Crystal structure, Hirshfeld surface and computational study of 1-(9,10-dioxo-9,10-dihydroanthracen-1-yl)-3-propanoylthiourea

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The title compound, C_{18}H_{14}N_{2}O_{3}S, crystallizes in the orthorhombic crystal system and Pbca space group. The thiourea chromophore is planar to an r.m.s deviation of 0.032 Å with the thiolate sulfur atom being the most deviated. Bifurcated N—H···O intramolecular hydrogen bonds result in an S(6) supramolecular synthon. In the crystal, molecules are linked by N—H···O intermolecular hydrogen-bonding interactions and stabilized by C—H···C and π···π interactions. Hirshfeld surface analysis and fingerprint plot indicate the H···H intermolecular contacts as the highest contributor to the overall surface contacts (38%) and this is supported by the high dispersive and electrostatic interaction energies.

1. Chemical context

Anthraquinones, a group of tricyclic aromatic organic compounds, are the largest group of natural and synthetic quinones. A large number of them are well-known natural pigments found in plants, lichens, and fungi (Duval et al., 2016). These compounds exhibit important biological activities, including antitumor (Huang et al., 2007; Murdock et al., 1979, Shrestha et al., 2014, 2015; Chien et al., 2015), anti-inflammatory (Chien et al., 2015; Khan et al., 2011), diuretic (Chien et al., 2015), antiarthritic (Davis et al., 1986), antifungal (Wuthi-udomlert et al., 2010), antibacterial (Fosso et al., 2012), antimalarial (Winter et al., 1996), antioxidant (Dave & Ledwani, 2012), antileukemic (Chang & Lee, 1984; Ismail et al., 1997), antiviral and anti-HIV properties (Alves et al., 2004; Barnard et al., 1992; Schinazi et al., 1990; Schrader et al., 2000). Some aminoanthraquinone derivatives have also been reported to be good DNA intercalators (Hande, 2008; Schrader et al., 2000). The versatility of acyl thioureas stems from their ease of preparation and ability to introduce different functionalities, resulting in compounds with very interesting biological properties including antifungal (del Campo et al., 2002, 2004), antitumor (Sacht & Datt, 2000; Sacht et al., 2000; Hernández et al., 2005), antiviral, antibacterial, herbicidal, insecticidal and pharmacological activities (Binzet et al., 2006; Saeed et al., 2010). Recently, our research group reported the synthesis and crystal structures of a number of thiourea derivatives (Asegbeloyin et al., 2018, 2019; Okpareke et al., 2020, 2022; Oyeka et al., 2021). In a continuation of our series on thiourea derivatives, we present
herein the crystal structure, Hirshfeld surface and computational study of a new potential biologically active thiourea derivative with an aminoanthraquinone moiety.

2. Structural commentary

The title compound crystallizes in the orthorhombic crystal system and $Pbca$ space group. The molecular structure (Fig. 1) shows a central thiourea chromophore flanked on either side by methylene and anthraquinone units. The central thiourea moiety is essentially planar with an r.m.s deviation of 0.032 Å with the thiolate S atom being the most deviated out of the plane with a deviation of 0.044 (3) Å. The torsion angles between the thiourea and the adjoining methylene and anthraquinone moieties are $/C0177.5 (2)$ and $/C0140.8 (2)$, respectively, indicating that the anthraquinone moiety is slightly deviated from the thiourea plane, compared to the methylene moiety. The $C1—N1—C5$ bond angle of $126.09 (19)^\circ$ subtended at the N1 atom is smaller than the less encumbered $C2—N2—C1$ angle $[129.79 (19)]^\circ$ subtended at N2 and larger than the central $N1—C1—N2$ $[114.5 (2)]^\circ$ bond angle subtended at the thiolate C1 carbon atom. The $C1—N2$ bond $[1.395 (3)$ Å$]$ is slightly longer than $C1—N1$ $[1.364 (3) $Å$]$. The thiourea carbonyl oxygen and imine groups are involved in a strong intramolecular N1—H1···O hydrogen bond (Table 1). The second amine nitrogen N2 is also involved in a hydrogen-bonding $S(6)$ graph-set (Kansiz et al., 2022) interaction.

