

# Diethyl 2-[[[(5-oxo-5H-thiochromeno-[2,3-b]pyridin-7-yl)amino]methylidene]-propanedioate

Muhammad Naeem Khan,<sup>a,b</sup> M. Nawaz Tahir,<sup>c\*</sup> Misbahul Ain Khan,<sup>a</sup> Munawar Ali Munawar<sup>d</sup> and Abdul Qayyum Ather<sup>b</sup>

<sup>a</sup>Department of Chemistry, Islamia University, Bahawalpur, Pakistan, <sup>b</sup>Applied Chemistry Research Center, PCSIR Laboratories complex, Lahore 54600, Pakistan, <sup>c</sup>University of Sargodha, Department of Physics, Sargodha, Pakistan, and <sup>d</sup>Institute of Chemistry, University of the Punjab, Lahore, Pakistan  
Correspondence e-mail: dmntahir\_uos@yahoo.com

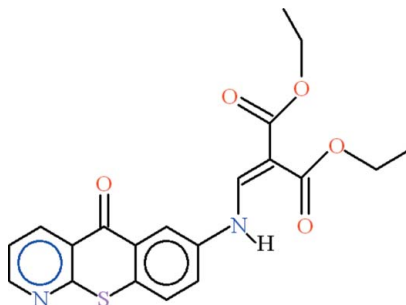
Received 17 April 2011; accepted 29 April 2011

Key indicators: single-crystal X-ray study;  $T = 296$  K; mean  $\sigma(\text{C}-\text{C}) = 0.005$  Å; disorder in main residue;  $R$  factor = 0.054;  $wR$  factor = 0.130; data-to-parameter ratio = 12.3.

In the title compound,  $\text{C}_{15}\text{H}_{14}\text{O}_5\text{S}$ , the three fused rings are roughly coplanar, the largest deviation from the mean plane being 0.1285 (13) Å for the S atom. An intramolecular  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bond generates an  $S_6$  ring. In the crystal, intermolecular  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds form  $R_2^2(14)$ ,  $R_2^2(13)$  and  $R_3^2(17)$  ring motifs, building a layer parallel to (100).

## Related literature

For related structures, see: Khan *et al.* (2008a,b); Lokaj *et al.* (1994); Lynch & McClenaghan (2003); For graph-set notation, see: Etter *et al.* (1990); Bernstein *et al.* (1995).



## Experimental

### Crystal data

$\text{C}_{20}\text{H}_{18}\text{N}_2\text{O}_5\text{S}$   
 $M_r = 398.42$   
Monoclinic,  $C2/c$   
 $a = 13.8013$  (7) Å

$b = 7.5180$  (3) Å  
 $c = 36.2743$  (15) Å  
 $\beta = 94.330$  (3)°  
 $V = 3753.0$  (3) Å<sup>3</sup>

$Z = 8$   
Mo  $K\alpha$  radiation  
 $\mu = 0.21$  mm<sup>-1</sup>

$T = 296$  K  
 $0.35 \times 0.18 \times 0.15$  mm

### Data collection

Bruker Kappa APEXII CCD diffractometer  
Absorption correction: multi-scan (SADABS; Bruker, 2005)  
 $T_{\min} = 0.968$ ,  $T_{\max} = 0.985$

13274 measured reflections  
3314 independent reflections  
1776 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.077$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.054$   
 $wR(F^2) = 0.130$   
 $S = 0.97$   
3314 reflections  
269 parameters

10 restraints  
H-atom parameters constrained  
 $\Delta\rho_{\max} = 0.20$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.18$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N2}-\text{H2}\cdots\text{O3}$	0.86	2.06	2.683 (3)	129
$\text{C11}-\text{H11}\cdots\text{O5}^i$	0.93	2.49	3.403 (4)	167
$\text{C12}-\text{H12}\cdots\text{O1}^i$	0.93	2.45	3.322 (4)	157
$\text{C17A}-\text{H17C}\cdots\text{O3}^{ii}$	0.96	2.58	3.516 (8)	165
$\text{C19A}-\text{H19B}\cdots\text{O3}^{iii}$	0.97	2.47	3.231 (11)	135

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

Data collection: APEX2 (Bruker, 2009); cell refinement: SAINT (Bruker, 2009); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEPIII (Burnett & Johnson, 1996), ORTEP-3 for Windows (Farrugia, 1997) and PLATON (Spek, 2009); software used to prepare material for publication: SHELXL97.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2678).

