Crystal structure of 2-[[5-amino-1-(phenylsulfonyl)-1H-pyrazol-3-yl]oxy]-1-(4-methylphenyl)ethan-1-one

Nadia H. Metwally, a Galal H. Elgemeieb and Peter G. Jonesc*

Chemistry Department, Faculty of Science, Cairo University, Giza, Egypt, b Chemistry Department, Faculty of Science, Helwan University, Cairo, Egypt, and c Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Hagenring 30, D-38106 Braunschweig, Germany. Correspondence e-mail: p.jones@tu-bs.de

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In the title compound, C_{18}H_{17}N_{3}O_{4}S, the pyrazole ring is planar, with the sulfur atom lying 0.558 (1) Å out of the ring plane. The NH_{2} group is involved in an intramolecular hydrogen bond to a sulfonyl oxygen atom; its other hydrogen atom forms an asymmetric three-centre hydrogen bond to the two oxygen atoms of the —O—CH_{2}—C==O— grouping, via the 2\_1 screw axis, forming a ribbon structure parallel to the b axis. Translationally adjacent, coplanar ribbons form a layer parallel to (10\_4).

1. Chemical context

We are interested in devising synthetic strategies for heterocyclic ring systems containing the N-sulfonyl- and N-sulfonylamino moiety, which have shown significant biological activity as novel antiviral and antimicrobial agents (Azzam et al., 2017, 2019, 2020; Elgemeie et al., 2017, 2019; Zhu et al., 2013). In addition, some of our recently published N-aryl-sulfonylpyrazoles (Elgemeie & Hanfy, 1999; Elgemeie et al., 1998, 2002, 2013) have been shown to be active as inhibitors of cathepsin B16 enzyme and NS2B-NS3 virus (Sidique et al., 2009; Myers et al., 2007). Based on these promising results, and in a continuation of our recent research to develop innovative and simple syntheses of other novel derivatives of N-sulfonylpyrazoles, we have begun to seek different scaffolds for use as potential pharmaceuticals (Zhang et al., 2020). In particular, we have now synthesized an O-alkyl derivative of N-sulfonylaminopyrazole 1.

Thus, the reaction of 5-amino-1-(phenylsulfonyl)-1,2-dihydro-3H-pyrazol-3-one 1 with 2-bromo-1-(p-toly)ethan-1-one 2 in DMF at 80 °C gives the title compound 3.

![Reaction scheme for the preparation of the title compound 4.](image-url)
one 2 in N,N-dimethylformamide in the presence of potassium carbonate at room temperature furnished an adduct for which two possible isomers, the O-alkylated or N-alkylated N-sulfonylpyrazole structures (3 or 4) were considered. The $^1$H NMR spectrum of the product showed four singlet signals at $\delta = 2.40, 4.91, 5.45$ and 6.34 ppm assigned for CH$_3$, CH-pyrazole, CH$_2$ and NH$_2$ protons, in addition to signals assigned to aromatic protons. The available spectroscopic data cannot differentiate between structures 3 and 4 (Fig. 1). Thus, the X-ray structure of this product was determined, indicating unambiguously the formation of the O-alkylated N-sulfonylpyrazole 4 as the sole product in the solid state.

### 2. Structural commentary

The molecular structure of 4 is shown in Fig. 2. Selected molecular dimensions are given in Table 1. An intramolecular hydrogen bond N3—H02 · · · O3 is observed. The pyrazole ring is planar (r.m.s. deviation 0.015 Å) and its dimensions may be regarded as normal. The sulfur atom lies 0.558 (1) Å outside the ring plane, and the nitrogen atom N1 is thus significantly pyramidalized; it lies 0.216 (1) Å out of the plane of the three atoms to which it binds. The atom sequence C4—C3—O1—C6—C7—C21—C22 presents an extended conformation, with all torsion angles close to $180^\circ$. The planes of the pyrazole and the tolyl rings are thus almost parallel [interplanar angle 14.46 (2)$^\circ$].

