Synthesis, crystal structure and Hirshfeld surface analysis of (1H-benzimidazol-2-yl)(morpholin-4-yl)-methanethione

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The title compound, C12H13N3OS, was synthesized via the Willgerodt–Kindler method. The benzimidazole moiety is essentially planar (r.m.s. deviation = 0.0084 Å). The thioamide group is inclined by 54.80 (14)° to the benzimidazole ring system. The morpholine ring is disordered over two sets of sites [ratio 0.841 (11):0.159 (11)], with chair conformations for both components. In the crystal, molecules are linked into N—H⋯C1/C1/C1 hydrogen-bonded chains running parallel to the c axis. Hirshfeld surface analysis was used to quantify the intermolecular interactions.

1. Chemical context

Benzimidazole is a biologically important compound and a useful structural motif for designing molecules of biochemical and pharmacological relevance. Numerous studies have confirmed that these molecules are effective against various strains of microorganisms (El Ashry et al., 2016). Likewise, substituted benzimidazole derivatives possess various biological activities, including antibacterial (Kazimierczuk et al., 2002), antifungal (Ansari & Lal, 2009), antinematode (Mavrova et al., 2006), antiviral (Pandey & Shukla, 1999), anticancer (Hranjec et al., 2011) and antiprotozoal (Mavrova et al., 2010) properties. Similarly, the morpholine moiety is a versatile and readily accessible synthetic building block; it is easily introduced as an amine reagent or can be built according to a variety of available synthetic methodologies. This versatile scaffold, appropriately substituted, possesses a wide range of biological activities (Walia et al., 2011). Additionally, most drugs containing a morpholine moiety in their structure have been found to exhibit significant biological properties (Basavaraja et al., 2010).

In this context, the title compound with its bifunctional properties (benzimidazole and morpholine derivative,
respectively) was synthesized and structurally characterized. The bifunctional properties predispose its potential biological activity, and the three nitrogen and one sulfur atoms can be used in reactions as electrophilic or nucleophilic sites for the formation of heterocyclic compounds.

2. Structural commentary

The title compound crystallizes with one molecule in the asymmetric unit (Fig. 1). The benzimidazole ring system is essentially planar, with a maximum deviation of 0.013 (3) Å for C6 from the mean plane (r.m.s. deviation = 0.0084 Å). The length of the C1—N2 bond is 1.353 (3) Å, slightly shorter than an isolated single C—N bond (1.382 Å; Berno & Gambarotta, 1994), while that of the C1—N1 bond is 1.322 (3) Å, slightly longer than an isolated C=N double bond (1.281 Å; Schmaunz et al., 2014), and the N3—C8 bond length of 1.322 (3) Å is the same as that of C1—N1, indicating conjugation of the p-orbital electrons over the imidazole ring. The thioamide group makes a dihedral angle of 54.80 (14)° with the benzimidazole ring system. Both components of the disordered morpholide ring [occupancy ratio 0.841 (11):0.159 (11)] adopt chair conformations. The puckering parameters (Cremer & Pople, 1975) of the ring (main occupancy component) are $Q = 0.521 (6)$ Å, $\theta = 176.8 (8)$°, $\varphi = 80 (8)$°. Weak intramolecular C12—H12A···N1 and C9—H9B···S1 hydrogen bonds help to consolidate the conformation of the molecule (Table 1).

3. Supramolecular features

In the crystal, molecules are linked by N2—H2···N1 hydrogen bonds into chains running parallel to the c axis (Table 1, Fig. 2).

Analysis and calculations of the Hirshfeld surface were carried out with CrystalExplorer17.5 (Spackman et al., 2021). The $d_{\text{norm}}$ plots were mapped with a colour scale between −0.182 a.u. (blue) and 1.195 a.u. (red) and are shown Fig. 3. The red spots indicate the contribution of N···H···N hydrogen bonds.

The expanded two-dimensional fingerprint plots (Seth, 2014; McKinnon et al., 2007) are displayed in Fig. 4 where $d_e$ and $d_i$ are the respective distances to the nearest nuclei outside and inside the surface from the Hirshfeld surface. The most important contributions to the crystal packing originate from H···H contacts (46.4%), followed by C···H/H···C contacts (21.0%) and S···H/H···S contacts (15.7%). Numerical data for other contributions are given in Fig. 4.