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**supplementary materials**

*Acta Cryst.* (2011). E67, o1348 [ doi:10.1107/S1600536811016291 ]

## Diethyl 2- $\{[(5\text{-oxo-}5H\text{-thiochromeno}[2,3\text{-}b]\text{pyridin-}7\text{-yl)amino]methylidene\}$ propanedioate

M. N. Khan, M. N. Tahir, M. A. Khan, M. A. Munawar and A. Q. Ather

### Comment

We reported the crystal structures of (II) *i.e.* 7-nitro-5*H*-thiochromeno[2,3-*b*]pyridin-5-one (Khan *et al.*, 2008*a*) and (III) *i.e.* 5*H*-thiochromeno[2,3-*b*]pyridin-5-one (Khan *et al.*, 2008*b*). The title compound (Fig. 1) is in continuation of our work to synthesize the derivatives of 5*H*-thiochromeno[2,3-*b*]pyridin-5-one. The crystal structures of (IV) *i.e.*, diethyl 2-(2,3-diphenylquinoxalin-6-ylaminomethylene)malonate (Lokaj *et al.*, 1994) and (V) *i.e.*, diethyl (4-*tert*-butyl-1,3-thiazol-2-ylaminomethylene)malonate (Lynch & McClenaghan, 2003) have been published. Both contain the diethyl (aminomethylidene)propanedioate moiety which is also present in (I).

In (I), the central heterocyclic ring A (C1/C2/C6/S1/C7/C8), the pyridinic group B (C2/C3/C4/C5/N1/C6) and benzene ring C (C7—C12) are planar with r. m. s. deviation of 0.0388, 0.0053 and 0.0049 Å, respectively. The carbonyl O-atom is at a distance of 0.1532 (35) Å from its parent ring A. The dihedral angle between A/B, A/C and B/C is 3.68 (12), 3.50 (9) and 7.19 (12)°, respectively. A strong intramolecular H-bonding of N—H $\cdots$ O type completes an S(6) (Etter *et al.*, 1990; Bernstein *et al.*, 1995) ring motif. Intermolecular C—H $\cdots$ O hydrogen bonds complete  $R_2^2(14)$ ,  $R_2^2(13)$  and  $R_3^2(17)$  ring motifs building a layer parallel to the (1 0 0) plane (Table 1, Fig 2).

### Experimental

Diethyl (ethoxymethylene)malonate (0.473 g, 2.1 mmol), 7-amino-5*H*-thiochromeno[2,3-*b*]pyridin-5-one (500 mg, 2.1 mmol) and 8.0 ml of ethyl alcohol was heated under reflux on water bath for 3 h. Completion of reaction was monitored by TLC. The product precipitated by the addition of n-hexane was filtered, washed, dried and recrystallized from chloroform to give the yellow needles of (I).

### Refinement

The diethyl groups are disordered over two set of sites with occupancy ratio of 0.75:0.25 and 0.53:0.47. The disordered positions were refined using O-C and C-C bond restraints to maintain chemically reasonable geometry. The disordered groups were refined anisotropically with however equal thermal parameters for the C-atoms.

The H-atoms were positioned geometrically (N—H = 0.86, C—H = 0.93–0.97 Å) and treated as riding with  $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{C}, \text{O})$ , where  $x = 1.5$  for methyl and  $x = 1.2$  for aryl H-atoms.

## Figures

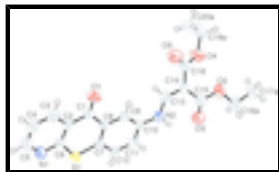


Fig. 1. View of the title compound with the atom numbering scheme. The thermal displacements are drawn at the 50% probability level. H-atoms are shown as small spheres of arbitrary radii. The disordered minority ethyl groups are omitted for clarity.

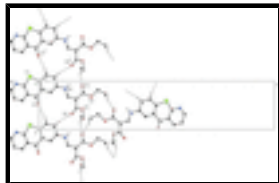


Fig. 2. Partial packing view showing the formation of different ring motifs through C-H...O hydrogen bonds. Only the major component of the disordered moieties are represented and H atoms not involved in hydrogen bondings have been omitted for clarity. [Symmetry code: (i)  $x, y-1, z$ .]