### 3. Supramolecular features

The classical hydrogen bond N3—H01 · · · O2 ($-x, y + \frac{1}{2}, -z + \frac{1}{2}$) links the molecules to form a broad ribbon structure parallel to the $b$ axis. H01 also has a short but non-linear contact to O1 (same operator), representing the weaker component of an asymmetric three-centre system (Fig. 3). The vector between translationally adjacent, coplanar ribbons is [401], so that the layer of ribbons is parallel to (104). The second amine hydrogen atom H02 is only involved in the intramolecular hydrogen bond (see above). The second amine hydrogen atom H02 is only involved in the intramolecular hydrogen bond (see above). The layers are linked by interactions C14—H14 · · · O2 ($x, -y + \frac{1}{2}, z + \frac{1}{2}$), which connect every second layer, penetrating the layer in between. See Table 2 for details of hydrogen bonding.

### Table 1

| Bond                  | Length (Å) | Angle (°) |
|-----------------------|------------|-----------|
| N1—C5                 | 1.3999 (7) |           |
| N1—N2                 | 1.4071 (7) |           |
| N1—S1                 | 1.6638 (5) |           |
| C5—N1—N2              | 111.51 (4) |           |
| C3—N2—N1              | 102.52 (4) |           |
| N2—C3—C4              | 115.07 (5) |           |
| C6—C7—C21             | 179.72 (5) |           |
| C4—C3—O1              | 174.99 (5) |           |

### Table 2

| Bond                  | Length (Å) | Distance (Å) | Angle (°) |
|-----------------------|------------|--------------|-----------|
| N3—H01—O1            | 0.869 (13) | 2.497 (14)   | 118.7 (11) |
| N3—H01—O2            | 0.869 (13) | 2.048 (13)   | 172.8 (13) |
| N3—H02—O3            | 0.863 (12) | 2.121 (13)   | 132.8 (11) |
| C14—H14—O2           | 0.95       | 2.54         | 132.8 (11) |

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

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**Figure 2**

The molecular structure of compound 4. Ellipsoids represent 50% probability levels. The dashed line indicates an intramolecular hydrogen bond.

**Figure 3**

Packing diagram of compound 4 viewed perpendicular to (104) and centred on (1/2, 1/2, 1/2). Two ribbons parallel to the $b$ axis are shown. Thick and thin dashed lines represent inter- and intramolecular hydrogen bonds, respectively. Hydrogen atoms not involved in hydrogen bonding are omitted for clarity. Selected atoms of the asymmetric unit are labelled.
4. Database survey

Version 5.41 of the Cambridge Structural Database (Groom et al., 2016) was used for a CSD search with CONQUEST (Bruno et al., 2002). The relative frequency of O- vs N2-alkylation of such pyrazole ring systems was investigated by a search for pyrazoles with a C=O function at C3, H at C4, substituted at N2, no fused rings [as in our recent publication (Metwally et al., 2021); 23 hits] or with substitution at the oxygen atom, H at C4, no substituent at N2, no fused rings (as here; 36 hits). Only one hit was registered for a pyrazole similar to 4 bearing a substitute at the C3—O group together with an N-substituent at C5 and an S-substituent at N1, namely 1-(4-fluorobenzensulfonyl)-5-amino-1H-pyrazol-3-yl thiophene 2-carboxylate, refcode YILPUF (Myers et al., 2007).