4. Database survey

A search in the Cambridge Structural Database (CSD, version 2022; Groom et al., 2016) gave one match for the benzimida-
Soy-thiocarbonate moiety, CSD refcode FUTSOF (Ranskiy et al., 2016). In the latter compound, the N and S atoms are bound to a Cu²⁺ cation. The corresponding N—C bond lengths within the benzimidazole ring exhibit little difference from those of the title compound, except that the C8—S1 bond length is slightly longer [1.708 (7) Å] than in the title compound, except that the C8—S1 bond length is about 0.5, 0.26 and 0.24 e⁻ Å⁻³ near the morpholide ring, resulting in R1[Fo > 4σ(Fo)] = 0.039. Introduction of a disorder model including split positions for C9, C10, C11 and C12 of the morpholide ring resulted in a occupancy ratio of 0.841 (11):0.159 (11) for the major and minor components (atoms of the minor component denoted by the B). For atom pair C10/C10B, the SHELXL command EADP was used. All C-bound H atoms were positioned geometrically, with C—H = 0.96 Å (for methylene H atoms) and C—H = 0.93 Å (for aromatic H atoms), and were refined with Uiso(H) = 1.2Ueq(C). The H atom bound to N2 was located in a difference-Fourier map, and its coordinates and isotropic displacement parameter were refined freely.

5. Synthesis and crystallization

1H-Benzimidazol-2-yl(morpholin-4-yl)methanethione was synthesized using a previously reported procedure with minor modifications (Klingele & Brooker, 2004; Okamoto et al., 2007), as shown in Fig. 5.

Method (i): A reaction mixture consisting of 1.32 g (10 mmol) of 2-methylbenzimidazole (1), 1.68 ml (1.7 g, d = 1.01 g ml⁻¹, 20 mmol) of morpholine and 0.96 g (30 mmol) of sulfur was heated in a round-bottomed flask at 448–453 K for 18 h. The excess of morpholine was evaporated, and the residue was treated with methanol. The resulting solid was filtered off and recrystallized from benzene and dried again. Yield 1.91 g (77.0%). Melting point 513–515 K, Rf = 0.25 (benzene:acetone 3:1 v/v).

1H NMR (400 MHz, DMSO-d₆): 12.9 (1H, s, NH), 7.7 (1H, d, J = 8.0, H-4), 7.54 (1H, d, J = 7.9, H-7), 7.24–7.33 (2H, m, H-5,6), 4.37 (2H, br.t, J = 4.7, NCH2-morpholine), 4.22 (2H, br.t, J = 4.7, NCH2-morpholine), 3.82 (2H, br.t, J = 4.9, OCH2-morpholine), 3.71 (2H, br.t, J = 4.8, OCH2-morpholine). ¹³C NMR (400 MHz, DMSO-d₆): 50.19 (NCH2-morpholine), 52.95 (NCH2-morpholine), 65.94 (OCH2-morpholine), 66.62 (OCH2-morpholine), 112.2 (C-3a), 120.06 (C-4), 121.3 (C-5), 122.6 (C-6), 124.0 (C-7), 133.9 (C-7a), 142.2 (C-2), 148.9 (C=S). IR (ν, cm⁻¹): 1614 (C==N), 1377 (C==S).

A single crystal suitable for X-ray diffraction was selected from crystals obtained by method (ii).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Refinement of the structure with an ordered model gave remaining electron difference peaks about 0.5, 0.26 and 0.24 e⁻ Å⁻³ near the morpholide ring, resulting in R1[Fo > 4σ(Fo)] = 0.039. Introduction of a disorder model including split positions for C9, C10, C11 and C12 of the morpholide ring resulted in an occupancy ratio of 0.841 (11):0.159 (11) for the major and minor components (atoms of the minor component denoted by the B). For atom pair C10/C10B, the SHELXL command EADP was used. All C-bound H atoms were positioned geometrically, with C—H = 0.96 Å (for methylene H atoms) and C—H = 0.93 Å (for aromatic H atoms), and were refined with Uiso(H) = 1.2Ueq(C). The H atom bound to N2 was located in a difference-Fourier map, and its coordinates and isotropic displacement parameter were refined freely.
Table 2
Experimental details.

