

Crystal structure of 1-ethyl-3-(2-oxo-1,3-dithiol-4-yl)quinoxalin-2(1H)-one

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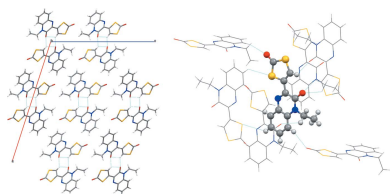
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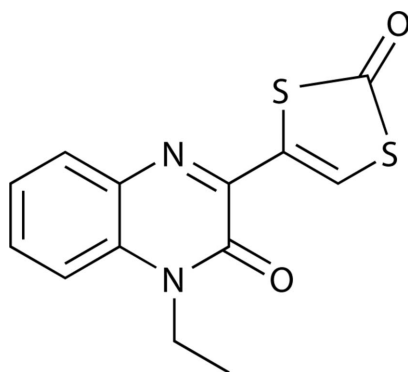
The title compound **I**, C₁₃H₁₀N₂O₂S₂, crystallizes in the monoclinic space group *C2/c* with eight molecules in the unit cell. Excluding for the ethyl substituent, the molecule of **I** adopts a nearly coplanar conformation (r.m.s. deviations is 0.058 Å), which is supported by the intramolecular C—H···O hydrogen-bonding interaction between the two ring systems [C···O = 2.859 (3) Å]. In the crystal, the molecules form dimeric associates *via* two bifurcated C—H···O hydrogen-bonding interactions between an ene hydrogen atom and a carbonyl functional group of an adjacent molecule [C···O = 3.133 (3) Å] and *vice versa*. The crystal structure is further stabilized by a three-dimensional network of weak hydrogen bonds between one molecule and six adjacent molecules as well as offset π – π stacking. The combination of the quinoxaline 2(1*H*)-one moiety with the dithiocarbonate moiety extends the aromaticity of the quinoxaline scaffold towards the substituent as well as influencing the π -system of the quinoxaline. The title compound is the direct precursor for a dithiolene ligand mimicking the natural cofactor ligand molybdopterin.

1. Chemical context

Non-innocent dithiolenes and their role as interesting ligand systems were discovered in the early 1960s. As a result of their unusual redox and structural characteristics and those of their metal complexes, they immediately attracted considerable scientific interest (Schrauzer & Mayweg, 1962). Initially, dithiolene systems were studied predominantly in the context of electronic and photonic conductors (Wudl *et al.*, 1972; Ferraris *et al.*, 1973). Later, metal dithiolene complexes found application in the purification and separation of olefins (Wang & Stiefel, 2001). In the early 1980s Rajagopalan and co-workers discovered and characterized the natural molybdopterin ligand (mpt) in the active sites of enzymes. Mpt is present in nearly all molybdenum enzymes and all tungsten enzymes and binds the respective central metal by a dithiolene moiety. As these enzymes are ubiquitous to all kingdoms of life, this brought dithiolene chemistry again to the focus of scientific attention (Johnson *et al.*, 1980; Johnson & Rajagopalan, 1982; Kramer *et al.*, 1987). Quinoxaline constitutes a widely exploited platform in the development of pharmaceuticals (Shi *et al.*, 2018). The title compound is a dithiolene ligand precursor, which can be used for the synthesis of molybdopterin cofactor model complexes bearing quinoxaline substituents. The target dithiolene ligand replicates the pyrazine moiety of mpt in its half-reduced form and in addition contains an oxofunction in the position of the pyran ring of the natural product. By itself it is an interesting example of an



extended π -system involving (by resonance) three different heteroatoms (N, O and S).



