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Crystal structure and Hirshfeld surface analysis of ethyl 2-{[4-ethyl-5-(quinolin-8-yloxymethyl)-4*H*-1,2,4-triazol-3-yl]sulfanyl}acetate

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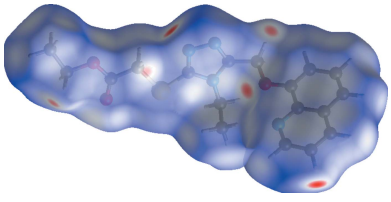
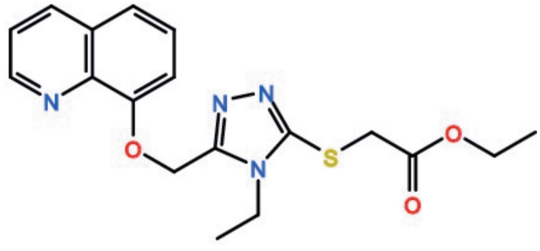
In the title compound, $C_{18}H_{20}N_4O_3S$, the 1,2,4-triazole ring is twisted with respect to the mean plane of quinoline moiety at 65.24 (4)°. In the crystal, molecules are linked by weak C—H···O and C—H···N hydrogen bonds, forming the three-dimensional supramolecular packing. π–π stacking between the quinoline ring systems of neighbouring molecules is also observed, the centroid-to-centroid distance being 3.6169 (6) Å. Hirshfeld surface (HS) analyses were performed.

1. Chemical context

Quinoline derivatives are a very important class of nitrogen-containing heterocycles, which display a broad range of biological activities (Srikanth *et al.*, 2010). In addition, quinolines have suitable electron mobility and other important properties which are crucial for their use in organic light-emitting diodes (OLEDs) (Chen & Shi, 1998; Kulkarni *et al.*, 2004). They are also used in the synthesis of molecules having non-linear optical properties (MacDiarmid *et al.*, 1997; Epstein, 1997). The 1,2,4-triazole ring is also a major five-membered heterocyclic ring, which serves as the core component of many substances that display a wide range of biological activities (Mathew *et al.*, 2007; Pelz *et al.*, 2001). This heterocycle is an important structural motif in the design of new drugs (Catarzi *et al.*, 2004). Here we report the molecular and crystal structure of the title 1,2,4-triazole derivative.





2. Structural commentary

The molecular structure with atomic numbering scheme for the title compound is given in Fig. 1. The geometric parameters of the ester group are within normal ranges. Likewise,

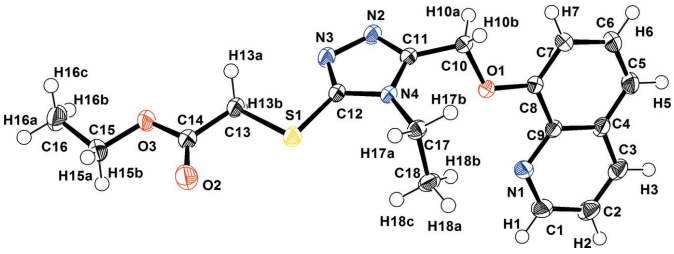


Figure 1
The molecular structure of the title molecule, showing the atomic numbering scheme (displacement ellipsoids are drawn at the 65% probability level). H atoms are shown as small spheres of arbitrary radii.

the S1—C12 and S1—C13 distances, being of 1.7480 (9) and 1.8082 (10) Å, are in agreement with single thioether C—S bonds. The C12—S1 bond is shorter than C13—S1 due to the presence of a delocalized π-electronic system throughout the triazole ring. The C—C bond lengths in the quinoline moiety are in the range 1.3691 (16)– 1.4328 (12) Å. The bond lengths are consistent with previous studies (Cabrera *et al.*, 2015; Sunitha *et al.*, 2015). The ethyl group C—C bond lengths are in the range 1.5083 (13)–1.5232 (13) Å and are consistent with previously reported values (Alshawi *et al.*, 2015). The C1—N1, C11—N2 and C12—N3 bonds have double-bond character