5. Synthesis and crystallization

A mixture of 5-amino-1-phenylsulfonyl-1,2-dihydro-3H-pyrazol-3-one 1 (0.01 mol), 2-bromo-1-(p-tolyl)ethan-1-one 2 (0.01 mol) and anhydrous potassium carbonate (0.01 mol) in N,N-dimethylformamide (5 mL) was stirred at room temperature for 3 h. The mixture was poured onto ice-water; the solid that formed was filtered off and recrystallized from ethanol to give pale-brown crystals in 70% yield, m.p. 445 K. The solid that formed was filtered off and recrystallized from dimethylformamide (5 mL) was stirred at room temperature to give pale-brown crystals in 70% yield, m.p. 445 K.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The hydrogen atoms of the NH2 group were refined freely. The methyl group was refined as an idealized rigid group allowed to rotate but not tip, with C—H = 0.98 Å and H—C—H = 109.5°. Other hydrogens were included using a riding model starting from calculated positions (C—Haromatic = 0.95, C—Hmethylene = 0.99 Å). The $U(H)$ values were fixed at 1.5 or 2 times the equivalent $U_{iso}$ value of the parent carbon atoms for methyl and non-methyl hydrogens, respectively. Six reflections were omitted because their calculated and measured $F^{2}$ values differed by more than 7 s.u. The occurrence of such apparent outliers seems to be a general consequence of collecting data to high $20$ values (here 76°), whereby spherical atom scattering factors become less applicable. Special refinements using aspherical atom scattering factors can lead to greatly improved $R$ values and thus fewer outliers, but this method is not yet widely employed. However, even for ‘normal’ refinement, it is still considered best practice to collect data to high diffraction angles wherever possible (Sanjuan-Szklarz et al., 2016).

| Crystal data | Chemical formula: C₁₈H₁₇N₃O₄S |
|--------------|-----------------------------|
| $M_r$: 371.40 | Monoclinic, $P2_1/c$ |
| Crystal system, space group | Temperature (K): 100 |
| $a$, $b$, $c$ (Å): 9.77236 (16), 11.98431 (18), 15.0131 (3) |
| $\beta$ (°): 95.4487 (16) |
| $\alpha$, $\beta$, $\gamma$ (°): 1750.32 (5) |
| Radiation type | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$): 0.21 |
| Crystal size (mm): 0.3 × 0.2 × 0.1 |
| No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections | $R_{w}$ |
| $R_{1}$, $wR_{2}$, $S$: 0.035, 0.093, 1.06 |
| No. of parameters | 9400 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |

| $\Delta$/$\Delta_{	ext{min}}$ (e Å$^{-3}$): 0.56, –0.43 |

Computer programs: CrysAlis PRO (Rigaku OD, 2021), SHELXT (Sheldrick, 2015a), SHELXL2018/3 (Sheldrick, 2015b) and Siemens XP (Siemens, 1994).

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Crystal structure of 2-[[5-amino-1-(phenylsulfonyl)-1H-pyrazol-3-yl]oxy]-1-(4-methylphenyl)ethan-1-one

Nadia H. Metwally, Galal H. Elgemeie and Peter G. Jones

Computing details

Data collection: CrysAlis PRO (Rigaku OD, 2021); cell refinement: CrysAlis PRO (Rigaku OD, 2021); data reduction: CrysAlis PRO (Rigaku OD, 2021); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2018/3 (Sheldrick, 2015b); molecular graphics: Siemens XP (Siemens, 1994); software used to prepare material for publication: SHELXL2018/3 (Sheldrick, 2015b).

2-[[5-Amino-1-(phenylsulfonyl)-1H-pyrazol-3-yl]oxy]-1-(4-methylphenyl)ethan-1-one

Crystal data

C₁₈H₁₇N₃O₄S  
Mr = 371.40  
Monoclinic, P2₁/c  
\( a = 9.77236 \) (16) Å  
\( b = 11.98431 \) (18) Å  
\( c = 15.0131 \) (3) Å  
\( \beta = 95.4487 \) (16)°  
\( V = 1750.32 \) (5) Å³  
Z = 4

F(000) = 776  
\( D_\lambda = 1.409 \) Mg m⁻³  
Mo Kα radiation, \( \lambda = 0.71073 \) Å  
Cell parameters from 110735 reflections  
\( \theta = 2.1^{\circ} \text{–} 38.3^{\circ} \)  
\( \mu = 0.21 \) mm⁻¹  
\( T = 100 \) K  
Irregular, colourless  
0.3 × 0.2 × 0.1 mm