2. Structural commentary

The title molecule **I** crystallizes in the monoclinic space group $C2/c$ with $Z = 8$. The quinoxaline ring system [C4–C11, N1, N2; largest deviation from plane = 0.041 (2) Å for C5] and the dithiolene ring [C1–C3, S1, S2; largest deviation from plane = 0.012 (1) Å for C3], which are connected by the C3–C4 bond [length = 1.465 (3) Å], are essentially coplanar, with an angle of only 4.89 (12)° between the two planes (Fig. 1). This planarity is supported by intramolecular hydrogen bonding between the dithiolene hydrogen atom and the quinoxaline carbonyl oxygen atom [C2–H2...O2 with $D\cdots A = 2.859$ (3) Å; Table 1]. Only the alkyl substituent C12–C13 subtends out of the planar geometry with an N1–C12–C13 torsion angle of 112.78 (18)°. While the N1–C12 bond [amine nitrogen and ethyl substituent; 1.475 (3) Å] is of explicit single-bond character, all other N–C distances are decidedly shorter, ranging from 1.296 (3) Å for the, according to the chemical structure, double bond of imine nitrogen (N2=C4) to 1.392 (3) Å for the amine nitrogen-to-benzene ring formal single bond (N1–C6). The longest C–C bond of the benzene ring is the one that is shared with the N-heterocycle [C6–C11, 1.411 (3) Å]. This, together with the adjacent N–C bonds [N1–C6, 1.392 (3) Å and C11–N2, 1.374 (3) Å] being significantly shorter than single bonds indicates resonance throughout the entire quinoxaline substituent. The C=O bond [1.212 (3) Å] of the carbonodithioate moiety is slightly shorter than the carbonyl C=O bond [1.232 (3) Å] of the quinoxaline substituent, suggesting that the latter might be involved to a small extent in resonance effects of the π -system, whereas the former is not. The C2=C3 double bond of the ene-dithiocarbonate moiety is at 1.341 (3) Å slightly longer than the average value for C=C double bonds of 1.331 (9) Å (Allen *et al.*, 1995), which again may be due to participation in resonance effects throughout the entire molecule. The deviation from the average value of 1.751 (17) Å for S–C sp^2 bonds (Allen *et al.*, 1995) of the S1–C2 bond [1.724 (2) Å] is substantial enough to suggest that the resonance effects extend up to this bond to which partial double-bond character can be assigned. All other C–S bonds concur with typical single bonds.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C2–H2...O2	0.95 (2)	2.30 (3)	2.859 (3)	117.2 (19)
C2–H2...O2 ⁱ	0.95 (2)	2.44 (2)	3.133 (3)	129 (2)
C7–H7...O1 ⁱⁱ	0.95	2.51	3.272 (3)	138
C9–H9...S2 ⁱⁱⁱ	0.95	2.99	3.652 (3)	128
C12–H12A...O2 ^{iv}	0.99	2.69	3.367 (3)	126

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

By bidirectional intermolecular hydrogen bonding, the title compound crystallizes as dimeric associate with the same donor and acceptor roles for both monomers [C2–H2...O2($-x, -y + 2, -z + 1$) and O2...H2–C2($-x, -y + 2, -z + 1$); $D\cdots A = 3.133$ (3) Å]. Here, the exact same atoms are involved as in the intramolecular hydrogen bond mentioned above. The respective hydrogen atom H2 is therefore bound to the ene carbon atom C2 and hydrogen bonded to the carbonyl oxygen (O2) of the quinoxaline moiety of the same molecule as well as that of the adjacent molecule (Fig. 2, left). There are only two crystal structures of very closely related systems reported in the literature. In one (A), the quinoxalin substituent of the present molecule is replaced by a coumarine (Ghosh *et al.*, 2016). In the other (B), the ene-dithiocarbonate is replaced by an aminothiazole (Mamedov *et al.*, 2005). The metrical parameters in both structures are, as far as comparable, very similar to the ones observed here. Notable differences comprise (i) a slightly stronger resonance involvement