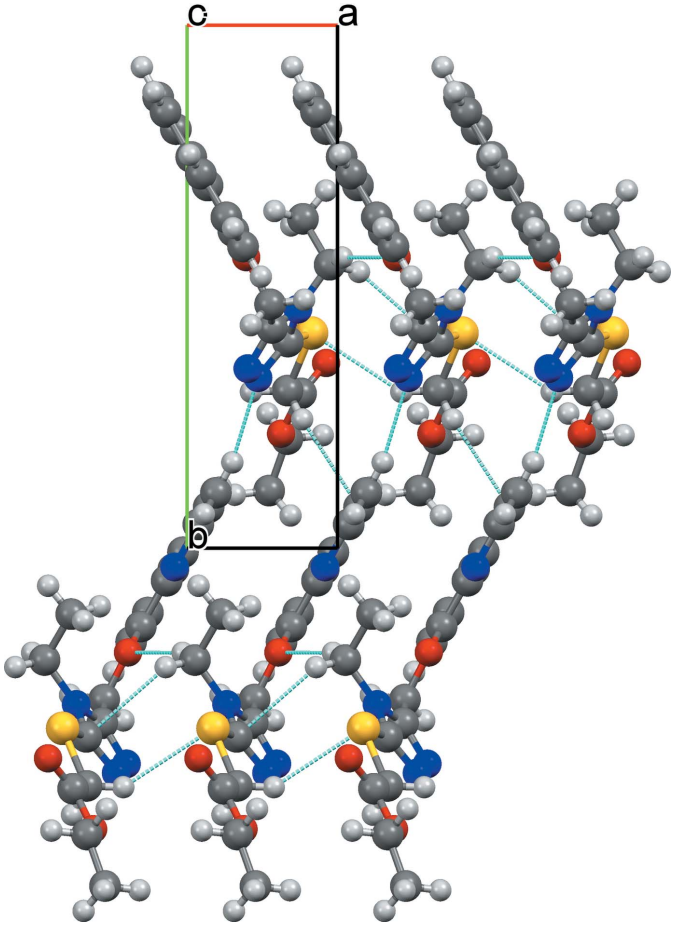


Figure 2
Crystal packing diagram of the title compound viewed along the *c* axis with hydrogen bonds shown as dashed lines.

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

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2···N3^{i}	0.95	2.51	3.4444 (14)	167
C10—H10A···O2^{ii}	0.99	2.52	3.4637 (13)	159
C15—H15B···N2^{iii}	0.99	2.58	3.4636 (14)	148
C17—H17B···O1^{iv}	0.99	2.50	3.4481 (12)	161

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

with bond lengths of 1.3222 (13), 1.3142 (12) and 1.3205 (12) Å, respectively, while the other C—N bonds in the triazole and quinoline rings (C9—N1, C11—N4 and C12—N4) have single-bond character with bond lengths of 1.3662 (12), 1.3699 (11) and 1.3647 (11) Å, respectively. The C14–O3 bond length [1.3326 (12) Å] is notably shorter than the normal C—O single bond (1.427 Å; Wan *et al.*, 2008) due to conjugation. The C15—O3 bond length [1.4605 (12) Å)] is normal for a C—O single bond. The 1,2,4-triazole ring is almost planar (r.m.s. deviation for the non-H atoms = 0.172 Å) and the ethyl acetate fragment adopts a fully extended conformation. The quinoline ring system and the 1,2,4 triazole ring are not coplanar but inclined to one another by 65.24 (4)°.

3. Supramolecular features

In the crystal, weak C—H···O and C—H···N hydrogen bonds (Table 1, Fig. 2) link the molecules into a three dimensional supramolecular architecture. π–π stacking involving the quinoline rings is also observed, with the intercentroid distance being 3.6169 (6) Å.