## Diethyl 2-[(5-oxo-5H-thiochromeno[2,3-b]pyridin-7-yl)amino]methylidene}propanedioate

### Crystal data

$C_{20}H_{18}N_2O_5S$

$M_r = 398.42$

Monoclinic,  $C2/c$

Hall symbol:  $-C\ 2yc$

$a = 13.8013\ (7)\ \text{\AA}$

$b = 7.5180\ (3)\ \text{\AA}$

$c = 36.2743\ (15)\ \text{\AA}$

$\beta = 94.330\ (3)^\circ$

$V = 3753.0\ (3)\ \text{\AA}^3$

$Z = 8$

$F(000) = 1664$

$D_x = 1.410\ \text{Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 1789 reflections

$\theta = 2.3\text{--}25.3^\circ$

$\mu = 0.21\ \text{mm}^{-1}$

$T = 296\ \text{K}$

Needle, yellow

$0.35 \times 0.18 \times 0.15\ \text{mm}$

### Data collection

Bruker Kappa APEXII CCD  
diffractometer

Radiation source: fine-focus sealed tube  
graphite

Detector resolution:  $8.10\ \text{pixels mm}^{-1}$

$\omega$  scans

Absorption correction: multi-scan  
(*SADABS*; Bruker, 2005)

$T_{\min} = 0.968$ ,  $T_{\max} = 0.985$

13274 measured reflections

3314 independent reflections

1776 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.077$

$\theta_{\max} = 25.0^\circ$ ,  $\theta_{\min} = 2.3^\circ$

$h = -16 \rightarrow 16$

$k = 0 \rightarrow 8$

$l = 0 \rightarrow 42$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

Primary atom site location: structure-invariant direct  
methods

Secondary atom site location: difference Fourier map

$$R[F^2 > 2\sigma(F^2)] = 0.054$$

$$wR(F^2) = 0.130$$

$$S = 0.97$$

3314 reflections

269 parameters

10 restraints

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0533P)^2]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

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

$$\Delta\rho_{\max} = 0.20 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.18 \text{ e } \text{\AA}^{-3}$$

### 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.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
S1	0.10364 (6)	-0.08366 (11)	-0.04024 (2)	0.0529 (3)	
O1	0.11162 (17)	0.4807 (3)	-0.00428 (6)	0.0604 (7)	
O2	0.3194 (2)	0.3243 (3)	0.21973 (6)	0.0911 (9)	
C16A	0.3217 (7)	0.1867 (9)	0.24963 (15)	0.1062 (19)	0.75
H16A	0.2563	0.1492	0.2540	0.127*	0.75
H16B	0.3585	0.0834	0.2428	0.127*	0.75
C17A	0.3688 (6)	0.2726 (9)	0.28278 (13)	0.1062 (19)	0.75
H17A	0.4333	0.3086	0.2780	0.159*	0.75
H17B	0.3718	0.1901	0.3030	0.159*	0.75
H17C	0.3318	0.3751	0.2890	0.159*	0.75
C16B	0.2928 (14)	0.259 (3)	0.2569 (5)	0.122 (7)	0.25
H16C	0.2441	0.1659	0.2556	0.147*	0.25
H16D	0.2762	0.3534	0.2736	0.147*	0.25
C17B	0.3965 (14)	0.192 (3)	0.2636 (8)	0.122 (7)	0.25
H17D	0.4131	0.1221	0.2429	0.184*	0.25
H17E	0.4019	0.1198	0.2855	0.184*	0.25
H17F	0.4401	0.2912	0.2668	0.184*	0.25
O3	0.2852 (2)	0.0944 (4)	0.18250 (6)	0.0853 (9)	
O4	0.40074 (19)	0.5902 (3)	0.18304 (7)	0.0793 (8)	
C19A	0.4388 (7)	0.7695 (14)	0.1889 (4)	0.105 (3)	0.53
H19A	0.4366	0.8060	0.2145	0.126*	0.53
H19B	0.4031	0.8548	0.1730	0.126*	0.53
C20A	0.5401 (7)	0.7499 (13)	0.1787 (3)	0.105 (3)	0.53
H20A	0.5726	0.6611	0.1941	0.157*	0.53