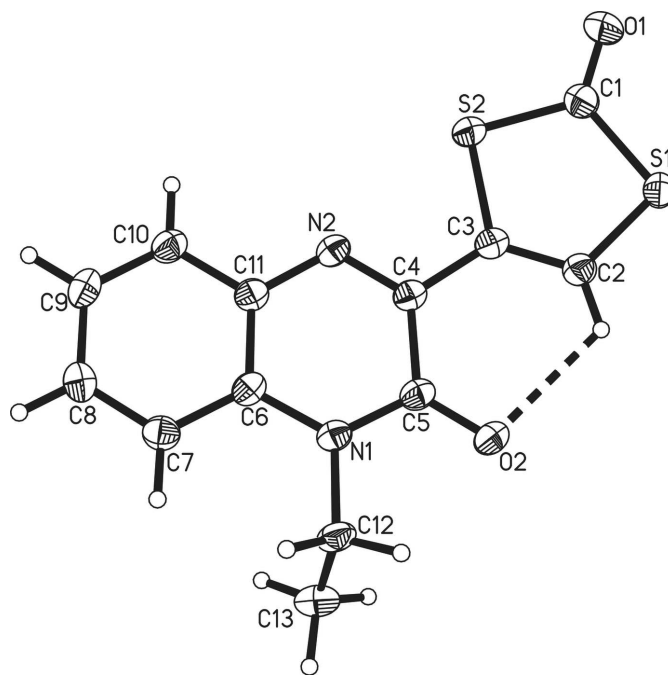


Figure 1
The molecular structure of 1-ethyl-3-(2-oxo-1,3-dithiol-4-yl)quinoxalin-2(1H)-one showing the atom labelling, 50% probability displacement ellipsoids and the intramolecular non-classical hydrogen bond (dashed line).

of the thiazole in *B* compared to the ene-dithiocarbonate while the quinoxalin carbonyl and amine functions are embraced to a lesser extent and (ii) an overall weaker resonance in *A*, in which the benzene ring C—C distances are all very similar (*i.e.* strongly resonant) whereas all other distances are of more pronounced single- and double-bond character and of less aromatic character.

3. Supramolecular features

In the crystal, the associated dimers are linked by (partly rather weak) C—H \cdots O and C—H \cdots S hydrogen-bonding interactions, forming a three-dimensional network (Fig. 2, Table 1). In the three-dimensional network, each molecule forms hydrogen-bonding interactions to six surrounding molecules. These are donor interactions involving C2 [C2—H2 \cdots O2($-x, -y + 2, -z + 1$); $D\cdots A = 3.133(3)$ Å], C7 [C7—H7 \cdots O1($x, -y + 1, z + \frac{1}{2}$); $D\cdots A = 3.272(3)$ Å], C9 [C9—H9 \cdots S2($-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$); $D\cdots A = 3.652(3)$ Å], C12 [C12—H12A \cdots O2($x, y - 1, z$); $D\cdots A = 3.367(3)$ Å] and acceptor interactions involving S2 [S2 \cdots H9—C9($-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$)], O2 [O2 \cdots H2—C2($-x, -y + 2, -z + 1$)], O2 \cdots H12A—C12($x, y - 1, z$)] and O1 [O1 \cdots H7—C7($x, -y + 1, z - \frac{1}{2}$)]. Even though there are coplanar alignments of layers, only offset π - π stacking was observed with centroid-centroid distances of 3.587(3) Å between the benzene ring of one molecule and the pyrazine ring of a molecule in the layer above or below.

4. Synthesis and crystallization

The title compound, 1-ethyl-3-(2-oxo-1,3-dithiol-4yl)-quinoxalin-2(1*H*)-one was synthesized based on a reported literature procedure (Mamedov *et al.*, 2005). The compound was synthesized in five steps starting from *o*-phenylenediamine. The last step in the synthetic pathway was carried out *via* an acid-catalysed Tchugaev ring closure reaction, which led to the formation of the dithiolene ring.

Synthesis of 1-ethyl-3-(2-oxo-1,3-dithiol-4yl)-quinoxalin-2(1*H*)-one: To a solution of *S*-2-(4-ethyl-3-oxo-4-dihydroquinoxalin-2-yl)-2-oxo-ethyl *o*-isopropyl carbonodithioate (11.180 g, 31.9 mmol) in 250 ml DCM/Et₂O 1:1 at ambient temperature, H₂SO₄ (25.50 ml) was added. The reaction mixture was stirred at room temperature for 2h. After that, the reaction was quenched by addition of 250 ml of ice and the mixture was stirred for 30 min. The organic phase was washed with brine and water 3 \times 250 ml. The solvent was reduced to 10 ml *in vacuo* and the greenish precipitate was filtered off and washed on the filter with cold acetone 3 \times 50 ml. The title compound was obtained as a greenish-white powder. Single crystals suitable for X-ray analysis were obtained by slow diffusion of solvents with chloroform and Et₂O Yield: 1.85g (20%).