4. Hirshfeld surface analysis

To understand the different interactions and contacts in the crystal structure, it is necessary to represent Hirshfeld surface (HS) and generate fingerprint plots which provide quantitative information for each intermolecular interaction. In order to highlight all intra- and intermolecular interactions, HS analyses were performed and fingerprint plots were drawn using *Crystal Explorer* (Wolff *et al.*, 2007). The three-dimensional Hirshfeld surface generated for the structure of the title crystal is presented in Fig. 3, which shows surfaces that have

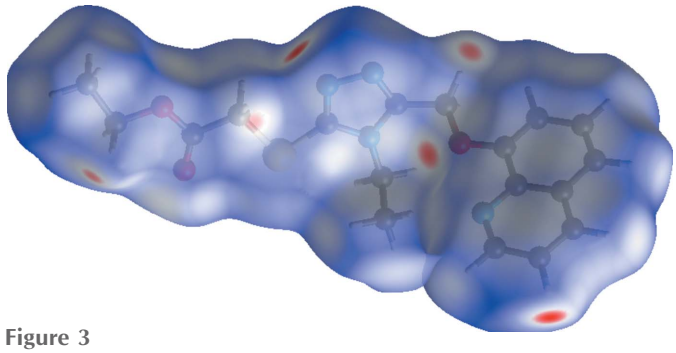


Figure 3
HS mapped over d_{norm}.

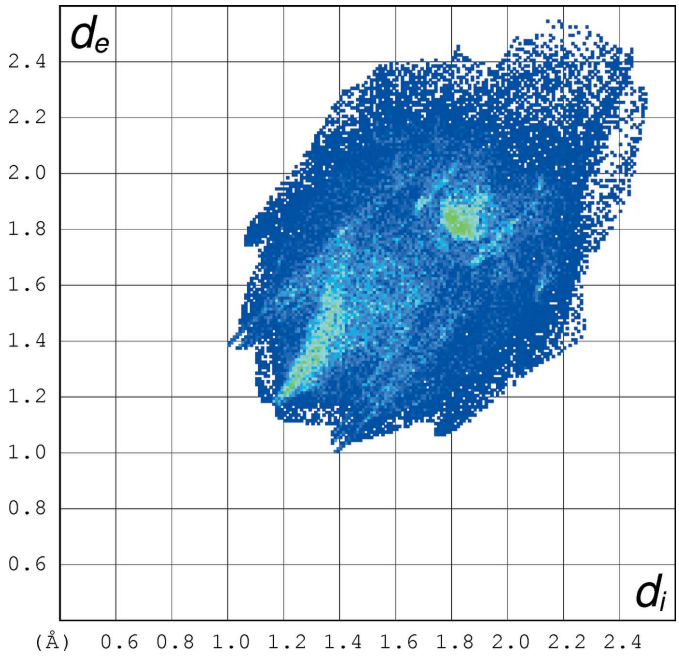


Figure 4
The two-dimensional fingerprint plot of the title molecule.

been mapped over a d_{norm} range of −0.191 to 1.247 Å. The large deep-red spots on the d_{norm} HS indicate the close-contact interactions, which are mainly responsible for significant hydrogen-bonding contacts. The 2D fingerprint plot is depicted in Fig. 4. This indicates that the most important contacts on the surface, which are necessary for organic molecules, are the H···H contacts with a percent contribution of 47.7% to the HS area of the title molecule.

5. Synthesis and crystallization

The synthesis of the title compound was performed according to the scheme in Fig. 5. Ethyl(quinoline-8-yloxy)acetate (2) was synthesized by condensation of 8-hydroxyquinoline (0.01 mol) (1) with ethyl bromoacetate (0.01 mol) in dry acetone for 12 h in the presence of anhydrous K_2CO_3. A mixture of compound (2) (0.01 mol) and hydrazine hydrate (0.02 mol) in ethanol was refluxed for 1 h. After cooling, the resulting solid was washed, dried and recrystallized from ethanol to afford 2-(quinolin-8-yloxy)acetohydrazide (3). Compound (3), on reaction with ethyl thiocyanate gave (quinolin-8-yloxy)-acetic acid *N*′-thiopropionyl-hydrazide (4).