| Crystal data | Chemical formula | C12H13N3OS |
|--------------|------------------|------------|
| M (g/mol)    |                  | 247.31     |
| Crystal system, space group | Monoclinic, Ia |
| Temperature (K) |                  | 293       |
| a, b, c (Å)  |                  | 8.1644 (2), 15.9237 (3), 9.6936 (2) |
| β (°)        |                  | 106.661 (2) |
| V (Å³)       |                  | 1207.33 (5) |
| Z            |                  | 4          |
| Radiation type | Cu Kα |
| μ (mm⁻¹)     |                  | 2.28       |
| Crystal size (mm) |           | 0.30 × 0.25 × 0.14 |

Data collection

Diffractometer: XtaLAB Synergy. Single source at home/near, HyPix3000

Absorption correction: Multi-scan (CrysAlis PRO; Rigaku OD, 2020)

Tmin, Tmax | 0.568, 1.000 |
No. of measured, independent and observed [I > 2σ(I)] reflections | 5160, 1724, 1692 |
R(int) | 0.022 |
(sin θ/λ)max (Å⁻¹) | 0.614 |

Refinement

R[F² > 2σ(F²)] | 0.030, 0.079, 1.10 |
No. of reflections | 1724 |
No. of parameters | 189 |
No. of restraints | 2 |
H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |

Δρmax, Δρmin (e Å⁻³) | 0.17, −0.19 |

Absolute structure

Flack x determined using 531 quotients [(Γ)−(−Γ)]/[(Γ)+(−Γ)] (Parsons et al., 2013)

Absolute structure parameter | −0.001 (13) |

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Synthesis, crystal structure and Hirshfeld surface analysis of (1H-benzimidazol-2-yl)(morpholin-4-yl)methanethione

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Computing details
Data collection: CrysAlis PRO (Rigaku OD, 2020); cell refinement: CrysAlis PRO (Rigaku OD, 2020); data reduction: CrysAlis PRO (Rigaku OD, 2020); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: SHELXL (Sheldrick, 2015b); molecular graphics: XP (Siemens, 1994), Mercury (Macrae et al. 2020); software used to prepare material for publication: PLATON (Spek, 2020).

(1H-Benzimidazol-2-yl)(morpholin-4-yl)methanethione

Crystal data

\[
C_{12}H_{13}N_3OS
\]

Mr = 247.31

Monoclinic, \( \text{Ia} \)

\( a = 8.1644 \pm 0.0002 \text{ Å} \)

\( b = 15.9237 \pm 0.0018 \text{ Å} \)

\( c = 9.6936 \pm 0.0002 \text{ Å} \)

\( \beta = 106.661 \pm 0.0002 \text{°} \)

\( V = 1207.33 \pm 0.20 \text{ Å}^3 \)

\( Z = 4 \)

\( F(000) = 520 \)

\( D_x = 1.361 \text{ Mg m}^{-3} \)

Melting point: 513(2) K

Cu Kα radiation, \( \lambda = 1.54184 \text{ Å} \)

Cell parameters from 4375 reflections

\( \theta = 5.5–71.1\text{°} \)

\( \mu = 2.28 \text{ mm}^{-1} \)

\( T = 293 \text{ K} \)

Needle, colourless

0.30 × 0.25 × 0.14 mm

Data collection

XtaLAB Synergy, Single source at home/near, HyPix3000 diffractometer

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

Mirror monochromator

Detector resolution: 10.0000 pixels mm\(^{-1}\)

\( \omega \) scans

Absorption correction: multi-scan

\( (\text{CrysAlisPro}; \text{Rigaku OD, 2020}) \)

Refinement

Refinement on \( F^2 \)

Least-squares matrix: full

\( R(F^2 > 2\sigma(F^2)) = 0.030 \)

\( wR(F^2) = 0.079 \)

\( S = 1.10 \)

1724 reflections

189 parameters

2 restraints

sup-1
Hydrogen site location: mixed
H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0448P)^2 + 0.2955P]$
where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta \rho_{\text{max}} = 0.17 \, \text{e} \, \text{Å}^{-3}$
$\Delta \rho_{\text{min}} = -0.19 \, \text{e} \, \text{Å}^{-3}$

Absolute structure: Flack $x$ determined using 531 quotients $[(I^{-})/(I^{+})]/[(I^{+})/(I^{-})]$ (Parsons et al., 2013)

