of neutral molecules and zwitterions. To get a better understanding of the structure of Form I, data were recollected at both room temperature and 150 K. Variable-temperature unit-cell determinations were also conducted, repeated every 20 K, starting from the complete dataset acquired at 150 K up to room temperature. This paper also describes for the first time the details of the crystal structure of a second polymorph (Form II) of psilocin, collected at room temperature in the space group $P2_1/n$ (preliminary data reported in a patent; Schultheiss *et al.*, 2022).



2. Structural commentary

Structural data for two polymorphic forms of psilocin, Forms I and II, were collected and analyzed. The two forms were obtained from different solvent mixtures: chloroform/heptane for Form I and chloroform for Form II. For Form II, the solution was acidified using HCl in attempts to form the psilocin hydrochloride salt. A single crystal from the sample was identified and isolated; however, the bulk material was not suitable for additional analytical characterization. The exact mechanism that induces the formation of the different polymorphs remains unclear and requires additional exploration.

The two forms crystallize in different settings of the same centrosymmetric monoclinic space group, $P2_1/c$ and $P2_1/n$ for Forms I and II, respectively. Each form has one crystallographically independent molecule ($Z^* = 1$, $Z = 4$) and similar molecular volume and density. Form I is more densely packed, with $\rho = 1.202$ rather than 1.190 g cm^{-3} for Form II (at room temperature). Although this difference could be attributed to the distinct molecular conformations and packing between the

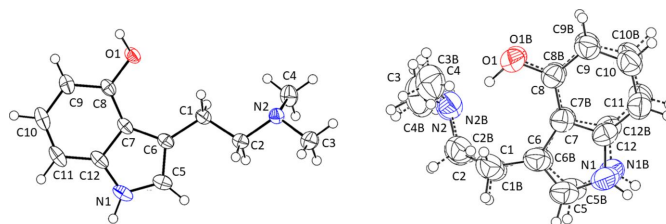


Figure 1

The molecular structures of psilocin (Form I left, Form II right) drawn at the 50% probability level. The major components of disorder are shown.

forms (see below), we do not consider this difference to be significant.

Displacement ellipsoid plots of the molecules for Form I and II are shown in Fig. 1. The molecules in both forms share the almost planar 4-hydroxy indole moiety. Bond lengths and angles in these moieties are unexceptional and as expected. The primary differences between the two forms lie in the molecular conformations of the psilocin molecules and the presence of disorder for Form II. Form I, previously described by Petcher and coworkers in 1974, exists in the crystal in its phenol–amine form, with the dimethylamine ethylene pendant grouping rotated away from the phenol oxygen atom and hydrogen-bonded to the phenol hydroxyl group of a neighboring molecule, forming centrosymmetric dimers (see *Supramolecular features* section). In contrast, Form II establishes an intramolecular $\text{O}–\text{H} \cdots \text{N}$ hydrogen bond, with the phenol $\text{O}–\text{H}$ group bonded to the dimethyl amine of the same molecule. Thus, the molecules in the two forms differ by the torsion angles of the dimethylamine chain. For Form I, the $\text{C6}–\text{C1}–\text{C2}–\text{N2}$ unit is *trans* with a torsion angle of $-172.27(11)^\circ$ [$-170.10(8)^\circ$ at 150 K]. The same unit in Form II adopts a *gauche* conformation, with a torsion angle of $-84.6(6)^\circ$ [$83.2(13)^\circ$ for the minor disorder component] for the equivalent atoms.

Another aspect that differentiates the two polymorphs is the presence of whole-molecule disorder in Form II. The entire molecule is disordered across its average plane, induced by an inversion at the two ethylene carbon atoms (C5 and C6). This is reflected in the already mentioned $\text{C6}–\text{C1}–\text{C2}–\text{N2}$ torsion angles, which are opposite in sign. The occupancy ratio refined to 0.689 (5):0.311 (5) (see the *Refinement* section for details). Consequently, the largest deviation between atom positions occurs at these two atoms (C1 and C2), but significant deviations are also observed for the disordered 4-hydroxy indole and dimethylamine fragments [$0.804(8) \text{ \AA}$ for the $\text{O1} \cdots \text{O1B}$ distance, for example].

The intramolecular $\text{O}–\text{H} \cdots \text{N}$ hydrogen bond is unaffected by the disorder; the acidic phenol proton is situated on the pseudo-mirror plane between the two moieties, maintaining the same position for both the major and minor moieties. As is typical for a strong hydrogen bond such as phenol-to-amine, the $\text{O}–\text{H}$ distance is elongated beyond the standard hydroxyl $\text{O}–\text{H}$ distance ($0.82–0.84 \text{ \AA}$ for X-ray based data): see Tables 1–3 for all metric parameters. The refined $\text{O}–\text{H}$ distances are $1.03(2) \text{ \AA}$ for Form I [$1.038(19) \text{ \AA}$ at 150 K], and $1.08(5)$ and $1.12(5) \text{ \AA}$ for the major and minor moieties of Form II,

respectively. These O—H bond lengths are slightly longer than those reported for similar compounds in the Cambridge Structural Database (CSD, 2023 version 5.45, including November 2023 update; Groom *et al.*, 2016): for 39 entries from 28 compounds featuring a phenol-to-dimethylamine hydrogen bond (excluding compounds where the O—H distance was constrained to a default value such as 0.82, 0.84 or 0.85 Å), an average O—H distance of 0.934 Å was reported. However, six of the 39 entries also feature O—H bond lengths greater than 1 Å, thus placing psilocin at the upper end of the observed range, although these values are not unprecedented. The H···N and O···N distances for Form I are 1.61 (2) and 2.6242 (14) Å [1.590 (19) and 2.6175 (10) Å at 150 K], and for Form II, they are 1.54 (5) and 2.584 (8) Å [1.43 (5) and 2.52 (2) Å for the minor moiety]. The average values from the CSD (for the same selection as for O—H distances) are 1.796 Å for H···N and 2.665 Å for the donor–acceptor distance, both significantly longer than the values found here, indicating that the elongated O—H distances in psilocin result from a very strong O—H···N hydrogen bond compared to other compounds with phenol to dimethylamine hydrogen bonds. This aligns with 4-hydroxy indole being more acidic than phenol itself or alkyl-substituted phenols, which constitute the majority of the 28 compounds from the CSD. However, the potential inaccuracy of refined H atom positions from X-ray data, especially for older or lower quality/resolution data, should be considered when comparing the data observed here with those from the CSD.

In their previous description of the structure of Form I, Petcher *et al.* (1974) were unable to locate the acidic hydrogen atom and speculated that the compound likely exists as a mixture of neutral molecules and zwitterions; that is, the phenol H atom might occasionally be transferred to the amine, forming a phenolate–ammonium proton-transfer complex. Proton transfer from a (relatively) strongly acidic phenol to an

amine would not be unprecedented. However, observations of this in the solid state are, with one exception, limited to very acidic di- and trinitro-substituted phenolates (25 entries in the CSD, excluding metal-coordinated phenolates). The one exception is a 4-bromo substituted phenolate (Ghosh *et al.*, 2022). In this case, the proton transfer to the dimethyl amine is facilitated by a second N—H group (from a hydrazinyl fragment) also hydrogen-bonded to the phenolate, thus stabilizing the anionic charge. No cases of a partial proton transfer, with an equilibrium between O—H···N and N—H⁺···O[−] states, have been reported for the solid state. With the new data now on hand, this can unequivocally be excluded as an option for psilocin. The electron densities of the acidic protons are well resolved for both polymorphic forms, and they are clearly associated with the phenol oxygen atom. The O—H bond lengths are elongated as expected for a strong hydrogen bond (as described above), but no split electron density or a full transfer of the proton is observed in either Form I (RT and 150 K) or in Form II.

To unequivocally exclude the possibility of partial proton transfer for psilocin in the solid state, low-temperature data were also collected for the better-defined, non-disordered polymorph, Form I. The refinement against the data collected at 150 K showed no indication of partial or full proton transfer, with well-defined and localized electron densities for the acidic hydrogen atoms. Variable-temperature unit-cell data were collected as well, showing a steady change in all unit-cell parameters between 300 and 150 K, with no indications of the presence of a discontinuity or phase change, see Fig. 2 and supporting information. The *a*- and *c*-axes exhibit a steady decline on cooling, while the *b*-axis marginally increases. The largest relative changes are observed for the *a*-axis and the unit-cell volume, which shrink by ~2 and 2.5%, respectively, upon cooling. The β angle increases from 90.8366 (24)° at 300 K to 92.6122 (19)° at 150 K (see supporting information). Overall, no unusual behavior is observed in the studied temperature range.

The closeness of the β angle to 90° allows for twinning by pseudo-merohedry. During the screening of crystals for data collection, twinning was indeed observed for some crystals (TWIN transformation matrix $-1\ 0\ 0 / 0\ -1\ 0 / 0\ 0\ 1$, corresponding to twofold rotation around the *c*-axis). Pseudo-merohedry led to twinning by non-merohedry upon cooling. All data reported here were collected from a crystal that was not twinned.

3. Supramolecular features

The difference between Forms I and II of psilocin are based on molecular conformations that lead to either intra- or intermolecular O—H···N bonds. Consequently, interactions between neighboring molecules also differ significantly between the two polymorphs. In Form I, all hydrogen-bonding interactions are intermolecular. Two types of classical hydrogen bonds involving acidic protons are observed: phenol OH to amine, and indole N—H to phenol. The O—H···N hydrogen bonds connect pairs of molecules into hydrogen-

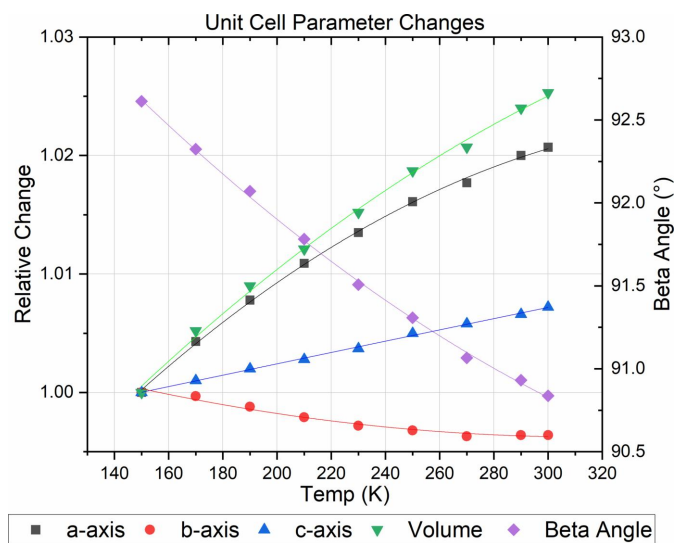


Figure 2
Variable-temperature unit-cell data of Form I from 150–300 K expressed as relative change compared to the 150 K values.