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{18}H_{20}N_4O_3S$
M_r	372.44
Crystal system, space group	Monoclinic, $P2_1$
Temperature (K)	100
a, b, c (Å)	4.0880 (3), 21.2246 (15), 10.2037 (7)
β (°)	99.407 (3)
V (Å^3)	873.43 (11)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.21
Crystal size (mm)	0.55 × 0.10 × 0.09
Data collection	
Diffractometer	Nonius KappaCCD
Absorption correction	ψ scan (North *et al.*, 1968)
T_{min}, T_{max}	0.973, 0.981
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	75160, 14165, 12491
R_{int}	0.045
(sin $\theta/\lambda)_{max}$ (Å^{-1})	1.002
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.036, 0.094, 1.06
No. of reflections	14165
No. of parameters	237
No. of restraints	1
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.41, −0.25
Absolute structure	Flack x determined using 5451 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter	0.253 (3)

Computer programs: *KappaCCD* Nonius (Nonius, 1998), *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2006).

To a solution of compound (4) (0.01 mol) in absolute ethanol and (2 eq) of anhydrous CH_3COONa, ethyl bromoacetate (0.01 mol) was added. After refluxing for 12 h, the formed precipitate was filtered off and recrystallized from ethanol to give the title compound (5) with moderate yield (75%, m.p. 284 K). Single crystals of the title compound suitable for X-ray diffraction were obtained from ethanol solution.

IR (KBr, cm^{-1}): 2967(CH3), 1730 (C═O), 1618–1486 (C═C), 1429 (C═N), 1174 (N—N), 819 (C—S). ^{1}H NMR, ($CDCl_3$, 300 MHz) δ (p.p.m.) J (Hz): 1.12 (*t*, 3H, J = 7.20 Hz, OCH_2CH_3), 1.27 (*t*, 3H, J = 7.21 Hz, NCH_2CH_3), 4.00 (*s*, 2H, S—CH_2), 4.07 (*q*, 2H, J = 7.17 Hz, N—CH_2), 4.16 (*q*, 2H, J = 7.25 Hz, O—CH_2CH_3), 5.50 (*s*, 2H, O—CH_2), 7.28–7.34 (*m*, 4H, Ar—H), 7.03 (*dd*, 1H, J = 1.56 Hz, J = 8.26 Hz, Ar—H),

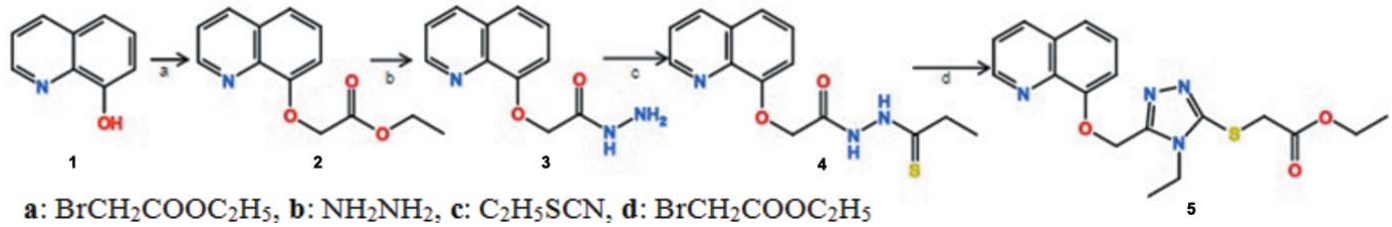


Figure 5
Chemical pathway showing the formation of the title compound.

8.81 (*dd*, 1H, J = 1.56 Hz, J = 4.13 Hz, Ar—H). ^{13}C NMR, ($CDCl_3$, 300 MHz) δ (p.p.m.): 14.03 (CH_3), 15.35(CH_3), 35.02(N—CH_2), 39.89 (S—CH_2), 61.41(O—CH_2), 62.09 (O—CH_2CH_3), 110.80, 121.08, 121.75, 126.72, 129.49, 136.02, 1140.15, 149.41, 150.75, 151.45, 153.04, 168.26 (C═O).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms in the title compound were placed in calculated positions (C—H = 0.96–1.08 Å) and allowed to ride on their parent atoms with U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms and 1.2U_{eq}(C) for other H atoms.

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Professor Dr Werner F. Kuhs and Dr S. Saouane from Georg-August-Universität Göttingen, GZG, Abt. Kristallographie (Germany) are gratefully acknowledged for the X-ray data collection.

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supporting information

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Computing details

Data collection: KappaCCD Nonius (Nonius, 1998); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015).