Absolute structure parameter: $-0.001 (13)$

**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 ($\text{Å}^2$)**

|        | x        | y        | z        | $U_{	ext{iso}}$/U$_{eq}$ | Occ. (<1) |
|--------|----------|----------|----------|---------------------------|-----------|
| S1     | 0.43314 (11) | 0.91597 (4) | 0.55516 (11) | 0.0555 (2) |           |
| O1     | 0.9333 (3)  | 0.79690 (17) | 0.3720 (4)  | 0.0726 (8)  |           |
| N1     | 0.3522 (3)  | 0.69924 (13) | 0.3950 (2)  | 0.0334 (4)  |           |
| N2     | 0.3362 (3)  | 0.72781 (14) | 0.6169 (3)  | 0.0354 (5)  |           |
| H2     | 0.350 (4)   | 0.754 (2)  | 0.695 (4)   | 0.038 (8)* |           |
| N3     | 0.6584 (3)  | 0.81395 (16) | 0.4919 (4)  | 0.0555 (8)  |           |
| C1     | 0.3992 (3)  | 0.74997 (16) | 0.5073 (3)  | 0.0316 (5)  |           |
| C2     | 0.1490 (4)  | 0.6052 (2)  | 0.6418 (4)  | 0.0490 (7)  |           |
| H2B    | 0.1429     | 0.6168     | 0.7342     | 0.059*      |           |
| C3     | 0.0676 (4)  | 0.5366 (2)  | 0.5648 (4)  | 0.0540 (8)  |           |
| H3A    | 0.0048     | 0.5012     | 0.6066     | 0.065*      |           |
| C4     | 0.0767 (4)  | 0.51882 (19) | 0.4256 (4)  | 0.0498 (7)  |           |
| H4A    | 0.0210     | 0.4716     | 0.3780     | 0.060*      |           |
| C5     | 0.1663 (3)  | 0.56963 (17) | 0.3576 (3)  | 0.0397 (6)  |           |
| H5A    | 0.1708     | 0.5581     | 0.2647     | 0.048*      |           |
| C6     | 0.2502 (3)  | 0.63938 (15) | 0.4345 (3)  | 0.0320 (5)  |           |
| C7     | 0.2407 (3)  | 0.65587 (16) | 0.5736 (3)  | 0.0337 (5)  |           |
| C8     | 0.5083 (3)  | 0.82515 (16) | 0.5156 (3)  | 0.0377 (6)  |           |
| C9     | 0.7777 (7)  | 0.8840 (3)  | 0.4960 (9)  | 0.0661 (16) | 0.841 (11) |
| H9A    | 0.8705     | 0.8823     | 0.5848     | 0.079*      | 0.841 (11) |
| H9B    | 0.7187     | 0.9373     | 0.4916     | 0.079*      | 0.841 (11) |
| C10    | 0.8473 (9)  | 0.8753 (4)  | 0.3682 (10) | 0.078 (2)   | 0.841 (11) |
| H10A   | 0.7541     | 0.8790     | 0.2799     | 0.093*      | 0.841 (11) |
| H10B   | 0.9263     | 0.9209     | 0.3686     | 0.093*      | 0.841 (11) |
| C11    | 0.8153 (7)  | 0.7297 (3)  | 0.3658 (7)  | 0.0530 (12) | 0.841 (11) |
| H11A   | 0.8722     | 0.6764     | 0.3637     | 0.064*      | 0.841 (11) |
| H11B   | 0.7213     | 0.7343     | 0.2782     | 0.064*      | 0.841 (11) |
| C12    | 0.7468 (6)  | 0.7322 (2)  | 0.4947 (7)  | 0.0466 (11) | 0.841 (11) |
| H12A   | 0.6675     | 0.6863     | 0.4903     | 0.056*      | 0.841 (11) |
| H12B   | 0.8397     | 0.7270     | 0.5828     | 0.056*      | 0.841 (11) |
| C9B    | 0.715 (5)   | 0.8869 (14) | 0.398 (5)   | 0.067 (10)  | 0.159 (11) |
| H9C    | 0.6680     | 0.8780     | 0.2957     | 0.080*      | 0.159 (11) |
| H9D    | 0.6840     | 0.9425     | 0.4236     | 0.080*      | 0.159 (11) |
**Atomic displacement parameters (Å²)**