Table 1

Hydrogen-bond geometry (Å, °) for Form I at 150 K.

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|---------------------------|-------------|---------------|-----------------------|-------------------------|
| O1—H1O...N2 ⁱ | 1.038 (19) | 1.590 (19) | 2.6175 (10) | 169.5 (16) |
| N1—H1N...O1 ⁱⁱ | 0.913 (16) | 1.995 (17) | 2.8867 (11) | 165.0 (15) |

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

Table 2

Hydrogen-bond geometry (Å, °) for Form I at 300 K.

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|---------------------------|-------------|---------------|-----------------------|-------------------------|
| O1—H1O...N2 ⁱ | 1.03 (2) | 1.61 (2) | 2.6242 (14) | 166.6 (18) |
| N1—H1N...O1 ⁱⁱ | 0.92 (2) | 1.99 (2) | 2.8944 (14) | 167.9 (18) |

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

Table 3

Hydrogen-bond geometry (Å, °) for Form II at 293 K.

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|-----------------------------|-------------|---------------|-----------------------|-------------------------|
| N1—H1N...O1 ⁱ | 0.86 | 1.99 | 2.823 (8) | 164 |
| N1B—H1NB...O1B ⁱ | 0.86 | 2.14 | 2.984 (18) | 169 |
| O1—H1...N2 | 1.08 (5) | 1.54 (5) | 2.584 (8) | 161 (4) |
| O1B—H1...N2B | 1.12 (5) | 1.43 (5) | 2.52 (2) | 162 (4) |

Symmetry code: (i) $x - \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$.

bonded dimers, see Fig. 3: molecules are inversion-related [symmetry operator: (i) $1 - x, 1 - y, 1 - z$]. The N—H...O hydrogen bonds operate perpendicular to the plane of the inversion dimers [symmetry operator: (ii) $x, \frac{1}{2} - y, \frac{1}{2} + z$], thus connecting the molecules to other dimers and creating infinite layers that extend perpendicular to the *a*-axis direction. Additional weak interactions enhance adhesion within the layers, such as a weak C—H...O interaction originating from methylene C atom C1, supporting the inversion dimer, and a C—H... π interaction of a pyrrole H atom to a neighboring phenyl ring [C5—H5 to C7^{iv}, symmetry operator: (iv) $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$]. Perpendicular to the layers, along [100], no hydrogen bonds are realized, and no other directional interactions such as C—H...O, C—H...N, C—H... π , or π -stacking interactions are present, thus creating a distinctly two-dimensional layered packing arrangement, see Fig. 4.

In Form II, the O—H...N hydrogen bond is intramolecular, as described above. An intermolecular indole N—H to phenol O bond is also present, as in Form I. This interaction connects

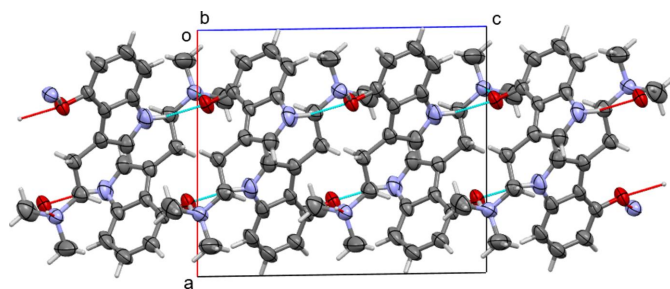


Figure 3

Intermolecular N—H...O hydrogen bonding between molecules of Form I.

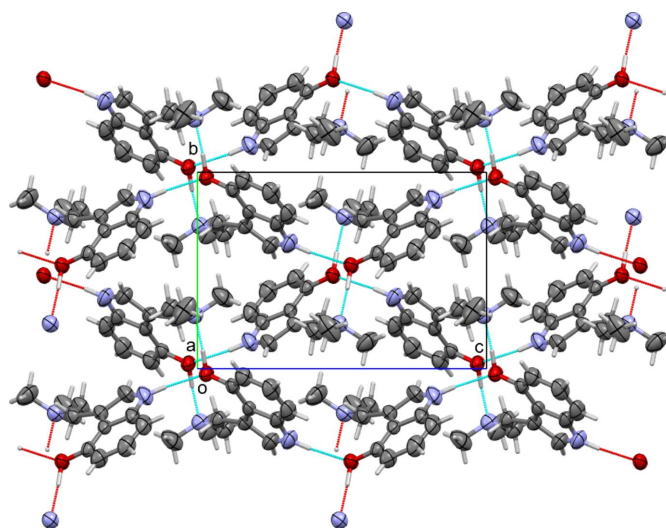


Figure 4

Intermolecular N—H...O and O—H...N hydrogen bonding between molecules of Form I resulting in two-dimensional layers.

molecules along the *ac*-diagonal (the [101] direction) into infinite chains. Parallel chains with opposite direction (inversion-related to the original chain) extend in parallel, thus creating an infinite array of N—H...O connected chains, see Fig. 5. Minor weak interactions connect neighboring chains. For the major disordered moiety, the most prominent interaction is a C—H... π interaction of a methyl group to C6 of a neighboring pyrrole ring (at $\frac{3}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$). For the minor moiety, a number of shorter-than-usual contacts involve close contacts between C atoms that are unlikely to be attractive interactions, like a 3.259 Å contact between methyl C atoms C3B and C3B^v [symmetry operator: (v) $2 - x, 1 - y, 1 - z$]. The most unfavorable interactions are present only between neighboring molecules of minor moieties, providing an explanation for why less than 50% of molecules are in the minor moiety orientation, as more than 50% occupancy would invariably lead to close and unfavorable contacts. The actual approximate 2:1 occupancy ratio [refined: 0.689 (5) to 0.311 (5)] avoids those close contacts.

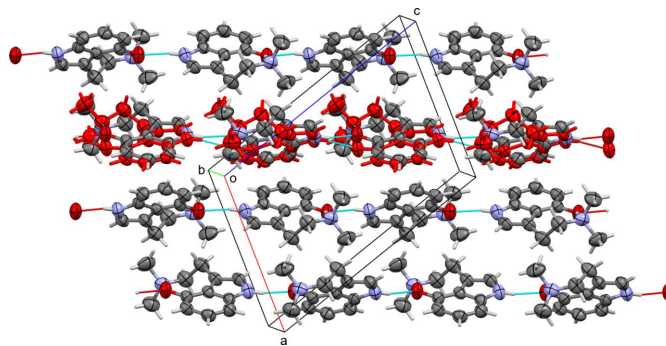


Figure 5

Hydrogen bonding in Form II with infinite chains along [101]. Minor moieties of the whole-molecule disorder are shown in red. Intermolecular N—H...O hydrogen bonds displayed in turquoise.

Table 4
Experimental details.

| | Form I at 150 K | Form I at 300 K | Form II at 293 K |
|---|--|--|--|
| Crystal data | | | |
| Chemical formula | C ₁₂ H ₁₆ N ₂ O | C ₁₂ H ₁₆ N ₂ O | C ₁₂ H ₁₆ N ₂ O |
| <i>M_r</i> | 204.27 | 204.27 | 204.27 |
| Crystal system, space group | Monoclinic, <i>P</i> 2 ₁ / <i>c</i> | Monoclinic, <i>P</i> 2 ₁ / <i>c</i> | Monoclinic, <i>P</i> 2 ₁ / <i>n</i> |
| Temperature (K) | 150 | 300 | 293 |
| <i>a</i> , <i>b</i> , <i>c</i> (Å) | 10.4041 (4), 8.5286 (3), 12.4087 (4) | 10.6228 (5), 8.4984 (4), 12.5073 (5) | 9.5331 (7), 8.9358 (3), 14.0279 (7) |
| β (°) | 92.5663 (19) | 90.807 (2) | 107.490 (7) |
| <i>V</i> (Å ³) | 1099.95 (7) | 1129.01 (9) | 1139.73 (11) |
| <i>Z</i> | 4 | 4 | 4 |
| Radiation type | Mo <i>K</i> α | Mo <i>K</i> α | Cu <i>K</i> α |
| μ (mm ⁻¹) | 0.08 | 0.08 | 0.61 |
| Crystal size (mm) | 0.43 × 0.29 × 0.06 | 0.43 × 0.29 × 0.06 | 0.37 × 0.16 × 0.04 |
| Data collection | | | |
| Diffractometer | Bruker AXS D8 Quest | Bruker AXS D8 Quest | SuperNova, Single source at offset, Pilatus 200/300K |
| Absorption correction | Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015) | Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015) | Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2015) |
| <i>T</i> _{min} , <i>T</i> _{max} | 0.663, 0.747 | 0.663, 0.747 | 0.675, 1.000 |
| No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections | 33575, 4199, 3116 | 34680, 4323, 2421 | 4929, 2329, 1754 |
| <i>R</i> _{int} | 0.051 | 0.066 | 0.019 |
| (<i>sin</i> θ / λ) _{max} (Å ⁻¹) | 0.770 | 0.771 | 0.634 |
| Refinement | | | |
| <i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i> | 0.046, 0.138, 1.05 | 0.052, 0.172, 1.03 | 0.065, 0.221, 1.13 |
| No. of reflections | 4199 | 4323 | 2329 |
| No. of parameters | 146 | 146 | 280 |
| No. of restraints | 0 | 0 | 532 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement | H atoms treated by a mixture of independent and constrained refinement | H atoms treated by a mixture of independent and constrained refinement |
| $\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³) | 0.35, -0.24 | 0.21, -0.19 | 0.18, -0.16 |

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *APEX4* (Bruker, 2022), *SAINTE* (Bruker, 2020), *SHELXT* (Sheldrick, 2015a), *SHELXL2019/2* (Sheldrick, 2015b), *ShelXle* (Hübschle *et al.*, 2011), *Mercury* (Macrae *et al.*, 2020) and *pubCIF* (Westrip, 2013).