Ethyl 2-{[4-ethyl-5-(quinolin-8-yloxymethyl)-4*H*-1,2,4-triazol-3-yl]sulfanyl}acetate

Crystal data

$C_{18}H_{20}N_4O_3S$
$M_r = 372.44$
Monoclinic, $P2_1$
$a = 4.0880$ (3) Å
$b = 21.2246$ (15) Å
$c = 10.2037$ (7) Å
$\beta = 99.407$ (3)°
$V = 873.43$ (11) Å^3
$Z = 2$
$F(000) = 392$
$D_x = 1.416$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 100 reflections
$\theta = 2$–29°
$\mu = 0.21$ mm^{-1}
$T = 100$ K
Prism, yellow
0.55 × 0.10 × 0.09 mm

Data collection

Nonius KappaCCD diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.973$, $T_{max} = 0.981$
75160 measured reflections
14165 independent reflections
12491 reflections with $I > 2\sigma(I)$
$R_{int} = 0.045$
$\theta_{max} = 45.4°$, $\theta_{min} = 1.9°$
$h = -7\rightarrow7$
$k = -42\rightarrow42$
$l = -20\rightarrow20$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.094$
$S = 1.06$
14165 reflections
237 parameters
1 restraint
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0538P)^2 + 0.0281P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.41$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ e Å^{-3}
Absolute structure: Flack *x* determined using 5451 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: 0.253 (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_{iso}*/U_{eq}
N1	0.9172 (2)	0.02368 (4)	0.62203 (8)	0.01693 (13)
C1	1.0744 (3)	−0.03017 (5)	0.61284 (11)	0.02013 (16)
H1	1.1114	−0.0430	0.5272	0.024*
C2	1.1915 (3)	−0.07009 (5)	0.72130 (12)	0.02139 (17)
H2	1.3007	−0.1086	0.7084	0.026*
C3	1.1431 (3)	−0.05183 (5)	0.84577 (11)	0.01943 (16)
H3	1.2234	−0.0772	0.9209	0.023*
C4	0.9726 (2)	0.00508 (4)	0.86158 (9)	0.01551 (13)
C5	0.9089 (3)	0.02636 (5)	0.98684 (10)	0.01889 (15)
H5	0.9840	0.0024	1.0646	0.023*
C6	0.7390 (3)	0.08139 (5)	0.99544 (9)	0.01881 (15)
H6	0.6948	0.0950	1.0795	0.023*
C7	0.6280 (3)	0.11840 (5)	0.88129 (9)	0.01619 (13)
H7	0.5097	0.1564	0.8890	0.019*
C8	0.6921 (2)	0.09907 (4)	0.75895 (9)	0.01349 (12)
C9	0.8639 (2)	0.04117 (4)	0.74566 (9)	0.01360 (12)
O1	0.6071 (2)	0.13178 (3)	0.64335 (7)	0.01586 (11)
C10	0.4482 (2)	0.19139 (4)	0.65147 (9)	0.01451 (12)
H10A	0.5765	0.2178	0.7217	0.017*
H10B	0.2217	0.1856	0.6720	0.017*
C11	0.4356 (2)	0.22133 (4)	0.51895 (8)	0.01328 (12)
N4	0.26324 (19)	0.19754 (3)	0.40309 (7)	0.01236 (10)
C12	0.3301 (2)	0.23854 (4)	0.30789 (8)	0.01341 (12)
N3	0.5287 (2)	0.28427 (4)	0.36011 (8)	0.01678 (13)
N2	0.5964 (2)	0.27277 (4)	0.49637 (8)	0.01664 (12)
S1	0.17236 (6)	0.22776 (2)	0.13959 (2)	0.01548 (4)
C13	0.3319 (2)	0.30058 (4)	0.08308 (9)	0.01582 (13)
H13A	0.2351	0.3369	0.1241	0.019*
H13B	0.5758	0.3021	0.1094	0.019*
C14	0.2422 (2)	0.30408 (4)	−0.06611 (9)	0.01528 (13)
O2	0.0756 (3)	0.26564 (5)	−0.13459 (9)	0.02499 (16)
O3	0.3753 (2)	0.35520 (4)	−0.11198 (8)	0.02008 (13)
C15	0.3339 (3)	0.36198 (5)	−0.25619 (10)	0.01947 (16)
H15A	0.0978	0.3570	−0.2961	0.023*
H15B	0.4652	0.3296	−0.2945	0.023*
C16	0.4544 (3)	0.42708 (6)	−0.28335 (12)	0.02388 (19)
H16A	0.4462	0.4326	−0.3792	0.036*
H16B	0.6831	0.4324	−0.2379	0.036*
H16C	0.3122	0.4586	−0.2506	0.036*