Data collection

XtaLAB Synergy, HyPix  
diffractometer  
Radiation source: micro-focus sealed X-ray tube  
Detector resolution: 10.0000 pixels mm⁻¹  
\( \omega \) scans  
Absorption correction: multi-scan  
(CrysAlisPro; Rigaku OD, 2021)  
\( T_{\text{min}} = 0.917, T_{\text{max}} = 1.000 \)

171365 measured reflections  
9400 independent reflections  
8324 reflections with \( I > 2\sigma(I) \)

Refinement

Refinement on \( F^2 \)  
Least-squares matrix: full  
\( R[F^2 > 2\sigma(F^2)] = 0.031 \)  
\( wR(F^2) = 0.093 \)  
\( S = 1.06 \)

9400 reflections  
244 parameters  
0 restraints  
Primary atom site location: dual  
Hydrogen site location: mixed  
H atoms treated by a mixture of independent and constrained refinement

\( w = 1/\left[\sigma^2(F_o^2) + (0.0533P)^2 + 0.2966P\right] \)  
where \( P = (F_o^2 + 2F_c^2)/3 \)

\( (\Delta\sigma)_{\text{max}} = 0.001 \)  
\( \Delta\rho_{\text{max}} = 0.56 \) e Å⁻³  
\( \Delta\rho_{\text{min}} = -0.43 \) 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.

Least-squares planes (x,y,z in crystal coordinates) and deviations from them (* indicates atom used to define plane)
- 4.1694 (0.0022) x - 1.2934 (0.0031) y + 14.0284 (0.0014) z = 3.1999 (0.0019)
* 0.0038 (0.0004) C21 * 0.0012 (0.0004) C22 * -0.0045 (0.0004) C23 * 0.0029 (0.0004) C24 * 0.0021 (0.0005) C25 * -0.0054 (0.0004) C26
Rms deviation of fitted atoms = 0.0036
- 3.9412 (0.0025) x + 1.7088 (0.0035) y + 14.0838 (0.0015) z = 3.9392 (0.0017)
Angle to previous plane (with approximate esd) = 14.458 (0.023)
* -0.0213 (0.0003) N1 * 0.0180 (0.0003) N2 * -0.0081 (0.0003) C3 * -0.0053 (0.0003) C4 * 0.0167 (0.0003) C5 0.5584 (0.0008) S1 -0.0703 (0.0009) O1 -0.0102 (0.0010) N3
Rms deviation of fitted atoms = 0.0151
0.7595 (0.0030) x + 11.8725 (0.0006) y + 1.5620 (0.0042) z = 8.2715 (0.0020)
Angle to previous plane (with approximate esd) = 77.814 (0.024)
* -0.0025 (0.0004) C11 * 0.0002 (0.0005) C12 * 0.0021 (0.0006) C13 * -0.0021 (0.0005) C14 * -0.0001 (0.0005) C15 * 0.0025 (0.0004) C16
Rms deviation of fitted atoms = 0.0019

**Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)**

| Atom | x    | y    | z    | Uiso*/Ueq |
|------|------|------|------|----------|
| N1   | 0.24056 (5) | 0.51243 (4) | 0.28333 (3) | 0.01335 (7) |
| N2   | 0.30323 (5) | 0.41284 (4) | 0.31574 (3) | 0.01269 (7) |
| C3   | 0.20639 (5) | 0.33841 (4) | 0.29582 (4) | 0.01215 (8) |
| C4   | 0.08065 (5) | 0.38197 (4) | 0.25555 (4) | 0.01363 (8) |
| H4   | -0.001094 | 0.342184 | 0.236726 | 0.016* |
| C5   | 0.10363 (5) | 0.49489 (5) | 0.24984 (4) | 0.01353 (8) |
| C6   | 0.36155 (5) | 0.19759 (5) | 0.34437 (4) | 0.01441 (8) |
| H6A  | 0.382782 | 0.227785 | 0.405500 | 0.017* |
| H6B  | 0.429311 | 0.227836 | 0.305692 | 0.017* |
| C7   | 0.36826 (5) | 0.07135 (4) | 0.34602 (4) | 0.01344 (8) |
| O1   | 0.22577 (4) | 0.22853 (3) | 0.31015 (3) | 0.01574 (7) |
| O2   | 0.26716 (5) | 0.01561 (4) | 0.32082 (4) | 0.01960 (9) |
| N3   | 0.02108 (6) | 0.57726 (5) | 0.21484 (5) | 0.02257 (11) |
| H01  | -0.0666 (14) | 0.5651 (12) | 0.2040 (8) | 0.036 (3)* |
| H02  | 0.0528 (13) | 0.6445 (10) | 0.2171 (8) | 0.028 (3)* |
| S1   | 0.30852 (2) | 0.62852 (2) | 0.32942 (2) | 0.01351 (4) |
| O3   | 0.23014 (5) | 0.71771 (4) | 0.28591 (3) | 0.01948 (8) |
| O4   | 0.45358 (5) | 0.62322 (4) | 0.32464 (3) | 0.01823 (8) |
| C11  | 0.27468 (6) | 0.62077 (5) | 0.44193 (4) | 0.01454 (9) |
| C12  | 0.13852 (7) | 0.62706 (6) | 0.46205 (4) | 0.02211 (12) |
| H12  | 0.066048 | 0.637804 | 0.416031 | 0.027* |
| C13  | 0.11104 (7) | 0.61728 (7) | 0.55093 (5) | 0.02584 (13) |
| H13  | 0.018996 | 0.621524 | 0.566106 | 0.031* |
| C14  | 0.21846 (7) | 0.60125 (6) | 0.61789 (4) | 0.02114 (11) |
| H14  | 0.198893 | 0.594176 | 0.678417 | 0.025* |
| C15  | 0.35380 (7) | 0.59553 (5) | 0.59684 (4) | 0.01925 (10) |
sup-3

Atomic displacement parameters (Å$^2$)