3. Supramolecular features

In the crystal, the molecules are linked by imine N—H···O (anthraquinone) hydrogen-bonding interactions, leading to supramolecular chains running along the $c$-axis direction (Fig. 2a). Supramolecular layers are obtained from self-assembly of these chains via anthraquinone $\pi$–$\pi$ stacking interactions along the $ab$ plane with centroid–centroid distances of 3.916(3), 3.531(5), 3.701(2) and 3.705(2) Å (Fig. 2b). These intermolecular interactions are balanced and stabilized by the phenyl C—H···O(carbonyl) and imine N—H···O(carbonyl) intramolecular $S(6)$ synthon.

4. Hirshfeld surface analysis and fingerprint plots

Hirshfeld surfaces (HS) and corresponding two-dimensional fingerprint plots (FPs) were calculated using the Crystal

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Table 1

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|------|-------|---------|
| N1—H1···O1 | 0.86 | 1.98 | 2.685 (2) | 138 |
| N1—H1···O2 | 0.86 | 2.14 | 2.652 (2) | 117 |
| N2—H2···O3 | 0.86 | 2.19 | 3.038 (2) | 167 |
| C3—H3B···O2w | 0.97 | 2.52 | 3.414 (3) | 153 |
| C15—H15···S1w | 0.93 | 2.87 | 3.553 (2) | 131 |
| C17—H17···O2w | 0.93 | 2.47 | 3.280 (3) | 145 |

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

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Figure 1

View of the molecular structure of the title compound, with the atom labeling. Displacement ellipsoids are drawn at the 30% probability level. Intramolecular hydrogen bonds are shown as dashed lines.

Figure 2

(a) Supramolecular 1-D hydrogen-bonding interactions along c-axis direction of the title compound and (b) molecular aggregation structure of the crystal along the $ab$ plane, showing repeating units of pairwise $\pi$–$\pi$ stacking interactions.
Explorer 17.5 software (Turner et al., 2017). The Hirshfeld surfaces mapped over $d_{\text{norm}}$ and shape-index were generated according to a procedure described by Tan et al. (2019) and used for further analysis of the intermolecular interactions. The HS mapped over $d_{\text{norm}}$ shows the most intense red regions around the thiourea N—H groups resulting from the amine-N—H—O (anthraquinone) hydrogen-bonding interactions (Fig. 3a). Other intense red spots can be identified around the thiourea carbonyl oxygen and resulting from carbonyl C17—H17· · ·O12 intermolecular interaction. Apart from the intense red spots, there are a number of other less intense red spots found around the alkyl C3 atom resulting from C3—H3B· · ·O1 intermolecular interaction. Other intermolecular interactions in the Hirshfeld surface are the anthraquinone C—H· · ·S(thiourea) and anthraquinone—C—H· · ·H(alkyl) interactions shown respectively as pink and green dotted lines in Fig. 3b. The anthraquinone π—π interactions can be seen in Fig. 3c. The C—H/H· · ·C contacts in the molecule are responsible for the molecular packing in the supramolecular structure and are the result of the C—H· · ·π and π—π interactions (Tan & Tiekink, 2020) and are depicted by mapping the structure over the shape-index isosurface as shown in Fig. 3d. The C—H· · ·π interactions appear as hollow orange areas (π· · ·H—C) and bulging blue areas (C—H· · ·π) in the compound. The small blue regions surrounding a bright orange spot within the anthraquinone rings of the molecule indicate π—π stacking interactions.