4. Database survey

A search of the CSD revealed one entry of 4-hydroxy-*N,N*-dimethyltryptamine (psilocin) and one entry of a structurally very similar molecule, 5-hydroxy-*N,N*-dimethyltryptamine (bufotenine). The Form I (*P*2₁/*c*) polymorph of 4-hydroxy-*N,N*-dimethyltryptamine, with data collected at room temperature, was reported in 1974 (CSD refcode PSILIN; Petcher *et al.*, 1974). The crystal structure of 5-hydroxy-*N,N*-dimethyltryptamine, also collected at room temperature, was reported in 1972 (CSD refcode BUFTEN; Falkenberg 1972). In this case, the molecule possesses two hydrogen-bond donors/acceptors; however, moving the hydroxyl group from the 4- to the 5-position results in one-dimensional strands formed through a series of O—H···N hydrogen bonds (O···N = 2.719 Å) from the hydroxyl group to the ethylamino nitrogen atom. The indole hydrogen-bond donor and hydroxyl oxygen hydrogen-bond acceptor do not participate significantly in the overall structure. A series of results featuring the 4-hydroxy-*N,N*-dialkyltryptamine structural backbone were identified. In each case, when the tryptamine molecule reacts with iodomethane (MeI), the ethylamino group is alkylated, resulting in the formation of iodide salts (CSD refcodes EDOYIJ, EDOYUV, EDOZIK, XUXFAA; Glatfelter *et al.*, 2022; Chadeayne *et al.*, 2020b). Similarly, when 4-hydroxy-*N,N*-dialkyltryptamine reacts with fumaric acid, the ethylamino

group protonates, resulting in fumarate salts (CSD refcodes RONSUL, TUFQAP, WUCGAF; Chadeayne *et al.*, 2019a,b, 2020a).

5. Synthesis and crystallization

Crystallization of Form I: 44.6 mg of psilocin (Cayman Chemical) was dissolved in a 20-ml solvent mixture of chloroform (Supelco) and heptane (Sigma-Aldrich) in a 1:4 volume-to-volume ratio. The clear solution obtained was left to evaporate at ambient conditions until dry, resulting in the formation of rosettes of crystalline plates.

Crystallization of Form II: a suspension of 129.4 mg of psilocin (Cayman Chemical) in 8 ml of chloroform (Macron Chemicals) was briefly sonicated in the presence of activated charcoal. After sonication, the mixture was filtered through a 0.2 μ m nylon filter to remove particulates. The resulting clear solution was then acidified by adding 52 ml of 37% HCl (Sigma-Aldrich) over dry ice. The mixture was left to stand in the freezer for one day to facilitate phase separation. Subsequently, the upper layer was decanted from the biphasic mixture. The supernatant was partially evaporated under a stream of dry nitrogen at room temperature until lamellar plates began to form.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. For both Forms I and II, the carbon-bound hydrogen atoms were refined isotropically at calculated positions using a riding model. The methyl H atoms were allowed to rotate but not to tip to best fit the experimental electron density. The positions and displacement parameters of acidic H atoms (O–H and N–H) were freely refined. The displacement parameter of the acidic phenol H atom of Form II was freely refined. U_{iso} values were constrained to 1.5 times the U_{eq} of their pivot atoms for the other acidic H atoms and methyl groups and 1.2 times for all other hydrogen atoms.

For Form II, disorder was observed and refined. A rotation of the ethylene bridge connecting the dimethyl amino group to the indole ring system induces whole-molecule disorder. The two disordered moieties were restrained to have similar geometries [SAME command in *SHELXL* (Sheldrick, 2015b)]. The indene fragment of the minor moiety, including the directly adjacent C and O atoms, was restrained to be close to planar (FLAT command). The acidic phenol H atom was excluded from the disorder, and its position and displacement parameter were freely refined. The U_{ij} components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar. Subject to these conditions, the occupancy ratio refined to 0.689 (5) to 0.311 (5).

For the variable temperature unit cell measurements, a colorless, plate-shaped crystal of Form I (the same as used for the full data collections) was mounted on a Mitegen micro-mesh mount in a random orientation. Data were collected on a Bruker AXS D8 Quest three-circle diffractometer with a fine-focus sealed tube X-ray source, using a Triumph curved graphite crystal as monochromator and a PhotonII charge-integrating pixel array (CPAD) detector. The diffractometer used Mo K_{α} radiation ($\lambda = 0.71073 \text{ \AA}$). The crystal was initially shock-cooled to 150 K, at which temperature a full dataset was collected. The temperature was then increased at a rate of 6° per minute to the next target temperature. After a waiting period of 15 minutes for temperature equilibration, a 180° φ scan ('Fast Scan') was collected (5 cm detector-to-crystal distance, $2\theta = 0^{\circ}$, shutterless continuous mode, 5 seconds exposure time per read out every 1°). The last 120 of the 180 frames of each run were integrated using *SAINTE V8.40B* (Bruker, 2020). The results (unit-cell parameters, orientation matrices, and correction parameters) were reimported, and the integration was repeated once. The procedure was repeated every 20 K, and the unit-cell data were obtained from the integration files (p4p files).

Acknowledgements

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supporting information

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Structural characterization and comparative analysis of polymorphic forms of psilocin (4-hydroxy-*N,N*-dimethyltryptamine)

Matthias Zeller, Stephan Parent and Nate Schultheiss

Computing details

3-[2-(Dimethylamino)ethyl]-1*H*-indol-4-ol (Form_II_293K)

Crystal data

$C_{12}H_{16}N_2O$

$M_r = 204.27$

Monoclinic, $P2_1/n$

$a = 9.5331$ (7) Å

$b = 8.9358$ (3) Å

$c = 14.0279$ (7) Å

$\beta = 107.490$ (7)°

$V = 1139.73$ (11) Å³

$Z = 4$

$F(000) = 440$

$D_x = 1.190$ Mg m⁻³

Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å

Cell parameters from 2141 reflections

$\theta = 4.9\text{--}77.1^\circ$

$\mu = 0.61$ mm⁻¹

$T = 293$ K

Plate, colourless

$0.37 \times 0.16 \times 0.04$ mm

Data collection

SuperNova, Single source at offset, Pilatus
200/300K

diffractometer

Radiation source: micro-focus sealed X-ray
tube, SuperNova (Cu) X-ray Source

ω scans

Absorption correction: multi-scan
(CrysAlisPro; Rigaku OD, 2015)

$T_{\min} = 0.675$, $T_{\max} = 1.000$

4929 measured reflections

2329 independent reflections

1754 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.019$

$\theta_{\max} = 78.0^\circ$, $\theta_{\min} = 5.0^\circ$

$h = -11 \rightarrow 8$

$k = -11 \rightarrow 11$

$l = -17 \rightarrow 17$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.065$

$wR(F^2) = 0.221$

$S = 1.13$

2329 reflections

280 parameters

532 restraints

Primary atom site location: dual

Secondary atom site location: difference Fourier
map

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.1062P)^2 + 0.3139P]$

where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{\max} = 0.18$ 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.

Refinement. Rotation of the ethylene bridge connecting the dimethyl amino group induces whole molecule disorder. The two disordered moieties were restrained to have similar geometries. The indene fragment of the minor moiety including the directly adjacent C and O atoms was restrained to be close to planar. The acidic phenol H atom was excluded from the disorder and its position and thermal parameter were freely refined. Uij components of ADPs for disordered atoms closer to each other than 2.0 Angstrom were restrained to be similar. Subject to these conditions the occupancy ratio refined to 0.689 (5) to 0.311 (5).

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

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ | Occ. (<1) |
|-----|-------------|-------------|------------|----------------------------------|-----------|
| H1 | 0.629 (5) | 0.548 (5) | 0.379 (3) | 0.120 (13)* | |
| C1 | 0.6049 (6) | 0.4321 (5) | 0.1961 (3) | 0.0786 (12) | 0.689 (5) |
| H1A | 0.701941 | 0.477062 | 0.218344 | 0.094* | 0.689 (5) |
| H1B | 0.598839 | 0.374580 | 0.136326 | 0.094* | 0.689 (5) |
| C2 | 0.5891 (7) | 0.3248 (5) | 0.2772 (3) | 0.0793 (11) | 0.689 (5) |
| H2A | 0.485373 | 0.309139 | 0.268700 | 0.095* | 0.689 (5) |
| H2B | 0.631533 | 0.228959 | 0.268722 | 0.095* | 0.689 (5) |
| N2 | 0.6602 (6) | 0.3790 (7) | 0.3790 (4) | 0.0700 (13) | 0.689 (5) |
| C3 | 0.8215 (7) | 0.3657 (8) | 0.4111 (6) | 0.0991 (18) | 0.689 (5) |
| H3A | 0.848490 | 0.262228 | 0.410669 | 0.149* | 0.689 (5) |
| H3B | 0.860680 | 0.405160 | 0.477477 | 0.149* | 0.689 (5) |
| H3C | 0.860535 | 0.420937 | 0.366147 | 0.149* | 0.689 (5) |
| C4 | 0.6000 (8) | 0.3008 (7) | 0.4497 (5) | 0.0880 (16) | 0.689 (5) |
| H4A | 0.496721 | 0.321472 | 0.433727 | 0.132* | 0.689 (5) |
| H4B | 0.649220 | 0.334574 | 0.516344 | 0.132* | 0.689 (5) |
| H4C | 0.614668 | 0.195002 | 0.445389 | 0.132* | 0.689 (5) |
| N1 | 0.3190 (10) | 0.6949 (9) | 0.0677 (6) | 0.0731 (15) | 0.689 (5) |
| H1N | 0.253727 | 0.724472 | 0.014198 | 0.110* | 0.689 (5) |
| C5 | 0.3974 (7) | 0.5670 (8) | 0.0772 (5) | 0.0692 (15) | 0.689 (5) |
| H5 | 0.387132 | 0.496668 | 0.026696 | 0.083* | 0.689 (5) |
| C6 | 0.4918 (6) | 0.5555 (6) | 0.1692 (4) | 0.0646 (11) | 0.689 (5) |
| C7 | 0.4692 (9) | 0.6852 (8) | 0.2248 (5) | 0.0557 (14) | 0.689 (5) |
| C8 | 0.5353 (6) | 0.7405 (7) | 0.3216 (4) | 0.0573 (12) | 0.689 (5) |
| C9 | 0.4903 (8) | 0.8781 (8) | 0.3460 (6) | 0.0651 (16) | 0.689 (5) |
| H9 | 0.533483 | 0.918116 | 0.409263 | 0.078* | 0.689 (5) |
| C10 | 0.3792 (13) | 0.9580 (11) | 0.2755 (6) | 0.0687 (18) | 0.689 (5) |
| H10 | 0.346823 | 1.047946 | 0.294841 | 0.082* | 0.689 (5) |
| C11 | 0.3173 (13) | 0.9095 (11) | 0.1803 (6) | 0.0683 (17) | 0.689 (5) |
| H11 | 0.249568 | 0.967390 | 0.133219 | 0.082* | 0.689 (5) |
| C12 | 0.3599 (13) | 0.7700 (10) | 0.1570 (6) | 0.0570 (13) | 0.689 (5) |
| O1 | 0.6453 (5) | 0.6668 (4) | 0.3906 (3) | 0.0720 (9) | 0.689 (5) |
| C1B | 0.5012 (11) | 0.3867 (10) | 0.2090 (7) | 0.078 (2) | 0.311 (5) |
| H1C | 0.478936 | 0.323039 | 0.150278 | 0.094* | 0.311 (5) |
| H1D | 0.446315 | 0.348423 | 0.251780 | 0.094* | 0.311 (5) |