|     | U¹¹  | U¹²  | U¹³  | U²²  | U²³  | U³³  |
|-----|------|------|------|------|------|------|
| S1  | 0.0713 (5) | 0.0311 (3) | 0.0723 (5) | 0.0025 (3) | 0.0340 (4) | -0.0069 (4) |
| O1  | 0.0627 (14) | 0.0675 (16) | 0.104 (2) | -0.0080 (12) | 0.0499 (15) | -0.0086 (15) |
| N1  | 0.0392 (10) | 0.0334 (10) | 0.0311 (11) | -0.0016 (8) | 0.0157 (9) | -0.0017 (8) |
| N2  | 0.0419 (12) | 0.0381 (11) | 0.0294 (12) | -0.0055 (9) | 0.0151 (9) | -0.0052 (10) |
| N3  | 0.0524 (15) | 0.0346 (13) | 0.092 (2) | -0.0092 (10) | 0.0407 (16) | -0.0091 (13) |
| C1  | 0.0349 (13) | 0.0307 (11) | 0.0307 (12) | -0.0001 (9) | 0.0121 (10) | -0.0004 (9) |
| C2  | 0.0532 (17) | 0.0567 (16) | 0.0425 (16) | -0.0104 (14) | 0.0226 (14) | 0.0030 (14) |
| C3  | 0.0517 (17) | 0.0498 (16) | 0.064 (2) | -0.0166 (14) | 0.0231 (16) | 0.0053 (15) |
| C4  | 0.0434 (15) | 0.0411 (15) | 0.065 (2) | -0.0097 (11) | 0.0154 (14) | -0.0078 (14) |
| C5  | 0.0369 (12) | 0.0408 (13) | 0.0410 (15) | -0.0029 (10) | 0.0105 (11) | -0.0085 (12) |
| C6  | 0.0314 (11) | 0.0330 (11) | 0.0325 (12) | 0.0012 (9) | 0.0107 (10) | -0.0017 (10) |
| C7  | 0.0351 (11) | 0.0350 (11) | 0.0329 (13) | -0.0020 (10) | 0.0127 (10) | -0.0002 (10) |
| C8  | 0.0460 (14) | 0.0318 (12) | 0.0375 (14) | -0.0042 (10) | 0.0153 (12) | -0.0009 (10) |
| C9  | 0.066 (3) | 0.052 (2) | 0.094 (5) | -0.027 (2) | 0.045 (3) | -0.021 (3) |
| C10 | 0.093 (4) | 0.057 (2) | 0.108 (5) | -0.012 (3) | 0.067 (5) | -0.003 (4) |
| C11 | 0.047 (3) | 0.052 (2) | 0.061 (3) | 0.0026 (18) | 0.017 (2) | -0.007 (2) |
| C12 | 0.0397 (19) | 0.0437 (19) | 0.059 (3) | 0.0014 (16) | 0.019 (2) | -0.0024 (19) |
| C9B | 0.09 (2) | 0.030 (9) | 0.11 (3) | 0.002 (11) | 0.07 (2) | 0.009 (14) |
| C10B| 0.093 (4) | 0.057 (2) | 0.108 (5) | -0.012 (3) | 0.067 (5) | -0.003 (4) |
| C11B| 0.049 (14) | 0.062 (14) | 0.058 (17) | 0.015 (10) | 0.010 (12) | -0.002 (13) |
| C12B| 0.050 (13) | 0.029 (8) | 0.08 (2) | -0.005 (8) | 0.040 (14) | 0.002 (10) |