The overall two-dimensional fingerprint plot (Spackman & McKinnon, 2002; Tan & Tiekink, 2020) and those delineated into H· · ·H, H· · ·O/O· · ·H, H· · ·C/C· · ·H, C· · ·C, S· · ·H/H· · ·S and C· · ·O/O· · ·C interactions are illustrated in Fig. 4, and their percentage contributions are presented in Table 2. The overall fingerprint plot comprises all intermolecular contacts in the molecule and exhibits a shield-like profile with two symmetric spikes on each side of a triangular protrusion. These spikes are also observed in the fingerprint plots for the O· · ·H/H· · ·O contacts, which make a 19.5% contribution to the overall surface contact, but not in the other surface contacts. These spikes are due to the C—H· · ·O and N2—H2· · ·O3 hydrogen-bonding interactions in the crystal structure of the title compound. H· · ·H contacts are the single highest contributor to the overall surface with a 38.0% contribution and and result from C—H· · ·H and H· · ·H dispersion interactions. The other major surface contacts are C· · ·H/H· · ·C (13.0%), S· · ·H/H· · ·S (10.8%), and C· · ·C (11.2%), showing that C· · ·H and π intermolecular contacts contribute significantly to the overall stability of the supramolecular architecture in the crystal structure (Ekowo et al., 2020; Izuogu et al., 2020).

![Figure 3](image1.png)

**Figure 3**
Hirshfeld surfaces mapped over (a), (b) and (c) $d_{\text{norm}}$ and (d) shape-index showing intermolecular atom-to-atom and π—π interactions in the crystal structure.

![Figure 4](image2.png)

**Figure 4**
The overall and individual two-dimensional fingerprint plots for intermolecular contacts in the crystal structure.

| Contact | Percentage contribution |
|---------|-------------------------|
| H· · ·H  | 38.0                    |
| H· · ·O/O· · ·H | 19.5              |
| C· · ·H/H· · ·C | 13.0              |
| C· · ·C  | 26.3                    |
| H· · ·H  | 11.2                    |
| S· · ·H/H· · ·S | 10.8              |
| C· · ·O/O· · ·C | 2.7               |
| N· · ·H/H· · ·N | 1.4                |
| C· · ·O/O· · ·C | 1.3                |

Table 2
Percentage contributions of intermolecular contacts to the Hirshfeld surface.
5. Interaction energy calculations

The interaction energies between pairs of molecules within the crystal of the title compound were calculated by adding up the four energy components, viz. electrostatic ($E_{ele}$), polarization ($E_{pol}$), dispersion ($E_{dis}$), and exchange repulsion ($E_{rep}$) (Tan et al., 2019; Ayiya & Okpareke, 2021). The energies were obtained by calculating the wave function of each pair of molecules or atoms at the B3LYP/6-31G(d,p) level of theory (Ayiya & Okpareke, 2021; Izuogu et al., 2020). Quantitative estimations of the strength and nature of the intermolecular interactions in the crystal of the compound were calculated by adding up the four energy components ($E_{ele}$, $E_{pol}$, $E_{dis}$, and $E_{rep}$) as well as the sum of the energy components ($E_{tot}$) are presented in Table 3. This shows that the dispersive component of the energy makes the most significant contribution to the total interaction energy profile in the crystal structure, probably due to the intermolecular dispersive $\pi$ interactions resulting from the $\pi-\pi$ stacking of adjacent anthraquinone ring systems in the crystal. The electrostatic component is the second highest contributor to the total interaction energy and probably results from the C-H...H and H-H-H and van der Waals interactions. A graphical representation of the magnitude of the interaction energies is presented in Fig. 5a–d in the form of energy frameworks to show the supramolecular architecture using cylindrical poles joining the centroids of molecular pairs. The red, green, and blue color-coded frameworks in Fig. 5a, 5b, and 5c, respectively, represent the $E_{ele}$, $E_{dis}$ and $E_{tot}$ energy components for intermolecular interactions in the crystal of the title compound, while Fig. 5d shows the annotated $E_{tot}$ energy. The magnitude of the cylindrical pipes indicates the significance of the $E_{ele}$ energy component to the total interaction energy and the molecular packing in the crystal.

6. Database survey

Anthraquinones derivatives with thiourea unit are scarce and our search for the basic architecture of the compound in the Cambridge Structural Database (CSD, version 5.42, update of May 2021; Groom et al., 2016) did not reveal any structure similar to the title compound.