| | | | | | |
|------|-------------|-------------|-------------|-----------|-----------|
| C2B | 0.6645 (12) | 0.3715 (13) | 0.2644 (7) | 0.079 (2) | 0.311 (5) |
| H2C | 0.696312 | 0.270113 | 0.257242 | 0.095* | 0.311 (5) |
| H2D | 0.720114 | 0.439026 | 0.235409 | 0.095* | 0.311 (5) |
| N2B | 0.6939 (15) | 0.4062 (19) | 0.3706 (9) | 0.073 (3) | 0.311 (5) |
| C3B | 0.8539 (14) | 0.443 (2) | 0.4141 (14) | 0.105 (4) | 0.311 (5) |
| H3D | 0.911578 | 0.355453 | 0.411664 | 0.158* | 0.311 (5) |
| H3E | 0.872839 | 0.473878 | 0.482286 | 0.158* | 0.311 (5) |
| H3F | 0.879671 | 0.521794 | 0.376268 | 0.158* | 0.311 (5) |
| C4B | 0.6546 (16) | 0.2889 (18) | 0.4287 (12) | 0.096 (3) | 0.311 (5) |
| H4D | 0.549796 | 0.276267 | 0.407503 | 0.143* | 0.311 (5) |
| H4E | 0.687337 | 0.315529 | 0.498172 | 0.143* | 0.311 (5) |
| H4F | 0.700690 | 0.197023 | 0.418951 | 0.143* | 0.311 (5) |
| N1B | 0.306 (2) | 0.722 (2) | 0.0774 (13) | 0.068 (2) | 0.311 (5) |
| H1NB | 0.248617 | 0.762923 | 0.024437 | 0.102* | 0.311 (5) |
| C5B | 0.3611 (15) | 0.5824 (19) | 0.0815 (11) | 0.065 (2) | 0.311 (5) |
| H5B | 0.343952 | 0.519523 | 0.026288 | 0.078* | 0.311 (5) |
| C6B | 0.4454 (12) | 0.5433 (12) | 0.1756 (10) | 0.067 (2) | 0.311 (5) |
| C7B | 0.446 (2) | 0.6822 (18) | 0.2322 (11) | 0.055 (2) | 0.311 (5) |
| C8B | 0.4966 (13) | 0.7291 (15) | 0.3325 (9) | 0.056 (2) | 0.311 (5) |
| C9B | 0.4612 (18) | 0.8680 (16) | 0.3603 (12) | 0.058 (2) | 0.311 (5) |
| H9B | 0.499146 | 0.895479 | 0.427087 | 0.070* | 0.311 (5) |
| C10B | 0.374 (3) | 0.968 (2) | 0.2955 (13) | 0.059 (2) | 0.311 (5) |
| H10B | 0.357485 | 1.063956 | 0.316512 | 0.071* | 0.311 (5) |
| C11B | 0.312 (3) | 0.924 (2) | 0.2009 (13) | 0.059 (2) | 0.311 (5) |
| H11B | 0.241889 | 0.984553 | 0.156808 | 0.071* | 0.311 (5) |
| C12B | 0.352 (3) | 0.788 (2) | 0.1687 (14) | 0.058 (2) | 0.311 (5) |
| O1B | 0.5739 (11) | 0.6420 (9) | 0.4069 (5) | 0.076 (2) | 0.311 (5) |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-----------|-------------|-------------|--------------|-------------|--------------|
| C1 | 0.106 (3) | 0.067 (2) | 0.072 (2) | 0.004 (2) | 0.041 (2) | −0.0041 (17) |
| C2 | 0.105 (3) | 0.055 (2) | 0.081 (2) | 0.003 (2) | 0.033 (2) | −0.0001 (17) |
| N2 | 0.078 (3) | 0.059 (3) | 0.080 (2) | 0.0124 (19) | 0.0338 (19) | 0.0092 (18) |
| C3 | 0.072 (3) | 0.097 (4) | 0.134 (4) | 0.026 (3) | 0.039 (3) | 0.019 (4) |
| C4 | 0.104 (4) | 0.076 (3) | 0.094 (3) | −0.002 (3) | 0.045 (3) | 0.015 (2) |
| N1 | 0.084 (3) | 0.078 (4) | 0.050 (2) | −0.007 (2) | 0.0099 (18) | −0.004 (2) |
| C5 | 0.084 (3) | 0.072 (3) | 0.0559 (19) | −0.008 (2) | 0.028 (2) | −0.0104 (18) |
| C6 | 0.082 (3) | 0.0618 (19) | 0.0557 (17) | −0.0055 (19) | 0.028 (2) | −0.0054 (14) |
| C7 | 0.064 (3) | 0.0537 (18) | 0.0522 (19) | −0.0065 (17) | 0.0216 (17) | 0.0023 (15) |
| C8 | 0.064 (3) | 0.0563 (19) | 0.0525 (19) | −0.0007 (19) | 0.0193 (18) | 0.0034 (15) |
| C9 | 0.081 (3) | 0.060 (2) | 0.059 (3) | 0.001 (2) | 0.028 (2) | −0.0028 (18) |
| C10 | 0.078 (2) | 0.063 (3) | 0.072 (4) | 0.009 (2) | 0.032 (3) | −0.004 (3) |
| C11 | 0.069 (2) | 0.070 (3) | 0.066 (3) | 0.011 (2) | 0.020 (3) | 0.005 (2) |
| C12 | 0.059 (2) | 0.063 (3) | 0.049 (2) | −0.009 (2) | 0.0173 (19) | 0.0030 (19) |
| O1 | 0.083 (2) | 0.0611 (17) | 0.0585 (17) | 0.0045 (16) | 0.0007 (15) | −0.0042 (12) |
| C1B | 0.095 (4) | 0.066 (4) | 0.073 (4) | −0.004 (3) | 0.026 (3) | −0.012 (3) |
| C2B | 0.096 (4) | 0.071 (4) | 0.076 (4) | 0.010 (4) | 0.035 (3) | −0.004 (3) |

| | | | | | | |
|------|-----------|-----------|-----------|------------|-----------|------------|
| N2B | 0.081 (5) | 0.065 (5) | 0.078 (4) | 0.009 (4) | 0.032 (4) | 0.001 (4) |
| C3B | 0.069 (6) | 0.113 (9) | 0.131 (8) | 0.016 (7) | 0.026 (6) | 0.003 (8) |
| C4B | 0.099 (7) | 0.086 (6) | 0.108 (7) | 0.012 (6) | 0.040 (6) | 0.023 (6) |
| N1B | 0.083 (4) | 0.064 (4) | 0.053 (4) | 0.001 (3) | 0.014 (3) | 0.002 (3) |
| C5B | 0.077 (4) | 0.068 (4) | 0.054 (3) | -0.006 (4) | 0.024 (3) | -0.012 (3) |
| C6B | 0.077 (4) | 0.063 (3) | 0.065 (3) | -0.001 (3) | 0.026 (3) | -0.008 (3) |
| C7B | 0.065 (4) | 0.053 (3) | 0.050 (3) | 0.000 (3) | 0.021 (3) | -0.001 (3) |
| C8B | 0.067 (4) | 0.054 (3) | 0.047 (3) | 0.000 (3) | 0.019 (3) | 0.001 (3) |
| C9B | 0.074 (4) | 0.054 (3) | 0.052 (4) | 0.000 (3) | 0.029 (3) | -0.001 (3) |
| C10B | 0.073 (4) | 0.053 (4) | 0.060 (4) | 0.009 (3) | 0.034 (4) | -0.007 (3) |
| C11B | 0.064 (4) | 0.061 (4) | 0.059 (5) | 0.011 (3) | 0.030 (4) | -0.001 (4) |
| C12B | 0.065 (4) | 0.061 (4) | 0.051 (4) | -0.006 (3) | 0.019 (3) | 0.000 (3) |
| O1B | 0.098 (5) | 0.066 (4) | 0.051 (3) | 0.014 (4) | 0.005 (3) | -0.002 (3) |

Geometric parameters (Å, °)

| | | | |
|---------|-----------|-----------|------------|
| C1—C6 | 1.509 (6) | C1B—C2B | 1.523 (12) |
| C1—C2 | 1.530 (6) | C1B—H1C | 0.9700 |
| C1—H1A | 0.9700 | C1B—H1D | 0.9700 |
| C1—H1B | 0.9700 | C2B—N2B | 1.463 (13) |
| C2—N2 | 1.466 (7) | C2B—H2C | 0.9700 |
| C2—H2A | 0.9700 | C2B—H2D | 0.9700 |
| C2—H2B | 0.9700 | N2B—C4B | 1.444 (14) |
| N2—C4 | 1.463 (7) | N2B—C3B | 1.498 (14) |
| N2—C3 | 1.471 (7) | N2B—H1 | 1.43 (5) |
| C3—H3A | 0.9600 | C3B—H3D | 0.9600 |
| C3—H3B | 0.9600 | C3B—H3E | 0.9600 |
| C3—H3C | 0.9600 | C3B—H3F | 0.9600 |
| C4—H4A | 0.9600 | C4B—H4D | 0.9600 |
| C4—H4B | 0.9600 | C4B—H4E | 0.9600 |
| C4—H4C | 0.9600 | C4B—H4F | 0.9600 |
| N1—C5 | 1.350 (7) | N1B—C5B | 1.347 (13) |
| N1—C12 | 1.370 (6) | N1B—C12B | 1.359 (13) |
| N1—H1N | 0.8600 | N1B—H1NB | 0.8600 |
| C5—C6 | 1.337 (7) | C5B—C6B | 1.368 (13) |
| C5—H5 | 0.9300 | C5B—H5B | 0.9300 |
| C6—C7 | 1.449 (6) | C6B—C7B | 1.472 (12) |
| C7—C8 | 1.403 (6) | C7B—C8B | 1.407 (12) |
| C7—C12 | 1.404 (6) | C7B—C12B | 1.416 (13) |
| C8—O1 | 1.364 (5) | C8B—O1B | 1.333 (11) |
| C8—C9 | 1.379 (7) | C8B—C9B | 1.374 (12) |
| C9—C10 | 1.408 (7) | C9B—C10B | 1.369 (13) |
| C9—H9 | 0.9300 | C9B—H9B | 0.9300 |
| C10—C11 | 1.358 (7) | C10B—C11B | 1.340 (13) |
| C10—H10 | 0.9300 | C10B—H10B | 0.9300 |
| C11—C12 | 1.380 (7) | C11B—C12B | 1.397 (13) |
| C11—H11 | 0.9300 | C11B—H11B | 0.9300 |
| O1—H1 | 1.08 (5) | O1B—H1 | 1.12 (5) |