C17	0.0521 (2)	0.14137 (4)	0.38461 (9)	0.01435 (12)
H17A	−0.1426	0.1503	0.3158	0.017*
H17B	−0.0302	0.1322	0.4687	0.017*
C18	0.2296 (3)	0.08330 (4)	0.34364 (10)	0.01737 (14)
H18A	0.0760	0.0475	0.3327	0.026*
H18B	0.4194	0.0734	0.4124	0.026*
H18C	0.3076	0.0916	0.2594	0.026*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0207 (3)	0.0149 (3)	0.0152 (3)	0.0034 (2)	0.0031 (2)	0.0000 (2)
C1	0.0242 (4)	0.0164 (4)	0.0196 (4)	0.0053 (3)	0.0030 (3)	−0.0012 (3)
C2	0.0238 (4)	0.0144 (4)	0.0248 (4)	0.0045 (3)	0.0007 (3)	0.0004 (3)
C3	0.0217 (4)	0.0139 (3)	0.0215 (4)	0.0020 (3)	0.0000 (3)	0.0033 (3)
C4	0.0176 (3)	0.0123 (3)	0.0157 (3)	−0.0008 (2)	0.0000 (2)	0.0022 (2)
C5	0.0236 (4)	0.0184 (4)	0.0140 (3)	−0.0005 (3)	0.0011 (3)	0.0033 (3)
C6	0.0238 (4)	0.0196 (4)	0.0131 (3)	−0.0006 (3)	0.0032 (3)	0.0011 (3)
C7	0.0203 (4)	0.0156 (3)	0.0129 (3)	0.0003 (3)	0.0035 (2)	−0.0001 (2)
C8	0.0161 (3)	0.0118 (3)	0.0125 (3)	0.0002 (2)	0.0022 (2)	0.0009 (2)
C9	0.0157 (3)	0.0113 (3)	0.0136 (3)	−0.0002 (2)	0.0015 (2)	0.0008 (2)
O1	0.0231 (3)	0.0119 (2)	0.0129 (2)	0.0043 (2)	0.0036 (2)	0.00195 (19)
C10	0.0182 (3)	0.0113 (3)	0.0142 (3)	0.0022 (2)	0.0029 (2)	0.0004 (2)
C11	0.0160 (3)	0.0102 (3)	0.0134 (3)	0.0002 (2)	0.0018 (2)	0.0003 (2)
N4	0.0143 (3)	0.0096 (2)	0.0132 (2)	−0.00051 (18)	0.00228 (19)	0.00067 (19)
C12	0.0161 (3)	0.0104 (3)	0.0136 (3)	−0.0003 (2)	0.0020 (2)	0.0013 (2)
N3	0.0229 (4)	0.0119 (3)	0.0148 (3)	−0.0035 (2)	0.0009 (2)	0.0014 (2)
N2	0.0221 (3)	0.0121 (3)	0.0150 (3)	−0.0029 (2)	0.0010 (2)	0.0005 (2)
S1	0.01887 (9)	0.01298 (8)	0.01402 (8)	−0.00283 (6)	0.00099 (6)	0.00105 (7)
C13	0.0207 (4)	0.0117 (3)	0.0144 (3)	−0.0014 (2)	0.0011 (2)	0.0015 (2)
C14	0.0183 (3)	0.0127 (3)	0.0147 (3)	−0.0004 (2)	0.0022 (2)	0.0008 (2)
O2	0.0335 (4)	0.0221 (4)	0.0177 (3)	−0.0115 (3)	−0.0007 (3)	−0.0001 (3)
O3	0.0313 (4)	0.0147 (3)	0.0141 (2)	−0.0057 (2)	0.0032 (2)	0.0012 (2)
C15	0.0256 (4)	0.0186 (4)	0.0142 (3)	−0.0015 (3)	0.0034 (3)	0.0018 (3)
C16	0.0293 (5)	0.0200 (4)	0.0235 (4)	0.0006 (3)	0.0078 (4)	0.0068 (4)
C17	0.0139 (3)	0.0121 (3)	0.0173 (3)	−0.0022 (2)	0.0032 (2)	−0.0002 (2)
C18	0.0204 (4)	0.0112 (3)	0.0206 (4)	−0.0017 (2)	0.0038 (3)	−0.0023 (3)