7. Synthesis and crystallization

A solution of propionyl chloride (1.85 g, 0.02 mol) dissolved in 40 mL of acetone was mixed with 30 mL of an acetone solution of potassium thiocyanate (1.94 g, 0.02 mol). The reaction mixture was refluxed for 30 min to give a suspension of propionylisothiocyanate, which was left to cool to room temperature. 1-Aminoanthraquinone (4.47 g, 0.02 mol) was dissolved in 40 mL of acetone and the resulting solution was mixed with the suspension of propionylisothiocyanate, and the mixture was stirred for 2 h. The resultant reddish suspension was filtered, and left at room temperature for 96 h to obtain a reddish crystalline solid of the title compound.

8. Refinement

Crystal data, collection and structure refinement details are summarized in Table 4. The carbon-bound H atoms were...
placed in calculated positions and were included in the refinement using the riding-model approximation with $U_{iso}(H)$ set to 1.2$U_{eq}$(C). The nitrogen-bound H atoms were located in the difference-Fourier maps and refined freely with appropriate RIGU restraints placed on the bonds.

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Crystal structure, Hirshfeld surface and computational study of 1-(9,10-dioxo-9,10-dihydroanthracen-1-yl)-3-propanoylthiourea

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Computing details

Data collection: Crystals PRO (Rigaku OD, 2018); cell refinement: Crystals PRO (Rigaku OD, 2018); data reduction: Crystals PRO (Rigaku OD, 2018); program(s) used to solve structure: ShelXT (Sheldrick, 2015a); program(s) used to refine structure: SHELXL (Sheldrick, 2015b); molecular graphics: OLEX2 (Dolomanov et al., 2009); software used to prepare material for publication: OLEX2 (Dolomanov et al., 2009).

1-(9,10-Dioxo-9,10-dihydroanthracen-1-yl)-3-propanoylthiourea

Crystal data

C_{18}H_{14}N_{2}O_{3}S  
Mr = 338.37  
Orthorhombic, Pbca  
a = 7.3003 (1) Å  
b = 18.9557 (3) Å  
c = 21.9045 (3) Å  
V = 3031.19 (8) Å³  
Z = 8  
F(000) = 1408

Data collection

XtaLAB Synergy, Dualflex, Pilatus 200K diffractometer  
Radiation source: micro-focus sealed X-ray tube, PhotonJet (Cu) X-ray Source  
Mirror monochromator  
ω scans  
Absorption correction: multi-scan  
(CrystalsPro; Rigaku OD, 2018)  
Tmin = 0.869, Tmax = 1.000  
18022 measured reflections  
3013 independent reflections  
2816 reflections with I > 2σ(I)  
Rint = 0.034  
θmax = 74.3°, θmin = 4.0°  
h = −8→8  
k = −23→22  
l = −26→26

Refinement

Refinement on F²  
Least-squares matrix: full  
R[F² > 2σ(F²)] = 0.048  
wR(F²) = 0.144  
S = 1.13  
3013 reflections  
218 parameters  
0 restraints  
Primary atom site location: dual  
Hydrogen site location: inferred from neighbouring sites  
H-atom parameters constrained  
w = 1/[σ²(Fo^2) + (0.0724P)^2 + 3.6939P]  
where P = (Fo^2 + 2Fc^2)/3
$(\Delta/\sigma)_{\text{max}} < 0.001$
\[ \Delta \rho_{\text{max}} = -0.64 \text{ e Å}^{-3} \]
\[ \Delta \rho_{\text{min}} = 0.67 \text{ e Å}^{-3} \]

**Special details**

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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