| | | | |
|------------|------------|---------------|------------|
| C1B—C6B | 1.521 (12) | | |
| C6—C1—C2 | 114.9 (4) | C2B—C1B—H1C | 108.1 |
| C6—C1—H1A | 108.5 | C6B—C1B—H1D | 108.1 |
| C2—C1—H1A | 108.5 | C2B—C1B—H1D | 108.1 |
| C6—C1—H1B | 108.5 | H1C—C1B—H1D | 107.3 |
| C2—C1—H1B | 108.5 | N2B—C2B—C1B | 110.8 (9) |
| H1A—C1—H1B | 107.5 | N2B—C2B—H2C | 109.5 |
| N2—C2—C1 | 113.5 (4) | C1B—C2B—H2C | 109.5 |
| N2—C2—H2A | 108.9 | N2B—C2B—H2D | 109.5 |
| C1—C2—H2A | 108.9 | C1B—C2B—H2D | 109.5 |
| N2—C2—H2B | 108.9 | H2C—C2B—H2D | 108.1 |
| C1—C2—H2B | 108.9 | C4B—N2B—C2B | 114.7 (13) |
| H2A—C2—H2B | 107.7 | C4B—N2B—C3B | 109.4 (12) |
| C4—N2—C2 | 110.0 (5) | C2B—N2B—C3B | 108.7 (12) |
| C4—N2—C3 | 109.9 (5) | C4B—N2B—H1 | 114 (2) |
| C2—N2—C3 | 113.9 (6) | C2B—N2B—H1 | 108.3 (19) |
| N2—C3—H3A | 109.5 | C3B—N2B—H1 | 101 (2) |
| N2—C3—H3B | 109.5 | N2B—C3B—H3D | 109.5 |
| H3A—C3—H3B | 109.5 | N2B—C3B—H3E | 109.5 |
| N2—C3—H3C | 109.5 | H3D—C3B—H3E | 109.5 |
| H3A—C3—H3C | 109.5 | N2B—C3B—H3F | 109.5 |
| H3B—C3—H3C | 109.5 | H3D—C3B—H3F | 109.5 |
| N2—C4—H4A | 109.5 | H3E—C3B—H3F | 109.5 |
| N2—C4—H4B | 109.5 | N2B—C4B—H4D | 109.5 |
| H4A—C4—H4B | 109.5 | N2B—C4B—H4E | 109.5 |
| N2—C4—H4C | 109.5 | H4D—C4B—H4E | 109.5 |
| H4A—C4—H4C | 109.5 | N2B—C4B—H4F | 109.5 |
| H4B—C4—H4C | 109.5 | H4D—C4B—H4F | 109.5 |
| C5—N1—C12 | 109.1 (6) | H4E—C4B—H4F | 109.5 |
| C5—N1—H1N | 125.4 | C5B—N1B—C12B | 110.4 (12) |
| C12—N1—H1N | 125.4 | C5B—N1B—H1NB | 124.8 |
| C6—C5—N1 | 110.7 (5) | C12B—N1B—H1NB | 124.8 |
| C6—C5—H5 | 124.7 | N1B—C5B—C6B | 112.7 (12) |
| N1—C5—H5 | 124.7 | N1B—C5B—H5B | 123.6 |
| C5—C6—C7 | 107.0 (5) | C6B—C5B—H5B | 123.6 |
| C5—C6—C1 | 121.4 (5) | C5B—C6B—C7B | 102.2 (10) |
| C7—C6—C1 | 131.3 (5) | C5B—C6B—C1B | 125.6 (11) |
| C8—C7—C12 | 119.4 (5) | C7B—C6B—C1B | 131.7 (10) |
| C8—C7—C6 | 134.9 (5) | C8B—C7B—C12B | 113.1 (11) |
| C12—C7—C6 | 105.5 (4) | C8B—C7B—C6B | 137.3 (12) |
| O1—C8—C9 | 118.9 (5) | C12B—C7B—C6B | 108.8 (10) |
| O1—C8—C7 | 122.9 (5) | O1B—C8B—C9B | 115.5 (10) |
| C9—C8—C7 | 118.2 (5) | O1B—C8B—C7B | 123.5 (11) |
| C8—C9—C10 | 120.1 (6) | C9B—C8B—C7B | 120.9 (10) |
| C8—C9—H9 | 119.9 | C10B—C9B—C8B | 123.9 (12) |
| C10—C9—H9 | 119.9 | C10B—C9B—H9B | 118.1 |
| C11—C10—C9 | 122.8 (7) | C8B—C9B—H9B | 118.1 |

| | | | |
|----------------|-------------|--------------------|-------------|
| C11—C10—H10 | 118.6 | C11B—C10B—C9B | 117.7 (14) |
| C9—C10—H10 | 118.6 | C11B—C10B—H10B | 121.2 |
| C10—C11—C12 | 116.7 (6) | C9B—C10B—H10B | 121.2 |
| C10—C11—H11 | 121.6 | C10B—C11B—C12B | 119.6 (14) |
| C12—C11—H11 | 121.6 | C10B—C11B—H11B | 120.2 |
| N1—C12—C11 | 129.5 (6) | C12B—C11B—H11B | 120.2 |
| N1—C12—C7 | 107.7 (5) | N1B—C12B—C11B | 129.8 (13) |
| C11—C12—C7 | 122.6 (6) | N1B—C12B—C7B | 105.7 (11) |
| C8—O1—H1 | 109 (2) | C11B—C12B—C7B | 124.4 (13) |
| C6B—C1B—C2B | 116.7 (8) | C8B—O1B—H1 | 111 (2) |
| C6B—C1B—H1C | 108.1 | | |
| C6—C1—C2—N2 | -84.6 (6) | C6B—C1B—C2B—N2B | 83.2 (13) |
| C1—C2—N2—C4 | 160.7 (5) | C1B—C2B—N2B—C4B | 76.8 (14) |
| C1—C2—N2—C3 | -75.4 (6) | C1B—C2B—N2B—C3B | -160.4 (12) |
| C12—N1—C5—C6 | -1.3 (8) | C12B—N1B—C5B—C6B | 1.6 (15) |
| N1—C5—C6—C7 | 1.9 (7) | N1B—C5B—C6B—C7B | -3.9 (10) |
| N1—C5—C6—C1 | -172.9 (5) | N1B—C5B—C6B—C1B | 168.7 (12) |
| C2—C1—C6—C5 | -117.6 (6) | C2B—C1B—C6B—C5B | 130.1 (10) |
| C2—C1—C6—C7 | 69.1 (8) | C2B—C1B—C6B—C7B | -59.5 (17) |
| C5—C6—C7—C8 | -177.2 (8) | C5B—C6B—C7B—C8B | 173 (2) |
| C1—C6—C7—C8 | -3.3 (13) | C1B—C6B—C7B—C8B | 1 (3) |
| C5—C6—C7—C12 | -1.6 (9) | C5B—C6B—C7B—C12B | 4.8 (19) |
| C1—C6—C7—C12 | 172.3 (7) | C1B—C6B—C7B—C12B | -167.2 (18) |
| C12—C7—C8—O1 | -177.9 (8) | C12B—C7B—C8B—O1B | 173.0 (19) |
| C6—C7—C8—O1 | -2.8 (12) | C6B—C7B—C8B—O1B | 5 (3) |
| C12—C7—C8—C9 | -0.4 (11) | C12B—C7B—C8B—C9B | -3 (3) |
| C6—C7—C8—C9 | 174.7 (8) | C6B—C7B—C8B—C9B | -171.8 (19) |
| O1—C8—C9—C10 | 178.6 (7) | O1B—C8B—C9B—C10B | -175.0 (17) |
| C7—C8—C9—C10 | 1.1 (10) | C7B—C8B—C9B—C10B | 2 (2) |
| C8—C9—C10—C11 | -3.6 (14) | C8B—C9B—C10B—C11B | 4 (3) |
| C9—C10—C11—C12 | 5.1 (16) | C9B—C10B—C11B—C12B | -8 (3) |
| C5—N1—C12—C11 | 174.9 (11) | C5B—N1B—C12B—C11B | -173 (3) |
| C5—N1—C12—C7 | 0.2 (10) | C5B—N1B—C12B—C7B | 2 (2) |
| C10—C11—C12—N1 | -178.3 (12) | C10B—C11B—C12B—N1B | -180 (3) |
| C10—C11—C12—C7 | -4.4 (16) | C10B—C11B—C12B—C7B | 6 (4) |
| C8—C7—C12—N1 | 177.3 (8) | C8B—C7B—C12B—N1B | -175.7 (18) |
| C6—C7—C12—N1 | 0.8 (10) | C6B—C7B—C12B—N1B | -4 (3) |
| C8—C7—C12—C11 | 2.2 (15) | C8B—C7B—C12B—C11B | 0 (4) |
| C6—C7—C12—C11 | -174.3 (10) | C6B—C7B—C12B—C11B | 171 (2) |

Hydrogen-bond geometry (\AA , $^\circ$)

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|------------------------------------|-------|-------------|-------------|---------------|
| N1—H1N \cdots O1 ⁱ | 0.86 | 1.99 | 2.823 (8) | 164 |
| N1B—H1NB \cdots O1B ⁱ | 0.86 | 2.14 | 2.984 (18) | 169 |

| | | | | |
|--------------|----------|----------|-----------|---------|
| O1—H1...N2 | 1.08 (5) | 1.54 (5) | 2.584 (8) | 161 (4) |
| O1B—H1...N2B | 1.12 (5) | 1.43 (5) | 2.52 (2) | 162 (4) |

Symmetry code: (i) $x-1/2, -y+3/2, z-1/2$.