Geometric parameters (Å, º)

N1—C1	1.3222 (13)	N4—C12	1.3647 (11)
N1—C9	1.3662 (12)	N4—C17	1.4660 (11)
C1—C2	1.4137 (15)	C12—N3	1.3205 (12)
C1—H1	0.9500	C12—S1	1.7480 (9)
C2—C3	1.3728 (17)	N3—N2	1.3941 (12)
C2—H2	0.9500	S1—C13	1.8082 (10)
C3—C4	1.4168 (14)	C13—C14	1.5083 (13)
C3—H3	0.9500	C13—H13A	0.9900

C4—C9	1.4183 (12)	C13—H13B	0.9900
C4—C5	1.4192 (14)	C14—O2	1.2092 (13)
C5—C6	1.3691 (16)	C14—O3	1.3326 (12)
C5—H5	0.9500	O3—C15	1.4605 (12)
C6—C7	1.4166 (14)	C15—C16	1.5078 (16)
C6—H6	0.9500	C15—H15A	0.9900
C7—C8	1.3792 (12)	C15—H15B	0.9900
C7—H7	0.9500	C16—H16A	0.9800
C8—O1	1.3638 (11)	C16—H16B	0.9800
C8—C9	1.4328 (12)	C16—H16C	0.9800
O1—C10	1.4309 (11)	C17—C18	1.5232 (13)
C10—C11	1.4872 (12)	C17—H17A	0.9900
C10—H10A	0.9900	C17—H17B	0.9900
C10—H10B	0.9900	C18—H18A	0.9800
C11—N2	1.3142 (12)	C18—H18B	0.9800
C11—N4	1.3699 (11)	C18—H18C	0.9800

C1—N1—C9	116.95 (9)	N3—C12—N4	111.28 (8)
N1—C1—C2	124.67 (10)	N3—C12—S1	126.62 (7)
N1—C1—H1	117.7	N4—C12—S1	122.08 (7)
C2—C1—H1	117.7	C12—N3—N2	106.41 (7)
C3—C2—C1	118.26 (9)	C11—N2—N3	107.27 (8)
C3—C2—H2	120.9	C12—S1—C13	96.14 (4)
C1—C2—H2	120.9	C14—C13—S1	108.85 (6)
C2—C3—C4	119.60 (9)	C14—C13—H13A	109.9
C2—C3—H3	120.2	S1—C13—H13A	109.9
C4—C3—H3	120.2	C14—C13—H13B	109.9
C3—C4—C9	117.29 (9)	S1—C13—H13B	109.9
C3—C4—C5	122.68 (9)	H13A—C13—H13B	108.3
C9—C4—C5	120.03 (9)	O2—C14—O3	124.76 (9)
C6—C5—C4	119.93 (9)	O2—C14—C13	124.82 (9)
C6—C5—H5	120.0	O3—C14—C13	110.41 (8)
C4—C5—H5	120.0	C14—O3—C15	116.57 (8)
C5—C6—C7	121.20 (9)	O3—C15—C16	106.73 (9)
C5—C6—H6	119.4	O3—C15—H15A	110.4
C7—C6—H6	119.4	C16—C15—H15A	110.4
C8—C7—C6	119.76 (9)	O3—C15—H15B	110.4
C8—C7—H7	120.1	C16—C15—H15B	110.4
C6—C7—H7	120.1	H15A—C15—H15B	108.6
O1—C8—C7	124.90 (8)	C15—C16—H16A	109.5
O1—C8—C9	114.47 (7)	C15—C16—H16B	109.5
C7—C8—C9	120.63 (8)	H16A—C16—H16B	109.5
N1—C9—C4	123.21 (8)	C15—C16—H16C	109.5
N1—C9—C8	118.36 (8)	H16A—C16—H16C	109.5
C4—C9—C8	118.42 (8)	H16B—C16—H16C	109.5
C8—O1—C10	117.00 (7)	N4—C17—C18	113.36 (7)
O1—C10—C11	105.89 (7)	N4—C17—H17A	108.9
O1—C10—H10A	110.6	C18—C17—H17A	108.9