|    | x       | y       | z       | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|----|---------|---------|---------|----------------------------------|
| S1 | 0.72292 (8) | 0.44246 (3) | 0.25812 (3) | 0.02439 (19) |
| O2 | 0.7597 (2) | 0.64440 (8) | 0.41206 (7) | 0.0228 (4)   |
| O3 | 0.6789 (2) | 0.46534 (8) | 0.60029 (7) | 0.0244 (4)   |
| O1 | 0.9337 (3) | 0.66694 (9) | 0.29076 (7) | 0.0287 (4)   |
| N1 | 0.8521 (3) | 0.53993 (9) | 0.33766 (8) | 0.0195 (4)   |
| H1 | 0.889018 | 0.582673 | 0.342345 | 0.023* |
| N2 | 0.8371 (3) | 0.57086 (10) | 0.23530 (8) | 0.0223 (4)   |
| H2 | 0.815839 | 0.557602 | 0.198428 | 0.027* |
| C12 | 0.6591 (3) | 0.62664 (11) | 0.51256 (9) | 0.0171 (4)   |
| C5 | 0.8416 (3) | 0.49780 (11) | 0.39044 (9) | 0.0172 (4)   |
| C13 | 0.6390 (3) | 0.58121 (11) | 0.56248 (9) | 0.0169 (4)   |
| C10 | 0.7788 (3) | 0.52594 (11) | 0.44627 (9) | 0.0154 (4)   |
| C11 | 0.7332 (3) | 0.60171 (11) | 0.45330 (9) | 0.0163 (4)   |
| C9 | 0.7647 (3) | 0.48093 (11) | 0.49745 (9) | 0.0159 (4)   |
| C6 | 0.9019 (3) | 0.42781 (11) | 0.38807 (10) | 0.0200 (5)   |
| H6 | 0.951456 | 0.410016 | 0.352119 | 0.024* |
| C7 | 0.8881 (3) | 0.38493 (11) | 0.43898 (10) | 0.0208 (5)   |
| H7 | 0.927247 | 0.338318 | 0.436683 | 0.025* |
| C15 | 0.5707 (3) | 0.60672 (12) | 0.61753 (10) | 0.0220 (5)   |
| H15 | 0.556732 | 0.576471 | 0.650632 | 0.026* |
| C8 | 0.8170 (3) | 0.41032 (11) | 0.49330 (10) | 0.0179 (4)   |
| H8 | 0.804179 | 0.380524 | 0.526757 | 0.022* |
| C14 | 0.6936 (3) | 0.50620 (11) | 0.55722 (9) | 0.0172 (4)   |
| C18 | 0.6119 (3) | 0.69770 (11) | 0.51866 (10) | 0.0223 (5)   |
| H18 | 0.625588 | 0.728232 | 0.485743 | 0.027* |
| C2 | 0.8937 (3) | 0.64023 (12) | 0.24157 (10) | 0.0230 (5)   |
| C17 | 0.5446 (3) | 0.72278 (13) | 0.57380 (11) | 0.0262 (5)   |
| H17 | 0.513700 | 0.770149 | 0.577811 | 0.031* |
| C1 | 0.8093 (3) | 0.51926 (12) | 0.27974 (10) | 0.0203 (5)   |
| C16 | 0.5234 (3) | 0.67731 (13) | 0.62298 (11) | 0.0254 (5)   |
| H16 | 0.477295 | 0.694251 | 0.659739 | 0.031* |
| C3 | 0.8997 (4) | 0.68035 (13) | 0.18245 (11) | 0.0298 (6)   |
| H3A | 0.777627 | 0.681545 | 0.164961 | 0.036* |
| H3B | 0.978880 | 0.655647 | 0.154039 | 0.036* |
| C4 | 0.9688 (5) | 0.75570 (14) | 0.19012 (13) | 0.0380 (6)   |
| H4A | 0.965684 | 0.779397 | 0.151405 | 0.057* |
| H4B | 1.092260 | 0.754860 | 0.205179 | 0.057* |
### Supporting Information