## supplementary materials

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H20B	0.5734	0.8614	0.1822	0.157*	0.53
H20C	0.5399	0.7146	0.1533	0.157*	0.53
C19B	0.4500 (8)	0.7644 (17)	0.1791 (5)	0.108 (4)	0.47
H19C	0.4098	0.8599	0.1874	0.130*	0.47
H19D	0.4615	0.7854	0.1534	0.130*	0.47
C20B	0.5450 (7)	0.7572 (16)	0.2024 (3)	0.108 (4)	0.47
H20D	0.5325	0.7451	0.2280	0.163*	0.47
H20E	0.5808	0.8647	0.1990	0.163*	0.47
H20F	0.5822	0.6571	0.1950	0.163*	0.47
O5	0.2939 (2)	0.6807 (4)	0.13788 (7)	0.0874 (9)	
N1	0.0155 (2)	0.0557 (4)	-0.09743 (7)	0.0591 (8)	
N2	0.23819 (19)	0.1593 (4)	0.11064 (7)	0.0544 (8)	
H2	0.2432	0.0765	0.1270	0.065*	
C1	0.1051 (2)	0.3242 (5)	-0.01327 (8)	0.0440 (8)	
C2	0.0601 (2)	0.2734 (4)	-0.05003 (8)	0.0446 (8)	
C3	0.0182 (2)	0.4052 (5)	-0.07279 (9)	0.0618 (10)	
H3	0.0195	0.5229	-0.0649	0.074*	
C4	-0.0251 (3)	0.3623 (6)	-0.10695 (10)	0.0737 (12)	
H4	-0.0542	0.4491	-0.1223	0.088*	
C5	-0.0242 (3)	0.1861 (6)	-0.11782 (9)	0.0719 (11)	
H5	-0.0533	0.1574	-0.1410	0.086*	
C6	0.0558 (2)	0.1015 (4)	-0.06379 (8)	0.0460 (8)	
C7	0.1410 (2)	0.0021 (4)	0.00313 (8)	0.0407 (8)	
C8	0.1395 (2)	0.1820 (4)	0.01247 (8)	0.0390 (8)	
C9	0.1711 (2)	0.2333 (4)	0.04837 (8)	0.0452 (8)	
H9	0.1691	0.3528	0.0549	0.054*	
C10	0.2052 (2)	0.1102 (5)	0.07425 (8)	0.0448 (8)	
C11	0.2065 (2)	-0.0693 (4)	0.06457 (8)	0.0507 (9)	
H11	0.2294	-0.1534	0.0819	0.061*	
C12	0.1743 (2)	-0.1219 (4)	0.02973 (8)	0.0468 (8)	
H12	0.1746	-0.2421	0.0237	0.056*	
C13	0.2620 (2)	0.3227 (5)	0.12156 (8)	0.0525 (9)	
H13	0.2555	0.4106	0.1035	0.063*	
C14	0.2949 (2)	0.3776 (4)	0.15601 (8)	0.0503 (9)	
C15	0.3008 (3)	0.2515 (6)	0.18640 (9)	0.0634 (10)	
C18	0.3268 (3)	0.5646 (5)	0.15800 (9)	0.0608 (10)	

### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
S1	0.0609 (6)	0.0445 (6)	0.0529 (5)	0.0014 (5)	0.0003 (4)	-0.0085 (4)
O1	0.0728 (18)	0.0357 (15)	0.0714 (15)	0.0011 (13)	-0.0036 (12)	-0.0025 (12)
O2	0.150 (3)	0.077 (2)	0.0444 (14)	-0.0195 (18)	-0.0106 (15)	0.0048 (13)
C16A	0.175 (6)	0.088 (4)	0.050 (2)	0.010 (4)	-0.023 (3)	0.004 (2)
C17A	0.175 (6)	0.088 (4)	0.050 (2)	0.010 (4)	-0.023 (3)	0.004 (2)
C16B	0.20 (2)	0.056 (13)	0.107 (13)	-0.034 (13)	0.004 (15)	0.009 (9)
C17B	0.20 (2)	0.056 (13)	0.107 (13)	-0.034 (13)	0.004 (15)	0.009 (9)
O3	0.135 (3)	0.0529 (19)	0.0666 (16)	-0.0019 (18)	0.0001 (15)	0.0044 (14)