¹H NMR (300MHz, CD₃Cl) δ 8.79 ppm (*s*, 1H), 7.87 ppm (*m*, 1H), 7.61 ppm (*m*, 1H), 7.4 ppm (*m*, 1H), 4.39 ppm (*q*, $J = 7.2$ Hz, 2H), 1.42 ppm (*t*, $J = 7.3$ Hz, 3H). ¹³C NMR (300MHz, CD₃Cl) δ 152.54 ppm, 144.75 ppm, 133.25 ppm, 132.58 ppm, 131.14 ppm, 130.32 ppm, 126.98 ppm, 124.00 ppm, 113.47 ppm, 37.47 ppm, 12.20 ppm. IR (KBr pellet): (ν cm⁻¹) = 3495 (*br*),

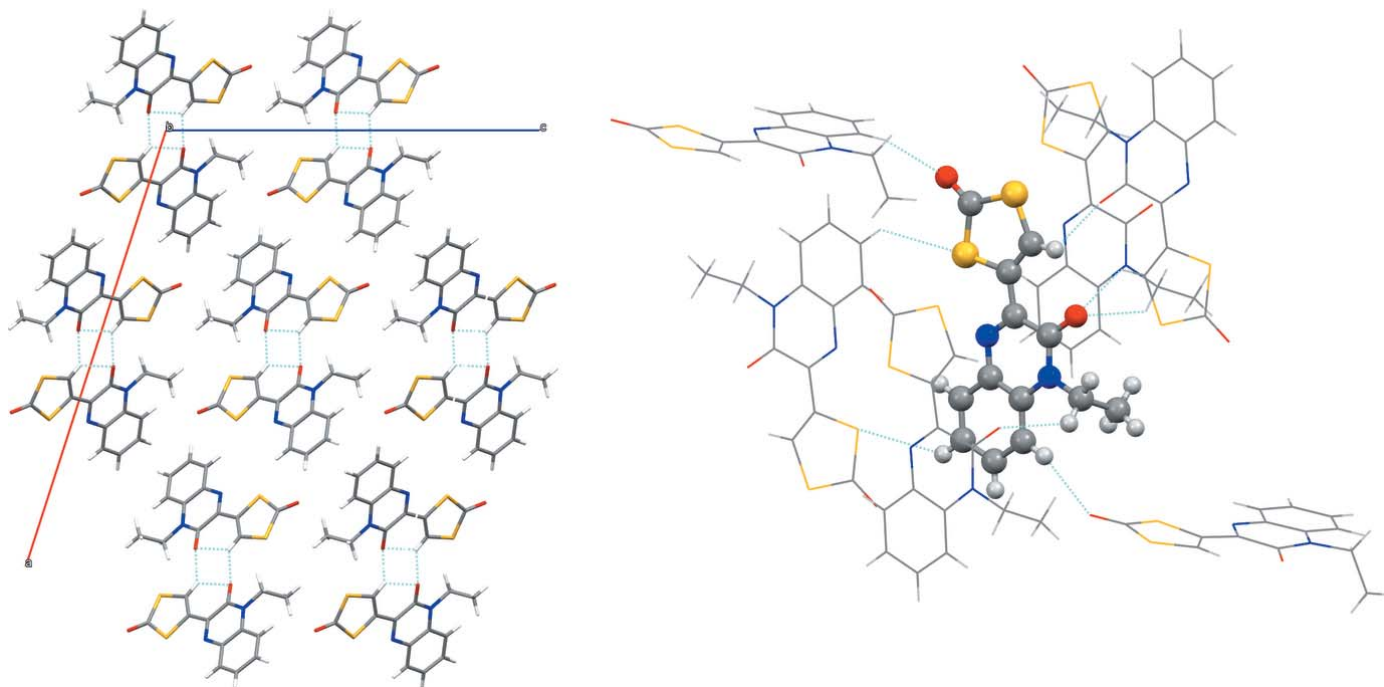


Figure 2

Crystal packing and intra- and intermolecular hydrogen-bonding interactions yielding the dimeric associates viewed along *b* (left) and hydrogen bonding contacts of an individual molecule to six adjacent molecules (right) (Mercury; Macrae *et al.*, 2006).