(Form_I_150K)

Crystal data

| | |
|---------------------------------|---|
| $C_{12}H_{16}N_2O$ | $F(000) = 440$ |
| $M_r = 204.27$ | $D_x = 1.233 \text{ Mg m}^{-3}$ |
| Monoclinic, $P2_1/c$ | Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$ |
| $a = 10.4041 (4) \text{ \AA}$ | Cell parameters from 9931 reflections |
| $b = 8.5286 (3) \text{ \AA}$ | $\theta = 3.1\text{--}33.1^\circ$ |
| $c = 12.4087 (4) \text{ \AA}$ | $\mu = 0.08 \text{ mm}^{-1}$ |
| $\beta = 92.5663 (19)^\circ$ | $T = 150 \text{ K}$ |
| $V = 1099.95 (7) \text{ \AA}^3$ | Plate, colourless |
| $Z = 4$ | $0.43 \times 0.29 \times 0.06 \text{ mm}$ |

Data collection

| | |
|--|---|
| Bruker AXS D8 Quest diffractometer | $T_{\min} = 0.663, T_{\max} = 0.747$ |
| Radiation source: fine focus sealed tube X-ray source | 33575 measured reflections |
| Triumph curved graphite crystal monochromator | 4199 independent reflections |
| Detector resolution: $7.4074 \text{ pixels mm}^{-1}$ | 3116 reflections with $I > 2\sigma(I)$ |
| ω and phi scans | $R_{\text{int}} = 0.051$ |
| Absorption correction: multi-scan (SADABS 2016/2; Krause <i>et al.</i> , 2015) | $\theta_{\max} = 33.2^\circ, \theta_{\min} = 2.9^\circ$ |
| | $h = -16 \rightarrow 16$ |
| | $k = -13 \rightarrow 13$ |
| | $l = -19 \rightarrow 18$ |

Refinement

| | |
|----------------------------------|--|
| Refinement on F^2 | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: mixed |
| $R[F^2 > 2\sigma(F^2)] = 0.046$ | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2) = 0.138$ | $w = 1/[\sigma^2(F_o^2) + (0.0713P)^2 + 0.1621P]$ |
| $S = 1.05$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| 4199 reflections | $(\Delta/\sigma)_{\max} < 0.001$ |
| 146 parameters | $\Delta\rho_{\max} = 0.35 \text{ e \AA}^{-3}$ |
| 0 restraints | $\Delta\rho_{\min} = -0.24 \text{ e \AA}^{-3}$ |
| Primary atom site location: dual | |

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. The atom naming scheme was adopted from an earlier determination of this structure (T. J. Petcher, H. P. Weber, J. C. S. Perkin *Trans.* 2, 1974, 946-948, <https://doi.org/10.1039/P29740000946>). Positions and isotropic displacement parameters of acidic H atoms (O-H and N-H) were freely refined.

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

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|----|-------------|-------------|-------------|----------------------------------|
| O1 | 0.70597 (7) | 0.47588 (8) | 0.47509 (5) | 0.03151 (16) |

| | | | | |
|-----|--------------|--------------|--------------|--------------|
| H1O | 0.7335 (17) | 0.592 (2) | 0.4841 (14) | 0.071 (5)* |
| N1 | 0.64472 (10) | 0.13425 (11) | 0.18670 (7) | 0.0385 (2) |
| H1N | 0.6505 (15) | 0.0898 (19) | 0.1202 (13) | 0.056 (4)* |
| N2 | 0.24988 (8) | 0.22499 (9) | 0.49394 (6) | 0.02849 (16) |
| C1 | 0.47558 (9) | 0.23991 (11) | 0.43345 (7) | 0.02952 (18) |
| H1A | 0.472877 | 0.351903 | 0.454214 | 0.035* |
| H1B | 0.513277 | 0.180568 | 0.495733 | 0.035* |
| C5 | 0.54133 (11) | 0.12554 (12) | 0.25174 (8) | 0.0350 (2) |
| H5 | 0.467292 | 0.062248 | 0.237856 | 0.042* |
| C6 | 0.56084 (9) | 0.22194 (10) | 0.33987 (7) | 0.02783 (18) |
| C7 | 0.68352 (9) | 0.29695 (10) | 0.32686 (7) | 0.02674 (18) |
| C8 | 0.75460 (9) | 0.41272 (10) | 0.38446 (7) | 0.02762 (18) |
| C9 | 0.87124 (10) | 0.46122 (13) | 0.34568 (9) | 0.0357 (2) |
| H9 | 0.920818 | 0.537842 | 0.384468 | 0.043* |
| C10 | 0.91725 (11) | 0.39842 (14) | 0.24952 (9) | 0.0415 (3) |
| H10 | 0.997389 | 0.433933 | 0.224968 | 0.050* |
| C11 | 0.84970 (11) | 0.28788 (14) | 0.19068 (9) | 0.0403 (3) |
| H11 | 0.881122 | 0.246287 | 0.125900 | 0.048* |
| C12 | 0.73231 (10) | 0.23859 (11) | 0.22993 (7) | 0.0324 (2) |
| C2 | 0.33887 (9) | 0.18255 (12) | 0.40912 (8) | 0.0326 (2) |
| H2A | 0.306539 | 0.227858 | 0.339629 | 0.039* |
| H2B | 0.339916 | 0.067070 | 0.401086 | 0.039* |
| C3 | 0.11742 (11) | 0.18671 (17) | 0.45855 (11) | 0.0477 (3) |
| H3A | 0.095506 | 0.240663 | 0.390463 | 0.072* |
| H3B | 0.058665 | 0.220643 | 0.513544 | 0.072* |
| H3C | 0.109444 | 0.073191 | 0.447973 | 0.072* |
| C4 | 0.28086 (12) | 0.14338 (14) | 0.59591 (9) | 0.0417 (2) |
| H4A | 0.274408 | 0.029888 | 0.584536 | 0.063* |
| H4B | 0.220221 | 0.175593 | 0.649912 | 0.063* |
| H4C | 0.368648 | 0.170138 | 0.621391 | 0.063* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|------------|------------|------------|-------------|------------|-------------|
| O1 | 0.0440 (4) | 0.0254 (3) | 0.0263 (3) | -0.0044 (3) | 0.0143 (3) | -0.0015 (2) |
| N1 | 0.0508 (5) | 0.0386 (5) | 0.0265 (4) | 0.0103 (4) | 0.0070 (3) | -0.0076 (3) |
| N2 | 0.0294 (4) | 0.0283 (4) | 0.0280 (3) | -0.0019 (3) | 0.0039 (3) | -0.0006 (3) |
| C1 | 0.0325 (4) | 0.0296 (4) | 0.0269 (4) | -0.0009 (3) | 0.0058 (3) | -0.0038 (3) |
| C5 | 0.0437 (5) | 0.0319 (5) | 0.0295 (4) | 0.0051 (4) | 0.0025 (4) | -0.0067 (4) |
| C6 | 0.0345 (4) | 0.0245 (4) | 0.0249 (4) | 0.0047 (3) | 0.0052 (3) | -0.0014 (3) |
| C7 | 0.0340 (4) | 0.0244 (4) | 0.0224 (3) | 0.0081 (3) | 0.0079 (3) | 0.0028 (3) |
| C8 | 0.0343 (4) | 0.0249 (4) | 0.0244 (4) | 0.0049 (3) | 0.0093 (3) | 0.0043 (3) |
| C9 | 0.0355 (5) | 0.0361 (5) | 0.0364 (5) | 0.0024 (4) | 0.0119 (4) | 0.0043 (4) |
| C10 | 0.0373 (5) | 0.0480 (6) | 0.0408 (5) | 0.0100 (4) | 0.0186 (4) | 0.0091 (4) |
| C11 | 0.0448 (6) | 0.0457 (6) | 0.0318 (5) | 0.0170 (5) | 0.0174 (4) | 0.0041 (4) |
| C12 | 0.0422 (5) | 0.0304 (4) | 0.0251 (4) | 0.0125 (4) | 0.0094 (3) | 0.0015 (3) |
| C2 | 0.0334 (4) | 0.0346 (5) | 0.0301 (4) | -0.0006 (4) | 0.0033 (3) | -0.0078 (4) |
| C3 | 0.0306 (5) | 0.0634 (8) | 0.0492 (6) | -0.0026 (5) | 0.0012 (4) | -0.0151 (6) |

| | | | | | | |
|----|------------|------------|------------|-------------|------------|------------|
| C4 | 0.0452 (6) | 0.0420 (6) | 0.0383 (5) | -0.0024 (5) | 0.0067 (4) | 0.0142 (4) |
|----|------------|------------|------------|-------------|------------|------------|

Geometric parameters (Å, °)