#### Atomic displacement parameters (Å²)

|     | \(U_{11}\) | \(U_{22}\) | \(U_{33}\) | \(U_{12}\) | \(U_{13}\) | \(U_{23}\) |
|-----|-----------|-----------|-----------|-----------|-----------|-----------|
| S1  | 0.0304 (3) | 0.0229 (3) | 0.0198 (3) | -0.0057 (2) | 0.0008 (2) | -0.0018 (2) |
| O2  | 0.0358 (9) | 0.0158 (7) | 0.0170 (7) | -0.0024 (6) | 0.0019 (7) | 0.0034 (6) |
| O3  | 0.0347 (10) | 0.0221 (8) | 0.0163 (8) | 0.0002 (7) | 0.0017 (6) | 0.0062 (6) |
| O1  | 0.0417 (11) | 0.0264 (9) | 0.0180 (8) | -0.0020 (7) | -0.0021 (7) | -0.0015 (6) |
| N1  | 0.0294 (10) | 0.0152 (8) | 0.0140 (9) | -0.0018 (7) | 0.0012 (7) | 0.0009 (7) |
| N2  | 0.0289 (10) | 0.0232 (10) | 0.0148 (9) | -0.0010 (8) | -0.0003 (8) | -0.0001 (7) |
| C12 | 0.0153 (10) | 0.0190 (10) | 0.0168 (10) | -0.0003 (8) | -0.0012 (8) | 0.0007 (8) |
| C5  | 0.0192 (11) | 0.0175 (10) | 0.0149 (10) | -0.0025 (8) | -0.0018 (8) | 0.0025 (8) |
| C13 | 0.0142 (10) | 0.0199 (10) | 0.0165 (10) | -0.0004 (8) | -0.0019 (8) | 0.0005 (8) |
| C10 | 0.0151 (10) | 0.0146 (10) | 0.0165 (10) | -0.0016 (7) | -0.0031 (8) | 0.0013 (8) |
| C11 | 0.0168 (10) | 0.0166 (10) | 0.0156 (10) | -0.0022 (8) | -0.0032 (8) | 0.0005 (8) |
| C9  | 0.0138 (10) | 0.0178 (10) | 0.0162 (10) | -0.0028 (8) | -0.0021 (8) | 0.0014 (8) |
| C6  | 0.0224 (11) | 0.0189 (10) | 0.0187 (10) | 0.0014 (8) | 0.0004 (8) | -0.0010 (8) |
| C7  | 0.0240 (11) | 0.0146 (10) | 0.0239 (11) | 0.0015 (9) | -0.0020 (9) | 0.0013 (8) |
| C15 | 0.0208 (11) | 0.0289 (12) | 0.0164 (10) | 0.0010 (9) | 0.0004 (8) | 0.0016 (9) |
| C8  | 0.0183 (10) | 0.0164 (10) | 0.0190 (10) | -0.0011 (8) | -0.0024 (8) | 0.0042 (8) |
| C14 | 0.0158 (10) | 0.0202 (10) | 0.0156 (10) | -0.0026 (8) | -0.0033 (8) | 0.0022 (8) |
| C18 | 0.0267 (11) | 0.0174 (10) | 0.0228 (11) | 0.0025 (9) | 0.0006 (9) | 0.0015 (8) |
| C2  | 0.0235 (11) | 0.0230 (11) | 0.0226 (11) | 0.0006 (9) | 0.0019 (9) | 0.0008 (9) |
| C17 | 0.0277 (12) | 0.0211 (11) | 0.0298 (12) | 0.0043 (9) | 0.0021 (10) | -0.0033 (9) |
| C1  | 0.0205 (11) | 0.0218 (11) | 0.0185 (10) | 0.0013 (8) | 0.0006 (8) | 0.0017 (8) |
| C16 | 0.0258 (12) | 0.0293 (12) | 0.0212 (11) | 0.0037 (9) | 0.0028 (9) | -0.0048 (9) |
| C3  | 0.0398 (14) | 0.0298 (13) | 0.0199 (11) | -0.0015 (11) | 0.0037 (10) | 0.0016 (9) |
| C4  | 0.0559 (18) | 0.0280 (13) | 0.0302 (13) | -0.0085 (12) | 0.0012 (12) | 0.0085 (10) |

#### Geometric parameters (Å, °)

|     |     |              |     |     |     |
|-----|-----|--------------|-----|-----|-----|
| S1  |      | C9—C14       |     |     |     |
| O2  |      | C6—H6        |     |     |     |
| O3  |      | C6—C7        |     |     |     |
| O1  |      | C7—H7        |     |     |     |
| N1  |      | C7—C8        |     |     |     |
| N1  |      | C15—H15      |     |     |     |
| N1  |      | C15—C16      |     |     |     |
| N2  |      | C8—H8        |     |     |     |
| N2  |      | C18—H18      |     |     |     |
| N2  |      | C18—C17      |     |     |     |
| N2  |      | C2—C3        |     |     |     |
| C12 |      | C17—H17      |     |     |     |
| C12 |      | C17—C16      |     |     |     |
| C12 |      | C3—H3A       |     |     |     |
| C13 |      | C3—H3B       |     |     |     |