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₁₃ H ₁₀ N ₂ O ₂ S ₂
<i>M_r</i>	290.35
Crystal system, space group	Monoclinic, C2/c
Temperature (K)	170
<i>a</i> , <i>b</i> , <i>c</i> (Å)	25.531 (6), 4.8522 (10), 20.861 (4)
β (°)	107.81 (3)
<i>V</i> (Å ³)	2460.4 (10)
<i>Z</i>	8
Radiation type	Mo Kα
μ (mm ⁻¹)	0.43
Crystal size (mm)	0.48 × 0.46 × 0.04
Data collection	
Diffractometer	Stoe IPDS 2T
Absorption correction	Numerical (<i>X-RED32</i> and <i>X-SHAPE</i> ; Stoe & Cie, 2010)
<i>T_{min}</i> , <i>T_{max}</i>	0.680, 0.887
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	10078, 2599, 2052
<i>R_{int}</i>	0.107
(sin θ/λ) _{max} (Å ⁻¹)	0.633
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.043, 0.113, 1.03
No. of reflections	2599
No. of parameters	177
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.39, -0.44

Computer programs: *X-AREA* (Stoe & Cie, 2010), *SIR92* (Altomare *et al.*, 1994), *SHELXL2016/6* (Sheldrick, 2015), *XP* in *SHELXTL* (Sheldrick, 2008), *Mercury* (Macrae *et al.*, 2006) and *CIFTAB* (Sheldrick, 2013).

1734 (*w*), 1646 (*sst*), 1601 (*st*), 1579 (*st*), 1535 (*st*), 1463 (*st*), 1383 (*w*), 1280 (*st*), 1248 (*w*), 1216 (*w*), 1173 (*st*), 1128 (*w*), 1087 (*w*), 1045 (*w*), 950 (*w*), 892 (*st*), 868 (*w*), 825 (*st*), 785 (*w*), 758 (*st*), 631 (*w*), 554 (*w*), 529 (*w*), 467 (*w*), 432 (*w*). APCI-MS (*m/s*) = 291 (*M*⁺ + *H*⁺). Analysis calculated for C₁₃H₁₀N₂O₂S₂: C, 53.78; H 3.47; N 9.65; S 22.09. Found: C, 53.41; H 3.25; N 9.86; S 22.32.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The hydrogen atom of the dithiolene unit (H2) was refined freely without any constraints or restraints. All other C-bound hydrogen atoms were attached in calculated positions and treated as riding: C—H =

0.98 Å with *U*_{iso}(H) = 1.5*U*_{eq}(C) for the methyl group, C—H = 0.99 Å with *U*_{iso}(H) = 1.2*U*_{eq}(C) for the methylene group and C—H = 0.95 Å with *U*_{iso}(H) = 1.2*U*_{eq}(C) for the aromatic atoms.

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Crystal structure of 1-ethyl-3-(2-oxo-1,3-dithiol-4-yl)quinoxalin-2(1H)-one

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Computing details

Data collection: *X-AREA* (Stoe & Cie, 2010); cell refinement: *X-AREA* (Stoe & Cie, 2010); data reduction: *X-AREA* (Stoe & Cie, 2010); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL2016/6* (Sheldrick, 2015); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *CIFTAB* (Sheldrick, 2013) and *Mercury* (Macrae *et al.*, 2006).