|   | $U^{11}$   | $U^{22}$   | $U^{33}$   | $U^{12}$   | $U^{13}$   | $U^{23}$   |
|---|------------|------------|------------|------------|------------|------------|
| N1| 0.01169 (17) | 0.01073 (16) | 0.01710 (18) | -0.00019 (13) | -0.00153 (14) | -0.00017 (13) |
| N2| 0.01097 (16) | 0.01076 (16) | 0.01599 (18) | 0.00054 (13) | -0.00050 (13) | -0.00021 (13) |
| C3| 0.01059 (18) | 0.01128 (18) | 0.01451 (19) | 0.00047 (14) | 0.00092 (14) | 0.00002 (14) |
| C4| 0.00988 (18) | 0.01317 (19) | 0.0175 (2) | -0.00025 (14) | -0.00052 (15) | 0.00061 (15) |
| C5| 0.01098 (18) | 0.01337 (19) | 0.0159 (2) | 0.00071 (15) | -0.00055 (15) | 0.00110 (15) |
| C6| 0.01131 (18) | 0.01194 (18) | 0.0195 (2) | 0.00104 (15) | -0.00122 (16) | -0.00021 (16) |
| C7| 0.01256 (19) | 0.01213 (18) | 0.0153 (2) | 0.00107 (15) | -0.00068 (15) | -0.00064 (15) |
| O1| 0.01125 (15) | 0.01075 (15) | 0.02455 (19) | 0.00083 (12) | -0.00184 (13) | 0.00110 (13) |
| O2| 0.01475 (18) | 0.01379 (17) | 0.0288 (2) | -0.00047 (13) | -0.00554 (15) | -0.00210 (15) |
| N3| 0.0147 (2) | 0.0154 (2) | 0.0360 (3) | 0.00168 (16) | -0.00609 (19) | 0.00591 (19) |
| S1| 0.01339 (6) | 0.01073 (6) | 0.01621 (6) | -0.00151 (4) | 0.00040 (4) | 0.00007 (4) |
| O3| 0.0232 (2) | 0.01187 (16) | 0.0226 (2) | 0.00004 (14) | -0.00214 (16) | 0.00320 (14) |
| O4| 0.01387 (17) | 0.01884 (19) | 0.0222 (2) | -0.00499 (14) | 0.00286 (14) | -0.00164 (14) |
| C11| 0.0134 (2) | 0.01384 (19) | 0.0161 (2) | 0.00121 (15) | -0.00008 (16) | -0.00136 (15) |
| C12| 0.0142 (2) | 0.0340 (3) | 0.0179 (2) | 0.0062 (2) | 0.00046 (18) | 0.00004 (2) |
| C13| 0.0176 (3) | 0.0408 (4) | 0.0194 (3) | 0.0068 (2) | 0.0032 (2) | 0.0007 (2) |
| C14| 0.0224 (3) | 0.0240 (3) | 0.0170 (2) | 0.0040 (2) | 0.00141 (19) | -0.00039 (19) |
| C15| 0.0192 (2) | 0.0198 (2) | 0.0179 (2) | 0.00189 (19) | -0.00336 (18) | -0.00113 (18) |
| C16| 0.0139 (2) | 0.0173 (2) | 0.0192 (2) | 0.00034 (17) | -0.00162 (17) | -0.00173 (17) |
| C21| 0.01182 (19) | 0.01317 (19) | 0.0149 (2) | 0.00123 (15) | -0.00019 (15) | 0.00002 (15) |
| C22| 0.0156 (2) | 0.0138 (2) | 0.0195 (2) | 0.00256 (16) | -0.00126 (17) | -0.00044 (17) |
| C23| 0.0175 (2) | 0.0172 (2) | 0.0199 (2) | 0.00551 (18) | -0.00005 (18) | 0.00038 (18) |
| C24| 0.0140 (2) | 0.0233 (3) | 0.0162 (2) | 0.00563 (18) | 0.00076 (16) | 0.00157 (18) |
| C25| 0.0126 (2) | 0.0226 (3) | 0.0223 (3) | 0.00085 (18) | -0.00198 (18) | -0.00033 (19) |
| C26| 0.0131 (2) | 0.0165 (2) | 0.0208 (2) | 0.00012 (16) | -0.00120 (17) | -0.00043 (18) |
| C27| 0.0176 (3) | 0.0355 (3) | 0.0242 (3) | 0.0113 (2) | -0.0016 (2) | 0.0022 (3) |
Geometric parameters (Å, °)