**Geometric parameters (Å, °)**

|     | C5—C6 | C5—H5A | C6—C7 | C9—C10 | C9—H9A | C9—H9B |
|-----|-------|--------|-------|--------|--------|--------|
| S1—C8 | 1.658 (3) | C5—H5A | 1.402 (3) |
| O1—C10 | 1.427 (7) | C5—H5A | 0.9300 |
| O1—C11 | 1.430 (5) | C6—C7 | 1.399 (4) |
| O1—C11B | 1.43 (3) | C9—C10 | 1.511 (10) |
| O1—C10B | 1.48 (4) | C9—H9A | 0.9700 |
| N1—C1 | 1.322 (3) | C9—H9B | 0.9700 |
| N1—C6 | 1.390 (3) | C10—H10A | 0.9700 |
| N2—C1 | 1.353 (3) | C10—H10B | 0.9700 |
| N2—C7 | 1.382 (3) | C11—C12 | 1.508 (8) |
| N2—H2 | 0.84 (4) | C11—H11A | 0.9700 |
| N3—C8 | 1.322 (3) | C11—H11B | 0.9700 |
| Bond                  | Length (Å) | Bond                  | Length (Å) |
|-----------------------|------------|-----------------------|------------|
| N3—C9                 | 1.475 (5)  | C12—H12A              | 0.9700     |
| N3—C12                | 1.485 (5)  | C12—H12B              | 0.9700     |
| N3—C12B               | 1.60 (2)   | C9B—C10B              | 1.47 (6)   |
| N3—C9B                | 1.62 (2)   | C9B—H9C               | 0.9700     |
| C1—C8                 | 1.480 (3)  | C9B—H9D               | 0.9700     |
| C2—C3                 | 1.380 (5)  | C10B—H10C             | 0.9700     |
| C2—C7                 | 1.390 (4)  | C10B—H10D             | 0.9700     |
| C2—H2B                | 0.9300     | C11B—C12B             | 1.44 (4)   |
| C3—C4                 | 1.401 (5)  | C11B—H11C             | 0.9700     |
| C3—H3A                | 0.9300     | C11B—H11D             | 0.9700     |
| C4—C5                 | 1.379 (4)  | C12B—H12C             | 0.9700     |
| C4—H4A                | 0.9300     | C12B—H12D             | 0.9700     |

C10—O1—C11

| Bond                  | Length (Å) | Bond                  | Length (Å) |
|-----------------------|------------|-----------------------|------------|
| C11B—O1—C10B         | 102 (2)    | O1—C10—H10A          | 109.5      |
| C1—N1—C6             | 104.3 (2)  | C9—C10—H10A          | 109.5      |
| C1—N2—C7             | 106.6 (2)  | O1—C10—H10B          | 109.5      |
| C1—N2—H2             | 127 (2)    | C9—C10—H10B          | 109.5      |
| C7—N2—H2             | 127 (2)    | H10A—C10—H10B        | 108.0      |
| C8—N3—C9             | 122.1 (3)  | O1—C11—C12           | 110.5 (4)  |
| C8—N3—C12            | 125.8 (3)  | O1—C11—H11A          | 109.5      |
| C9—N3—C12            | 110.4 (3)  | C12—C11—H11A         | 109.5      |
| C8—N3—C12B           | 120.0 (9)  | O1—C11—H11B          | 109.5      |
| C8—N3—C9B            | 115.3 (10) | C12—C11—H11B         | 109.5      |
| C12B—N3—C9B          | 97.8 (16)  | H11A—C11—H11B        | 108.1      |
| N1—C1—N2             | 113.7 (2)  | N3—C12—C11           | 107.6 (4)  |
| N1—C1—C8             | 124.5 (2)  | N3—C12—H12A          | 110.2      |
| N2—C1—C8             | 121.8 (2)  | C11—C12—H12A         | 110.2      |
| C3—C2—C7             | 116.4 (3)  | N3—C12—H12B          | 110.2      |
| C3—C2—H2B            | 121.8      | C11—C12—H12B         | 110.2      |
| C7—C2—H2B            | 121.8      | H12A—C12—H12B        | 108.5      |
| C2—C3—C4             | 122.0 (3)  | C10B—C9B—N3           | 99 (3)     |
| C2—C3—H3A            | 119.0      | C10B—C9B—H9C         | 112.1      |
| C4—C3—H3A            | 119.0      | N3—C9B—H9C           | 112.1      |
| C5—C4—C3             | 121.6 (3)  | C10B—C9B—H9D         | 112.1      |
| C5—C4—H4A            | 119.2      | N3—C9B—H9D           | 112.1      |
| C3—C4—H4A            | 119.2      | H9C—C9B—H9D          | 109.7      |
| C4—C5—C6             | 117.2 (3)  | C9B—C10B—O1          | 106 (3)    |
| C4—C5—H5A            | 121.4      | C9B—C10B—H10C        | 110.5      |
| C6—C5—H5A            | 121.4      | O1—C10B—H10C         | 110.5      |
| N1—C6—C7             | 109.9 (2)  | C9B—C10B—H10D        | 110.5      |
| N1—C6—C5             | 129.6 (2)  | O1—C10B—H10D         | 110.5      |
| C7—C6—C5             | 120.5 (2)  | H10C—C10B—H10D       | 108.7      |
| N2—C7—C2             | 132.2 (3)  | O1—C11B—C12B         | 107 (2)    |
| N2—C7—C6             | 105.4 (2)  | O1—C11B—H11C         | 110.3      |
| C2—C7—C6             | 122.4 (2)  | C12B—C11B—H11C       | 110.3      |
| N3—C8—C1             | 117.1 (2)  | O1—C11B—H11D         | 110.3      |
| N3—C8—S1             | 125.5 (2)  | C12B—C11B—H11D       | 110.3      |
| Bond | Angles (°) | Bond | Angles (°) |
|------|-----------|------|-----------|
| C1—C8—S1 | 117.5 (2) | H11C—C11B—H11D | 108.5 |
| N3—C9—C10 | 108.0 (5) | C11B—C12B—N3 | 100 (3) |
| N3—C9—H9A | 110.1 | C11B—C12B—H12C | 111.8 |
| C10—C9—H9A | 110.1 | N3—C12B—H12C | 111.8 |
| N3—C9—H9B | 110.1 | C11B—C12B—H12D | 111.8 |
| C10—C9—H9B | 110.1 | N3—C12B—H12D | 111.8 |
| H9A—C9—H9B | 108.4 | H12C—C12B—H12D | 109.5 |