1-Ethyl-3-(2-oxo-1,3-dithiol-4-yl)quinoxalin-2(1H)-one

Crystal data

$C_{13}H_{10}N_2O_2S_2$

$M_r = 290.35$

Monoclinic, *C2/c*

$a = 25.531$ (6) Å

$b = 4.8522$ (10) Å

$c = 20.861$ (4) Å

$\beta = 107.81$ (3)°

$V = 2460.4$ (10) Å³

$Z = 8$

$F(000) = 1200$

$D_x = 1.568$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 10798 reflections

$\theta = 3.4$ – 53.5 °

$\mu = 0.43$ mm⁻¹

$T = 170$ K

Platelet, green

$0.48 \times 0.46 \times 0.04$ mm

Data collection

Stoe IPDS2T

diffractometer

Radiation source: fine-focus sealed tube

Detector resolution: 6.67 pixels mm⁻¹

ω scans

Absorption correction: numerical

(X-Red32 and X-Shape; Stoe & Cie, 2010)

$T_{\min} = 0.680$, $T_{\max} = 0.887$

10078 measured reflections

2599 independent reflections

2052 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.107$

$\theta_{\max} = 26.7$ °, $\theta_{\min} = 1.7$ °

$h = -32$ → 32

$k = -6$ → 6

$l = -26$ → 23

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.043$

$wR(F^2) = 0.113$

$S = 1.03$

2599 reflections

177 parameters

0 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent

and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0557P)^2 + 1.3022P]$

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

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

$\Delta\rho_{\max} = 0.39$ e Å⁻³

$\Delta\rho_{\min} = -0.44$ 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.06586 (2)	1.17332 (13)	0.38431 (3)	0.02924 (17)
S2	0.16189 (2)	0.80790 (12)	0.43550 (3)	0.02882 (17)
O1	0.14629 (7)	1.1274 (4)	0.32955 (8)	0.0379 (4)
O2	0.04198 (6)	0.7134 (3)	0.56260 (8)	0.0296 (4)
N1	0.09576 (7)	0.3591 (4)	0.61708 (9)	0.0233 (4)
N2	0.16734 (7)	0.4593 (4)	0.54239 (9)	0.0242 (4)
C1	0.12850 (9)	1.0512 (5)	0.37418 (11)	0.0290 (5)
C2	0.06873 (9)	0.9742 (5)	0.45374 (11)	0.0258 (5)
C3	0.11163 (9)	0.8032 (5)	0.47709 (11)	0.0237 (4)
C4	0.12261 (8)	0.6022 (5)	0.53199 (10)	0.0229 (4)
C5	0.08324 (8)	0.5692 (5)	0.57104 (10)	0.0236 (4)
C6	0.14444 (8)	0.2091 (5)	0.63101 (11)	0.0231 (4)
C7	0.15922 (9)	0.0081 (5)	0.68143 (11)	0.0263 (5)
H7	0.135972	-0.028724	0.708326	0.032*
C8	0.20757 (9)	-0.1364 (5)	0.69197 (11)	0.0278 (5)
H8	0.217320	-0.273223	0.726147	0.033*
C9	0.24248 (9)	-0.0852 (5)	0.65328 (12)	0.0296 (5)
H9	0.275622	-0.187017	0.661099	0.036*
C10	0.22885 (9)	0.1124 (5)	0.60399 (11)	0.0273 (5)
H10	0.252595	0.147249	0.577626	0.033*
C11	0.17997 (9)	0.2633 (5)	0.59235 (11)	0.0237 (4)
C12	0.05590 (9)	0.2972 (5)	0.65349 (12)	0.0269 (5)
H12A	0.054369	0.095209	0.659446	0.032*
H12B	0.018905	0.359079	0.625995	0.032*
C13	0.07039 (10)	0.4352 (6)	0.72202 (12)	0.0353 (6)
H13A	0.108738	0.394349	0.747326	0.053*
H13B	0.046176	0.365385	0.746832	0.053*
H13C	0.065600	0.634974	0.716145	0.053*
H2	0.0387 (10)	0.987 (5)	0.4716 (12)	0.028 (6)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0263 (3)	0.0320 (3)	0.0296 (3)	0.0039 (2)	0.0086 (2)	0.0057 (2)
S2	0.0273 (3)	0.0336 (3)	0.0300 (3)	0.0057 (2)	0.0152 (2)	0.0046 (2)
O1	0.0404 (9)	0.0485 (11)	0.0299 (9)	0.0037 (8)	0.0181 (7)	0.0084 (8)
O2	0.0251 (8)	0.0323 (9)	0.0348 (9)	0.0061 (7)	0.0143 (6)	0.0034 (7)
N1	0.0206 (8)	0.0250 (9)	0.0262 (9)	-0.0011 (7)	0.0099 (7)	-0.0010 (8)
N2	0.0206 (8)	0.0252 (9)	0.0282 (9)	0.0001 (7)	0.0096 (7)	-0.0013 (8)