| Bond          | Distance (Å) | Bond          | Distance (Å) |
|---------------|--------------|---------------|--------------|
| N1—C5         | 1.3999 (7)   | C22—C23       | 1.3869 (8)   |
| N1—N2         | 1.4071 (7)   | C23—C24       | 1.3976 (9)   |
| N1—S1         | 1.6638 (5)   | C24—C25       | 1.3987 (9)   |
| N2—C3         | 1.3141 (7)   | C24—C27       | 1.5047 (9)   |
| C3—O1         | 1.3447 (7)   | C25—C26       | 1.3898 (8)   |
| C3—C4         | 1.4167 (7)   | C4—H4         | 0.9500       |
| C4—C5         | 1.3758 (8)   | C6—H6A        | 0.9900       |
| C5—N3         | 1.3494 (8)   | C6—H6B        | 0.9900       |
| C6—O1         | 1.4257 (7)   | N3—H01        | 0.869 (13)   |
| C6—C7         | 1.5144 (8)   | N3—H02        | 0.863 (12)   |
| C7—O2         | 1.2226 (7)   | C12—H12       | 0.9500       |
| C7—C21        | 1.4802 (8)   | C13—H13       | 0.9500       |
| S1—O4         | 1.7542 (6)   | C14—H14       | 0.9500       |
| S1—O3         | 1.4355 (5)   | C15—H15       | 0.9500       |
| S1—C11        | 1.3910 (8)   | C16—H16       | 0.9500       |
| C11—C16       | 1.3942 (9)   | C25—H25       | 0.9500       |
| C13—C14       | 1.3961 (10)  | C25—H26       | 0.9500       |
| C14—C15       | 1.3904 (10)  | C26—H26       | 0.9500       |
| C15—C16       | 1.3938 (9)   | C27—H27A      | 0.9800       |
| C21—C26       | 1.3976 (8)   | C27—H27B      | 0.9800       |
| C21—C22       | 1.3984 (8)   |               |              |
| C5—N1—N2      | 111.51 (4)   | C25—C24—C27   | 120.59 (6)   |
| C5—N1—S1      | 127.24 (4)   | C26—C25—C24   | 120.87 (6)   |
| N2—N1—S1      | 114.96 (4)   | C25—C26—C21   | 120.10 (6)   |
| C3—N2—N1      | 102.52 (4)   | C5—C4—H4      | 127.8        |
| N2—C3—O1      | 122.74 (5)   | C3—C4—H4      | 127.8        |
| N2—C3—C4      | 115.07 (5)   | O1—C6—H6A     | 110.2        |
| O1—C3—C4      | 122.17 (5)   | C7—C6—H6A     | 110.2        |
| C5—C4—C3      | 104.42 (5)   | O1—C6—H6B     | 110.2        |
| N3—C5—C4      | 130.45 (5)   | C7—C6—H6B     | 110.2        |
| N3—C5—N1      | 123.07 (5)   | H6A—C6—H6B    | 108.5        |
| C4—C5—N1      | 106.35 (5)   | C5—N3—H01     | 119.6 (9)    |
| O1—C6—C7      | 107.65 (4)   | C5—N3—H02     | 117.9 (8)    |
| O2—C7—C21     | 121.83 (5)   | H01—N3—H02    | 120.5 (12)   |
| O2—C7—C6      | 120.55 (5)   | C13—C12—H12   | 120.7        |
| C21—C7—C6     | 117.62 (5)   | C11—C12—H12   | 120.7        |
| C3—O1—C6      | 115.11 (4)   | C12—C13—H13   | 119.9        |
| O4—S1—O3      | 119.98 (3)   | C14—C13—H13   | 119.9        |
| O4—S1—N1      | 107.51 (3)   | C15—C14—H14   | 119.7        |
| O3—S1—N1      | 104.99 (3)   | C13—C14—H14   | 119.7        |
| O4—S1—C11     | 108.96 (3)   | C14—C15—H15   | 120.1        |
| O3—S1—C11     | 109.66 (3)   | C16—C15—H15   | 120.1        |
| N1—S1—C11     | 104.59 (3)   | C11—C16—H16   | 120.5        |
### Hydrogen-bond geometry (Å, º)

| D—H···A     | D—H   | H···A  | D···A  | D—H···A |
|-------------|-------|-------|-------|---------|
| N3—H01···O1i| 0.869 (13) | 2.497 (14) | 3.0124 (7) | 118.7 (11) |
| N3—H01···O2i| 0.869 (13) | 2.048 (13) | 2.9121 (7) | 172.8 (13) |

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**sup-5**
|                | d (Å)  | r (Å)  | R (Å)  | θ (°)  |
|----------------|--------|--------|--------|--------|
| N3—H02···O3   | 0.863 (12) | 2.121 (13) | 2.7806 (8) | 132.8 (11) |
| C14—H14···O2^i | 0.95   | 2.54   | 3.3458 (8) | 142    |

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