| | | | |
|------------|-------------|-------------|-------------|
| O1—C8 | 1.3645 (10) | C7—C12 | 1.4165 (12) |
| O1—H1O | 1.038 (19) | C8—C9 | 1.3884 (13) |
| N1—C12 | 1.3662 (15) | C9—C10 | 1.4110 (15) |
| N1—C5 | 1.3755 (14) | C9—H9 | 0.9500 |
| N1—H1N | 0.913 (16) | C10—C11 | 1.3674 (18) |
| N2—C3 | 1.4644 (14) | C10—H10 | 0.9500 |
| N2—C4 | 1.4672 (13) | C11—C12 | 1.3995 (15) |
| N2—C2 | 1.4776 (12) | C11—H11 | 0.9500 |
| C1—C6 | 1.5004 (12) | C2—H2A | 0.9900 |
| C1—C2 | 1.5215 (14) | C2—H2B | 0.9900 |
| C1—H1A | 0.9900 | C3—H3A | 0.9800 |
| C1—H1B | 0.9900 | C3—H3B | 0.9800 |
| C5—C6 | 1.3759 (13) | C3—H3C | 0.9800 |
| C5—H5 | 0.9500 | C4—H4A | 0.9800 |
| C6—C7 | 1.4432 (13) | C4—H4B | 0.9800 |
| C7—C8 | 1.4090 (13) | C4—H4C | 0.9800 |
| | | | |
| C8—O1—H1O | 110.8 (10) | C11—C10—C9 | 121.84 (10) |
| C12—N1—C5 | 109.28 (8) | C11—C10—H10 | 119.1 |
| C12—N1—H1N | 123.8 (10) | C9—C10—H10 | 119.1 |
| C5—N1—H1N | 126.4 (10) | C10—C11—C12 | 117.19 (9) |
| C3—N2—C4 | 108.68 (9) | C10—C11—H11 | 121.4 |
| C3—N2—C2 | 110.07 (8) | C12—C11—H11 | 121.4 |
| C4—N2—C2 | 112.18 (8) | N1—C12—C11 | 129.50 (9) |
| C6—C1—C2 | 113.17 (8) | N1—C12—C7 | 107.71 (9) |
| C6—C1—H1A | 108.9 | C11—C12—C7 | 122.78 (10) |
| C2—C1—H1A | 108.9 | N2—C2—C1 | 112.95 (8) |
| C6—C1—H1B | 108.9 | N2—C2—H2A | 109.0 |
| C2—C1—H1B | 108.9 | C1—C2—H2A | 109.0 |
| H1A—C1—H1B | 107.8 | N2—C2—H2B | 109.0 |
| N1—C5—C6 | 110.04 (10) | C1—C2—H2B | 109.0 |
| N1—C5—H5 | 125.0 | H2A—C2—H2B | 107.8 |
| C6—C5—H5 | 125.0 | N2—C3—H3A | 109.5 |
| C5—C6—C7 | 106.01 (8) | N2—C3—H3B | 109.5 |
| C5—C6—C1 | 127.22 (9) | H3A—C3—H3B | 109.5 |
| C7—C6—C1 | 126.71 (8) | N2—C3—H3C | 109.5 |
| C8—C7—C12 | 118.49 (8) | H3A—C3—H3C | 109.5 |
| C8—C7—C6 | 134.47 (8) | H3B—C3—H3C | 109.5 |
| C12—C7—C6 | 106.95 (8) | N2—C4—H4A | 109.5 |
| O1—C8—C9 | 122.01 (9) | N2—C4—H4B | 109.5 |
| O1—C8—C7 | 119.29 (8) | H4A—C4—H4B | 109.5 |
| C9—C8—C7 | 118.69 (8) | N2—C4—H4C | 109.5 |
| C8—C9—C10 | 120.99 (11) | H4A—C4—H4C | 109.5 |
| C8—C9—H9 | 119.5 | H4B—C4—H4C | 109.5 |

| | | | |
|--------------|--------------|----------------|--------------|
| C10—C9—H9 | 119.5 | | |
| C12—N1—C5—C6 | -1.19 (12) | C7—C8—C9—C10 | 1.12 (15) |
| N1—C5—C6—C7 | 1.10 (11) | C8—C9—C10—C11 | -0.03 (17) |
| N1—C5—C6—C1 | -176.13 (9) | C9—C10—C11—C12 | -0.17 (17) |
| C2—C1—C6—C5 | -19.25 (14) | C5—N1—C12—C11 | -178.23 (10) |
| C2—C1—C6—C7 | 164.07 (9) | C5—N1—C12—C7 | 0.76 (11) |
| C5—C6—C7—C8 | 175.89 (10) | C10—C11—C12—N1 | 178.11 (10) |
| C1—C6—C7—C8 | -6.86 (16) | C10—C11—C12—C7 | -0.75 (16) |
| C5—C6—C7—C12 | -0.61 (10) | C8—C7—C12—N1 | -177.24 (8) |
| C1—C6—C7—C12 | 176.64 (8) | C6—C7—C12—N1 | -0.08 (10) |
| C12—C7—C8—O1 | 176.77 (8) | C8—C7—C12—C11 | 1.83 (14) |
| C6—C7—C8—O1 | 0.57 (15) | C6—C7—C12—C11 | 178.99 (9) |
| C12—C7—C8—C9 | -1.96 (13) | C3—N2—C2—C1 | 171.85 (9) |
| C6—C7—C8—C9 | -178.15 (10) | C4—N2—C2—C1 | -67.00 (11) |
| O1—C8—C9—C10 | -177.57 (9) | C6—C1—C2—N2 | -170.10 (8) |

Hydrogen-bond geometry (Å, °)

| <i>D</i> —H··· <i>A</i> | <i>D</i> —H | H··· <i>A</i> | <i>D</i> ··· <i>A</i> | <i>D</i> —H··· <i>A</i> |
|---------------------------|-------------|---------------|-----------------------|-------------------------|
| O1—H1O···N2 ⁱ | 1.038 (19) | 1.590 (19) | 2.6175 (10) | 169.5 (16) |
| N1—H1N···O1 ⁱⁱ | 0.913 (16) | 1.995 (17) | 2.8867 (11) | 165.0 (15) |

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

(Form_I_300K)

Crystal data

C₁₂H₁₆N₂O*M_r* = 204.27Monoclinic, *P*2₁/*c**a* = 10.6228 (5) Å*b* = 8.4984 (4) Å*c* = 12.5073 (5) Å β = 90.807 (2)°*V* = 1129.01 (9) Å³*Z* = 4*F*(000) = 440*D_x* = 1.202 Mg m⁻³Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 7001 reflections

 θ = 3.1–30.2° μ = 0.08 mm⁻¹*T* = 300 K

Plate, colourless

0.43 × 0.29 × 0.06 mm

Data collection

Bruker AXS D8 Quest

diffractometer

Radiation source: fine focus sealed tube X-ray

source

Triumph curved graphite crystal

monochromator

Detector resolution: 7.4074 pixels mm⁻¹ ω and ϕ scans

Absorption correction: multi-scan

(SADABS 2016/2; Krause *et al.*, 2015)*T_{min}* = 0.663, *T_{max}* = 0.747

34680 measured reflections

4323 independent reflections

2421 reflections with *I* > 2σ(*I*)*R_{int}* = 0.066 θ_{\max} = 33.2°, θ_{\min} = 2.9°*h* = -16→16*k* = -13→13*l* = -19→18

*Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.052$ $wR(F^2) = 0.172$ $S = 1.03$

4323 reflections

146 parameters

0 restraints

Primary atom site location: isomorphous
structure methodsSecondary atom site location: difference Fourier
map

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement $w = 1/[\sigma^2(F_o^2) + (0.0782P)^2 + 0.1036P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.21 \text{ e } \text{Å}^{-3}$ $\Delta\rho_{\min} = -0.19 \text{ e } \text{Å}^{-3}$ *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.

Refinement. The structure was solved from its 150 K analogue by isomorphous replacement. The atom naming scheme was adopted from an earlier determination of this structure (T. J. Petcher, H. P. Weber, J. C. S. Perkin *Trans. 2*, 1974, 946-948, <https://doi.org/10.1039/P29740000946>).

Positions and isotropic displacement parameters of acidic H atoms (O-H and N-H) were freely refined.

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

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|--------------|--------------|----------------------------------|
| O1 | 0.69993 (9) | 0.47438 (10) | 0.46870 (6) | 0.0560 (2) |
| H1O | 0.7313 (19) | 0.588 (3) | 0.4810 (15) | 0.103 (6)* |
| N1 | 0.64455 (13) | 0.13744 (16) | 0.18151 (10) | 0.0705 (4) |
| H1N | 0.6508 (18) | 0.095 (2) | 0.1144 (16) | 0.093 (6)* |
| N2 | 0.25313 (10) | 0.22804 (13) | 0.49141 (9) | 0.0552 (3) |
| C1 | 0.47404 (11) | 0.24181 (16) | 0.42811 (10) | 0.0541 (3) |
| H1A | 0.473533 | 0.351254 | 0.450111 | 0.065* |
| H1B | 0.507116 | 0.180151 | 0.487413 | 0.065* |
| C5 | 0.54246 (14) | 0.12965 (17) | 0.24671 (11) | 0.0639 (4) |
| H5 | 0.471156 | 0.068880 | 0.233330 | 0.077* |
| C6 | 0.55999 (12) | 0.22397 (14) | 0.33453 (9) | 0.0502 (3) |
| C7 | 0.68108 (11) | 0.29721 (13) | 0.32125 (8) | 0.0464 (3) |
| C8 | 0.75013 (11) | 0.41104 (14) | 0.37825 (9) | 0.0483 (3) |
| C9 | 0.86570 (13) | 0.45722 (18) | 0.33999 (12) | 0.0636 (3) |
| H9 | 0.913117 | 0.531082 | 0.377831 | 0.076* |
| C10 | 0.91262 (14) | 0.3942 (2) | 0.24471 (13) | 0.0739 (4) |
| H10 | 0.990900 | 0.427232 | 0.221063 | 0.089* |
| C11 | 0.84729 (15) | 0.2863 (2) | 0.18597 (12) | 0.0709 (4) |
| H11 | 0.879046 | 0.245610 | 0.122822 | 0.085* |
| C12 | 0.73034 (13) | 0.23927 (16) | 0.22452 (10) | 0.0567 (3) |
| C2 | 0.34100 (13) | 0.19072 (18) | 0.40446 (11) | 0.0620 (3) |
| H2A | 0.311821 | 0.241790 | 0.339330 | 0.074* |
| H2B | 0.340035 | 0.078053 | 0.392046 | 0.074* |
| C3 | 0.12307 (15) | 0.2040 (3) | 0.45468 (18) | 0.1042 (7) |
| H3A | 0.105329 | 0.272151 | 0.395138 | 0.156* |