*Acta Cryst. (2022). E78, 439-444*
C13—C14 1.481 (3)  C3—C4 1.524 (4)
C10—C11 1.482 (3)  C4—H4A 0.9600
C10—C9 1.412 (3)  C4—H4B 0.9600
C9—C8 1.395 (3)  C4—H4C 0.9600

C5—N1—H1 117.0  C9—C8—H8 120.3
C1—N1—H1 117.0  C7—C8—C9 119.49 (19)
C1—N1—C5 126.06 (19)  C7—C8—H8 120.3
C2—N2—H2 115.1  O3—C14—C13 121.5 (2)
C2—N2—C1 129.79 (19)  O3—C14—C9 120.32 (19)
C1—N2—H2 115.1  C4—H4A 0.9600
C13—C12—C11 121.73 (19)  C12—C18—H18 120.0
C18—C12—C13 119.5 (2)  C17—C18—C12 120.1 (2)
C18—C12—C11 118.74 (19)  C17—C18—H18 120.0
N1—C5—C10 121.02 (18)  O1—C2—N2 123.4 (2)
C6—C5—N1 119.38 (19)  O1—C2—C3 122.8 (2)
C6—C5—C10 119.54 (19)  N2—C2—C3 113.80 (19)
C12—C13—C14 120.11 (19)  C18—C17—H17 119.9
C15—C13—C12 120.1 (2)  C18—C17—C16 120.1 (2)
C15—C13—C14 119.83 (19)  C16—C17—H17 119.9
C5—C10—C14 121.97 (18)  N1—C1—S1 127.30 (17)
C5—C10—C9 118.90 (19)  N1—C1—N2 114.5 (2)
C9—C10—C11 119.10 (19)  N2—C1—S1 118.19 (16)
O2—C11—C12 119.42 (19)  C15—C16—C17 120.3 (2)
O2—C11—C10 121.78 (19)  C15—C16—H16 119.9
C10—C11—C12 118.78 (18)  C16—C17—H16 119.9
C10—C9—C14 121.97 (18)  C2—C3—H3A 109.0
C8—C9—C10 120.52 (19)  C2—C3—H3B 109.0
C8—C9—C14 117.50 (18)  C2—C3—C4 112.9 (2)
C5—C6—H6 119.9  H3A—C3—H3B 107.8
C7—C6—C5 120.3 (2)  C4—C3—H3A 109.0
C7—C6—H6 119.9  C4—C3—H3B 109.0
C6—C7—H7 119.5  C3—C4—H4A 109.5
C6—C7—C8 121.0 (2)  C3—C4—H4B 109.5
C8—C7—H7 119.5  C3—C4—H4C 109.5
C13—C15—H15 120.0  H4A—C4—H4B 109.5
C16—C15—C13 119.9 (2)  H4A—C4—H4C 109.5
C16—C15—H15 120.0  H4B—C4—H4C 109.5

*Hydrogen-bond geometry (Å, °)*

| D—H···A | D—H | H···A | D···A | D—H···A |
|----------|-----|-------|-------|--------|
| N1—H1···O1 | 0.86 | 1.98 | 2.685 (2) | 138 |
| N1—H1···O2 | 0.86 | 2.14 | 2.652 (2) | 117 |
| N2—H2···O3 | 0.86 | 2.19 | 3.038 (2) | 167 |
| C3—H3B···O2 | 0.97 | 2.52 | 3.414 (3) | 153 |
| Bond          | r (Å) | d (Å)  | d(H···A) (Å)  | ϕ (°) |
|--------------|-------|--------|--------------|-------|
| C15—H15···S1   | 0.93  | 2.87   | 3.553 (2)    | 131   |
| C17—H17···O2   | 0.93  | 2.47   | 3.280 (3)    | 145   |

Symmetry codes: (i) −x+3/2, −y+1, z−1/2; (ii) x+1/2, y, −z+1/2; (iii) −x+3/2, −y+1, z+1/2; (iv) x−1/2, −y+3/2, −z+1.