C1	0.0287 (11)	0.0313 (12)	0.0272 (11)	0.0004 (10)	0.0089 (9)	0.0011 (10)
C2	0.0228 (10)	0.0296 (12)	0.0260 (10)	-0.0002 (9)	0.0087 (8)	0.0003 (10)
C3	0.0221 (10)	0.0253 (11)	0.0245 (10)	-0.0006 (8)	0.0085 (8)	-0.0029 (9)
C4	0.0220 (10)	0.0239 (10)	0.0237 (10)	-0.0003 (8)	0.0083 (8)	-0.0029 (9)
C5	0.0202 (10)	0.0262 (11)	0.0251 (10)	-0.0015 (9)	0.0081 (8)	-0.0037 (9)
C6	0.0200 (10)	0.0228 (10)	0.0260 (10)	-0.0005 (8)	0.0065 (8)	-0.0038 (9)
C7	0.0268 (10)	0.0262 (11)	0.0269 (11)	-0.0030 (9)	0.0096 (8)	-0.0009 (9)
C8	0.0293 (11)	0.0238 (11)	0.0277 (11)	0.0007 (9)	0.0048 (9)	0.0018 (9)
C9	0.0255 (11)	0.0278 (12)	0.0340 (12)	0.0065 (9)	0.0067 (9)	-0.0016 (10)
C10	0.0223 (10)	0.0315 (12)	0.0287 (11)	0.0016 (9)	0.0088 (8)	-0.0022 (10)
C11	0.0226 (10)	0.0243 (10)	0.0247 (10)	-0.0009 (8)	0.0077 (8)	-0.0021 (9)
C12	0.0226 (10)	0.0282 (11)	0.0357 (12)	-0.0010 (9)	0.0173 (9)	0.0010 (10)
C13	0.0362 (12)	0.0401 (14)	0.0366 (13)	-0.0039 (11)	0.0215 (10)	-0.0032 (11)

Geometric parameters (Å, °)

S1—C2	1.724 (2)	C6—C11	1.411 (3)
S1—C1	1.778 (2)	C7—C8	1.378 (3)
S2—C3	1.755 (2)	C7—H7	0.9500
S2—C1	1.758 (2)	C8—C9	1.395 (3)
O1—C1	1.212 (3)	C8—H8	0.9500
O2—C5	1.232 (3)	C9—C10	1.371 (3)
N1—C5	1.370 (3)	C9—H9	0.9500
N1—C6	1.392 (3)	C10—C11	1.403 (3)
N1—C12	1.475 (3)	C10—H10	0.9500
N2—C4	1.296 (3)	C12—C13	1.519 (3)
N2—C11	1.374 (3)	C12—H12A	0.9900
C2—C3	1.341 (3)	C12—H12B	0.9900
C2—H2	0.95 (2)	C13—H13A	0.9800
C3—C4	1.465 (3)	C13—H13B	0.9800
C4—C5	1.483 (3)	C13—H13C	0.9800
C6—C7	1.399 (3)		
C2—S1—C1	96.00 (11)	C6—C7—H7	120.1
C3—S2—C1	95.93 (11)	C7—C8—C9	121.1 (2)
C5—N1—C6	122.51 (18)	C7—C8—H8	119.4
C5—N1—C12	117.57 (17)	C9—C8—H8	119.4
C6—N1—C12	119.91 (18)	C10—C9—C8	119.9 (2)
C4—N2—C11	119.18 (18)	C10—C9—H9	120.1
O1—C1—S2	123.50 (19)	C8—C9—H9	120.1
O1—C1—S1	123.48 (19)	C9—C10—C11	120.2 (2)
S2—C1—S1	113.02 (13)	C9—C10—H10	119.9
C3—C2—S1	118.16 (17)	C11—C10—H10	119.9
C3—C2—H2	124.3 (15)	N2—C11—C10	118.85 (19)
S1—C2—H2	117.4 (15)	N2—C11—C6	121.32 (19)
C2—C3—C4	129.5 (2)	C10—C11—C6	119.8 (2)
C2—C3—S2	116.86 (17)	N1—C12—C13	112.79 (18)
C4—C3—S2	113.64 (15)	N1—C12—H12A	109.0