| | | | | |
|-----|--------------|------------|--------------|------------|
| H3B | 0.066678 | 0.227621 | 0.511797 | 0.156* |
| H3C | 0.111940 | 0.096468 | 0.433020 | 0.156* |
| C4 | 0.27790 (19) | 0.1351 (2) | 0.58787 (15) | 0.0928 (6) |
| H4A | 0.263611 | 0.025763 | 0.572681 | 0.139* |
| H4B | 0.222611 | 0.168533 | 0.643515 | 0.139* |
| H4C | 0.363726 | 0.149990 | 0.610712 | 0.139* |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|--------------|-------------|--------------|
| O1 | 0.0711 (6) | 0.0524 (5) | 0.0450 (4) | −0.0088 (4) | 0.0212 (4) | −0.0048 (3) |
| N1 | 0.0868 (9) | 0.0741 (8) | 0.0509 (6) | 0.0118 (6) | 0.0123 (6) | −0.0191 (6) |
| N2 | 0.0498 (5) | 0.0578 (6) | 0.0582 (6) | −0.0052 (4) | 0.0087 (4) | −0.0046 (5) |
| C1 | 0.0550 (7) | 0.0573 (7) | 0.0502 (6) | −0.0007 (5) | 0.0100 (5) | −0.0069 (5) |
| C5 | 0.0720 (8) | 0.0631 (8) | 0.0568 (7) | 0.0026 (6) | 0.0053 (6) | −0.0161 (6) |
| C6 | 0.0567 (6) | 0.0473 (6) | 0.0467 (6) | 0.0075 (5) | 0.0080 (5) | −0.0035 (5) |
| C7 | 0.0546 (6) | 0.0456 (5) | 0.0393 (5) | 0.0132 (5) | 0.0115 (4) | 0.0027 (4) |
| C8 | 0.0538 (6) | 0.0504 (6) | 0.0412 (5) | 0.0077 (5) | 0.0128 (4) | 0.0061 (4) |
| C9 | 0.0558 (7) | 0.0719 (8) | 0.0635 (8) | 0.0007 (6) | 0.0169 (6) | 0.0038 (6) |
| C10 | 0.0583 (8) | 0.0934 (11) | 0.0709 (9) | 0.0135 (7) | 0.0281 (7) | 0.0103 (8) |
| C11 | 0.0722 (9) | 0.0856 (10) | 0.0557 (7) | 0.0240 (8) | 0.0278 (6) | 0.0008 (7) |
| C12 | 0.0669 (7) | 0.0587 (7) | 0.0449 (6) | 0.0190 (6) | 0.0142 (5) | −0.0003 (5) |
| C2 | 0.0589 (7) | 0.0664 (8) | 0.0609 (7) | −0.0042 (6) | 0.0082 (6) | −0.0170 (6) |
| C3 | 0.0523 (8) | 0.1488 (19) | 0.1117 (15) | −0.0096 (10) | 0.0041 (9) | −0.0549 (14) |
| C4 | 0.0979 (13) | 0.0873 (12) | 0.0940 (12) | 0.0032 (10) | 0.0288 (10) | 0.0360 (10) |

Geometric parameters (Å, °)

| | | | |
|------------|-------------|-------------|-------------|
| O1—C8 | 1.3678 (13) | C7—C12 | 1.4135 (15) |
| O1—H10 | 1.03 (2) | C8—C9 | 1.3809 (17) |
| N1—C12 | 1.362 (2) | C9—C10 | 1.405 (2) |
| N1—C5 | 1.3676 (19) | C9—H9 | 0.9300 |
| N1—H1N | 0.92 (2) | C10—C11 | 1.359 (2) |
| N2—C4 | 1.463 (2) | C10—H10 | 0.9300 |
| N2—C3 | 1.4640 (19) | C11—C12 | 1.397 (2) |
| N2—C2 | 1.4776 (16) | C11—H11 | 0.9300 |
| C1—C6 | 1.5022 (15) | C2—H2A | 0.9700 |
| C1—C2 | 1.5038 (18) | C2—H2B | 0.9700 |
| C1—H1A | 0.9700 | C3—H3A | 0.9600 |
| C1—H1B | 0.9700 | C3—H3B | 0.9600 |
| C5—C6 | 1.3703 (17) | C3—H3C | 0.9600 |
| C5—H5 | 0.9300 | C4—H4A | 0.9600 |
| C6—C7 | 1.4407 (17) | C4—H4B | 0.9600 |
| C7—C8 | 1.4026 (18) | C4—H4C | 0.9600 |
| C8—O1—H10 | 111.3 (11) | C11—C10—C9 | 122.10 (13) |
| C12—N1—C5 | 109.09 (11) | C11—C10—H10 | 118.9 |
| C12—N1—H1N | 123.6 (12) | C9—C10—H10 | 118.9 |

| | | | |
|--------------|--------------|----------------|--------------|
| C5—N1—H1N | 126.6 (12) | C10—C11—C12 | 117.14 (12) |
| C4—N2—C3 | 109.96 (15) | C10—C11—H11 | 121.4 |
| C4—N2—C2 | 112.52 (12) | C12—C11—H11 | 121.4 |
| C3—N2—C2 | 110.01 (12) | N1—C12—C11 | 129.70 (13) |
| C6—C1—C2 | 113.42 (11) | N1—C12—C7 | 107.80 (12) |
| C6—C1—H1A | 108.9 | C11—C12—C7 | 122.50 (14) |
| C2—C1—H1A | 108.9 | N2—C2—C1 | 113.26 (11) |
| C6—C1—H1B | 108.9 | N2—C2—H2A | 108.9 |
| C2—C1—H1B | 108.9 | C1—C2—H2A | 108.9 |
| H1A—C1—H1B | 107.7 | N2—C2—H2B | 108.9 |
| N1—C5—C6 | 110.47 (13) | C1—C2—H2B | 108.9 |
| N1—C5—H5 | 124.8 | H2A—C2—H2B | 107.7 |
| C6—C5—H5 | 124.8 | N2—C3—H3A | 109.5 |
| C5—C6—C7 | 105.78 (11) | N2—C3—H3B | 109.5 |
| C5—C6—C1 | 127.32 (12) | H3A—C3—H3B | 109.5 |
| C7—C6—C1 | 126.84 (11) | N2—C3—H3C | 109.5 |
| C8—C7—C12 | 118.56 (11) | H3A—C3—H3C | 109.5 |
| C8—C7—C6 | 134.49 (10) | H3B—C3—H3C | 109.5 |
| C12—C7—C6 | 106.86 (11) | N2—C4—H4A | 109.5 |
| O1—C8—C9 | 122.25 (12) | N2—C4—H4B | 109.5 |
| O1—C8—C7 | 118.99 (10) | H4A—C4—H4B | 109.5 |
| C9—C8—C7 | 118.75 (11) | N2—C4—H4C | 109.5 |
| C8—C9—C10 | 120.89 (15) | H4A—C4—H4C | 109.5 |
| C8—C9—H9 | 119.6 | H4B—C4—H4C | 109.5 |
| C10—C9—H9 | 119.6 | | |
| C12—N1—C5—C6 | -0.99 (17) | C7—C8—C9—C10 | 1.3 (2) |
| N1—C5—C6—C7 | 1.03 (15) | C8—C9—C10—C11 | 0.2 (2) |
| N1—C5—C6—C1 | -176.28 (12) | C9—C10—C11—C12 | -0.3 (2) |
| C2—C1—C6—C5 | -20.34 (19) | C5—N1—C12—C11 | -179.00 (15) |
| C2—C1—C6—C7 | 162.90 (12) | C5—N1—C12—C7 | 0.52 (15) |
| C5—C6—C7—C8 | 175.62 (13) | C10—C11—C12—N1 | 178.25 (14) |
| C1—C6—C7—C8 | -7.1 (2) | C10—C11—C12—C7 | -1.2 (2) |
| C5—C6—C7—C12 | -0.69 (13) | C8—C7—C12—N1 | -176.89 (11) |
| C1—C6—C7—C12 | 176.64 (11) | C6—C7—C12—N1 | 0.12 (14) |
| C12—C7—C8—O1 | 176.31 (10) | C8—C7—C12—C11 | 2.67 (19) |
| C6—C7—C8—O1 | 0.3 (2) | C6—C7—C12—C11 | 179.68 (12) |
| C12—C7—C8—C9 | -2.62 (17) | C4—N2—C2—C1 | -68.20 (16) |
| C6—C7—C8—C9 | -178.60 (13) | C3—N2—C2—C1 | 168.82 (15) |
| O1—C8—C9—C10 | -177.63 (12) | C6—C1—C2—N2 | -172.27 (11) |

Hydrogen-bond geometry (\AA , $^\circ$)

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|----------------------------------|----------|-------------|-------------|---------------|
| O1—H1O \cdots N2 ⁱ | 1.03 (2) | 1.61 (2) | 2.6242 (14) | 166.6 (18) |
| N1—H1N \cdots O1 ⁱⁱ | 0.92 (2) | 1.99 (2) | 2.8944 (14) | 167.9 (18) |

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

The unit-cell parameters of Form I as a function of temperature. Axes in [\AA], angle in [$^\circ$], volume in [\AA^3]. Alpha and gamma angles are 90° (monoclinic crystal system). Estimated standard deviations are given below each value.

| | a-axis | b-axis | c-axis | beta | Volume |
|-----|-------------------|------------------|-------------------|-------------------|-------------------|
| 150 | 10.4055 0.0004 | 8.5247 0.0003 | 12.4170 0.0004 | 92.6122 0.0019 | 1100.296 0.093 |
| 170 | 10.4506 0.0010 | 8.5219 0.0007 | 12.4289 0.0011 | 92.3237 0.0029 | 1106.001 0.278 |
| 190 | 10.4863 0.0011 | 8.5145 0.0007 | 12.4417 0.0012 | 92.0707 0.0031 | 1110.171 0.293 |
| 210 | 10.5185 0.0010 | 8.5072 0.0006 | 12.4516 0.0011 | 91.7817 0.0028 | 1113.659 0.262 |
| 230 | 10.5462 0.0011 | 8.5009 0.0008 | 12.4634 0.0013 | 91.5068 0.0032 | 1116.985 0.318 |
| 250 | 10.5728 0.0011 | 8.4975 0.0008 | 12.4790 0.0013 | 91.3072 0.0031 | 1120.845 0.315 |
| 270 | 10.5897 0.0009 | 8.4935 0.0006 | 12.4886 0.0010 | 91.0658 0.0026 | 1123.084 0.243 |
| 290 | 10.6137 0.0012 | 8.4937 0.0008 | 12.4994 0.0014 | 90.9311 0.0033 | 1126.671 0.337 |
| 300 | 10.6208 0.0005 | 8.4943 0.0004 | 12.5066 0.0005 | 90.8366 0.0024 | 1128.181 0.104 |

Relative changes of unit cell parameter as a function of temperature. Values relative to the 150 K number.

| | a-axis | b-axis | c-axis | Volume |
|-----|--------|--------|--------|--------|
| 150 | 1.00 | 1.00 | 1.00 | 1.00 |
| 170 | 1.0043 | 0.9997 | 1.0010 | 1.0052 |
| 190 | 1.0078 | 0.9988 | 1.0020 | 1.0090 |
| 210 | 1.0109 | 0.9979 | 1.0028 | 1.0121 |
| 230 | 1.0135 | 0.9972 | 1.0037 | 1.0152 |
| 250 | 1.0161 | 0.9968 | 1.0050 | 1.0187 |
| 270 | 1.0177 | 0.9963 | 1.0058 | 1.0207 |
| 290 | 1.0200 | 0.9964 | 1.0066 | 1.0240 |
| 300 | 1.0207 | 0.9964 | 1.0072 | 1.0253 |