C11—C10—H10A	110.6	N4—C17—H17B	108.9
O1—C10—H10B	110.6	C18—C17—H17B	108.9
C11—C10—H10B	110.6	H17A—C17—H17B	107.7
H10A—C10—H10B	108.7	C17—C18—H18A	109.5
N2—C11—N4	110.87 (8)	C17—C18—H18B	109.5
N2—C11—C10	124.77 (8)	H18A—C18—H18B	109.5
N4—C11—C10	124.31 (8)	C17—C18—H18C	109.5
C12—N4—C11	104.16 (7)	H18A—C18—H18C	109.5
C12—N4—C17	127.54 (8)	H18B—C18—H18C	109.5
C11—N4—C17	128.29 (7)		

C9—N1—C1—C2	−0.45 (17)	O1—C10—C11—N4	63.40 (11)
N1—C1—C2—C3	−0.74 (19)	N2—C11—N4—C12	−0.21 (10)
C1—C2—C3—C4	1.42 (17)	C10—C11—N4—C12	−178.06 (8)
C2—C3—C4—C9	−0.95 (15)	N2—C11—N4—C17	−179.65 (8)
C2—C3—C4—C5	178.93 (11)	C10—C11—N4—C17	2.50 (14)
C3—C4—C5—C6	−179.14 (10)	C11—N4—C12—N3	0.06 (10)
C9—C4—C5—C6	0.74 (15)	C17—N4—C12—N3	179.50 (9)
C4—C5—C6—C7	−0.84 (16)	C11—N4—C12—S1	178.60 (7)
C5—C6—C7—C8	−0.22 (16)	C17—N4—C12—S1	−1.95 (13)
C6—C7—C8—O1	−177.76 (9)	N4—C12—N3—N2	0.10 (11)
C6—C7—C8—C9	1.37 (14)	S1—C12—N3—N2	−178.36 (7)
C1—N1—C9—C4	0.96 (15)	N4—C11—N2—N3	0.27 (11)
C1—N1—C9—C8	−179.58 (9)	C10—C11—N2—N3	178.12 (8)
C3—C4—C9—N1	−0.28 (14)	C12—N3—N2—C11	−0.22 (11)
C5—C4—C9—N1	179.84 (9)	N3—C12—S1—C13	−6.16 (10)
C3—C4—C9—C8	−179.73 (9)	N4—C12—S1—C13	175.53 (8)
C5—C4—C9—C8	0.38 (14)	C12—S1—C13—C14	178.01 (7)
O1—C8—C9—N1	−1.71 (12)	S1—C13—C14—O2	3.55 (14)
C7—C8—C9—N1	179.08 (9)	S1—C13—C14—O3	−175.82 (7)
O1—C8—C9—C4	177.77 (8)	O2—C14—O3—C15	−4.60 (16)
C7—C8—C9—C4	−1.44 (13)	C13—C14—O3—C15	174.77 (9)
C7—C8—O1—C10	1.90 (14)	C14—O3—C15—C16	171.18 (10)
C9—C8—O1—C10	−177.28 (8)	C12—N4—C17—C18	83.62 (11)
C8—O1—C10—C11	170.64 (8)	C11—N4—C17—C18	−97.06 (11)
O1—C10—C11—N2	−114.16 (10)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···N3^{i}	0.95	2.51	3.4444 (14)	167
C10—H10*A*···O2^{ii}	0.99	2.52	3.4637 (13)	159
C15—H15*B*···N2^{iii}	0.99	2.58	3.4636 (14)	148
C17—H17*B*···O1^{iv}	0.99	2.50	3.4481 (12)	161

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