N2—C4—C3	115.80 (19)	C13—C12—H12A	109.0
N2—C4—C5	124.1 (2)	N1—C12—H12B	109.0
C3—C4—C5	120.11 (19)	C13—C12—H12B	109.0
O2—C5—N1	121.94 (19)	H12A—C12—H12B	107.8
O2—C5—C4	123.6 (2)	C12—C13—H13A	109.5
N1—C5—C4	114.42 (18)	C12—C13—H13B	109.5
N1—C6—C7	122.65 (19)	H13A—C13—H13B	109.5
N1—C6—C11	118.2 (2)	C12—C13—H13C	109.5
C7—C6—C11	119.16 (19)	H13A—C13—H13C	109.5
C8—C7—C6	119.8 (2)	H13B—C13—H13C	109.5
C8—C7—H7	120.1		
C3—S2—C1—O1	-178.3 (2)	N2—C4—C5—N1	-4.3 (3)
C3—S2—C1—S1	1.57 (15)	C3—C4—C5—N1	174.71 (18)
C2—S1—C1—O1	179.1 (2)	C5—N1—C6—C7	175.2 (2)
C2—S1—C1—S2	-0.82 (15)	C12—N1—C6—C7	-3.6 (3)
C1—S1—C2—C3	-0.6 (2)	C5—N1—C6—C11	-4.9 (3)
S1—C2—C3—C4	-176.09 (18)	C12—N1—C6—C11	176.29 (19)
S1—C2—C3—S2	1.9 (3)	N1—C6—C7—C8	178.9 (2)
C1—S2—C3—C2	-2.1 (2)	C11—C6—C7—C8	-0.9 (3)
C1—S2—C3—C4	176.21 (16)	C6—C7—C8—C9	0.3 (3)
C11—N2—C4—C3	-178.92 (19)	C7—C8—C9—C10	0.2 (4)
C11—N2—C4—C5	0.1 (3)	C8—C9—C10—C11	0.0 (3)
C2—C3—C4—N2	178.4 (2)	C4—N2—C11—C10	-179.0 (2)
S2—C3—C4—N2	0.4 (3)	C4—N2—C11—C6	1.9 (3)
C2—C3—C4—C5	-0.7 (4)	C9—C10—C11—N2	-179.8 (2)
S2—C3—C4—C5	-178.67 (16)	C9—C10—C11—C6	-0.7 (3)
C6—N1—C5—O2	-174.7 (2)	N1—C6—C11—N2	0.3 (3)
C12—N1—C5—O2	4.1 (3)	C7—C6—C11—N2	-179.8 (2)
C6—N1—C5—C4	6.6 (3)	N1—C6—C11—C10	-178.7 (2)
C12—N1—C5—C4	-174.59 (18)	C7—C6—C11—C10	1.2 (3)
N2—C4—C5—O2	177.0 (2)	C5—N1—C12—C13	-96.3 (2)
C3—C4—C5—O2	-4.0 (3)	C6—N1—C12—C13	82.5 (3)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C2—H2 \cdots O2	0.95 (2)	2.30 (3)	2.859 (3)	117.2 (19)
C2—H2 \cdots O2 ⁱ	0.95 (2)	2.44 (2)	3.133 (3)	129 (2)
C7—H7 \cdots O1 ⁱⁱ	0.95	2.51	3.272 (3)	138
C9—H9 \cdots S2 ⁱⁱⁱ	0.95	2.99	3.652 (3)	128
C12—H12A \cdots O2 ^{iv}	0.99	2.69	3.367 (3)	126

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