C6—N1—C1—N2 0.1 (3) C12—N3—C8—S1 162.8 (4)
C6—N1—C1—C8 −179.1 (2) C12B—N3—C8—S1 −156.9 (15)
C7—N2—C1—N1 0.6 (3) C9B—N3—C8—S1 −40.3 (4)
C7—N2—C1—C8 179.8 (2) N1—C1—C8—N3 −55.2 (4)
C7—C2—C3—C4 0.1 (5) N2—C1—C8—N3 125.7 (3)
C2—C3—C4—C5 −0.7 (5) N1—C1—C8—S1 125.4 (2)
C3—C4—C5—C6 0.9 (4) N2—C1—C8—S1 53.7 (3)
C1—N1—C6—C7 −0.7 (3) N3—C9—C10—O1 −59.2 (9)
C1—N1—C6—C5 −179.5 (3) C12—N3—C9—C10 58.2 (9)
C4—C5—C6—C7 180.0 (2) C11—O1—C10—C9 61.3 (8)
C4—C5—C6—N1 −0.5 (4) N3—C9—C10—O1 59.2 (9)
C1—N2—C7—C2 179.1 (3) C10—O1—C11—C12 62.0 (8)
C1—N2—C7—C6 −1.0 (3) C8—N3—C12—C11 135.6 (4)
C3—C2—C7—N2 −179.8 (3) C9—N3—C12—C11 −58.9 (7)
C3—C2—C7—C6 0.3 (5) O1—C11—C12—N3 60.2 (6)
N1—C6—C7—N2 1.1 (3) C8—N3—C12—N3 157 (2)
C5—C6—C7—N2 180.0 (2) C12B—N3—C9B—C10B 74 (3)
N1—C6—C7—C2 −179.0 (3) N3—C9B—C10B—O1 76 (3)
C5—C6—C7—C2 −0.1 (4) C11B—O1—C10B—C9B 73 (4)
C9—N3—C8—C1 179.5 (5) C12B—O1—C11B—C12B 74 (4)
C12—N3—C8—C1 −16.6 (5) O1—C11B—C12B—N3 77 (3)
C12B—N3—C8—C1 23.7 (15) C8—N3—C12B—C11B −160.0 (16)
C9B—N3—C8—C1 140.3 (19) C9B—N3—C12B—C11B 75 (3)
C9—N3—C8—S1 −1.1 (6)

Hydrogen-bond geometry (Å, °)

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|-------|----------|
| N2—H2···N1i | 0.84 (4) | 2.07 (4) | 2.903 (3) | 169 (3) |
| C9—H9B···S1 | 0.97 | 2.60 | 3.070 (5) | 110 |
| C12—H12A···N1 | 0.97 | 2.48 | 3.131 (5) | 124 |

Symmetry code: (i) x, −y+3/2, z+1/2.

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