O4	0.085 (2)	0.0608 (19)	0.0880 (18)	-0.0109 (15)	-0.0233 (15)	-0.0001 (14)
C19A	0.127 (9)	0.055 (5)	0.129 (7)	-0.022 (5)	-0.010 (6)	0.006 (4)
C20A	0.127 (9)	0.055 (5)	0.129 (7)	-0.022 (5)	-0.010 (6)	0.006 (4)
C19B	0.080 (8)	0.102 (8)	0.138 (8)	-0.009 (5)	-0.026 (5)	-0.044 (6)
C20B	0.080 (8)	0.102 (8)	0.138 (8)	-0.009 (5)	-0.026 (5)	-0.044 (6)
O5	0.115 (2)	0.063 (2)	0.0792 (18)	0.0021 (16)	-0.0280 (16)	0.0106 (15)
N1	0.058 (2)	0.072 (2)	0.0474 (17)	-0.0035 (16)	0.0008 (14)	-0.0064 (15)
N2	0.065 (2)	0.053 (2)	0.0452 (16)	-0.0068 (16)	0.0044 (13)	0.0012 (13)
C1	0.034 (2)	0.044 (2)	0.054 (2)	-0.0031 (17)	0.0088 (15)	0.0006 (17)
C2	0.038 (2)	0.046 (2)	0.0496 (19)	0.0001 (16)	0.0032 (15)	0.0073 (16)
C3	0.060 (2)	0.059 (3)	0.065 (2)	0.003 (2)	0.0019 (19)	0.003 (2)
C4	0.075 (3)	0.081 (3)	0.063 (3)	0.007 (2)	-0.008 (2)	0.016 (2)
C5	0.075 (3)	0.091 (4)	0.049 (2)	-0.001 (3)	-0.0056 (19)	0.000 (2)
C6	0.039 (2)	0.054 (2)	0.0446 (18)	-0.0004 (17)	0.0057 (15)	0.0009 (17)
C7	0.035 (2)	0.039 (2)	0.0479 (18)	-0.0044 (16)	0.0062 (15)	0.0002 (15)
C8	0.0351 (19)	0.037 (2)	0.0452 (18)	-0.0044 (15)	0.0061 (14)	-0.0006 (15)
C9	0.044 (2)	0.042 (2)	0.0507 (19)	-0.0033 (16)	0.0073 (16)	-0.0075 (16)
C10	0.047 (2)	0.050 (2)	0.0386 (17)	-0.0050 (17)	0.0066 (14)	0.0010 (16)
C11	0.053 (2)	0.046 (2)	0.053 (2)	-0.0014 (18)	0.0071 (17)	0.0101 (17)
C12	0.051 (2)	0.037 (2)	0.052 (2)	-0.0022 (16)	0.0077 (16)	-0.0007 (15)
C13	0.051 (2)	0.060 (3)	0.047 (2)	-0.0038 (19)	0.0060 (16)	0.0018 (17)
C14	0.059 (2)	0.049 (2)	0.0430 (18)	-0.0047 (18)	0.0061 (16)	0.0007 (16)
C15	0.072 (3)	0.066 (3)	0.051 (2)	0.003 (2)	-0.0017 (19)	-0.005 (2)
C18	0.067 (3)	0.064 (3)	0.050 (2)	0.001 (2)	-0.0044 (19)	-0.0032 (19)

*Geometric parameters (Å, °)*

S1—C6	1.737 (3)	C20B—H20D	0.9600
S1—C7	1.742 (3)	C20B—H20E	0.9600
O1—C1	1.222 (3)	C20B—H20F	0.9600
O2—C15	1.334 (4)	O5—C18	1.204 (4)
O2—C16A	1.497 (6)	N1—C5	1.321 (4)
O2—C16B	1.506 (14)	N1—C6	1.347 (4)
C16A—C17A	1.472 (7)	N2—C13	1.324 (4)
C16A—H16A	0.9700	N2—C10	1.413 (4)
C16A—H16B	0.9700	N2—H2	0.8600
C17A—H17A	0.9600	C1—C8	1.474 (4)
C17A—H17B	0.9600	C1—C2	1.478 (4)
C17A—H17C	0.9600	C2—C6	1.385 (4)
C16B—C17B	1.520 (10)	C2—C3	1.388 (4)
C16B—H16C	0.9700	C3—C4	1.373 (4)
C16B—H16D	0.9700	C3—H3	0.9300
C17B—H17D	0.9600	C4—C5	1.382 (5)
C17B—H17E	0.9600	C4—H4	0.9300
C17B—H17F	0.9600	C5—H5	0.9300
O3—C15	1.206 (4)	C7—C12	1.395 (4)
O4—C18	1.328 (4)	C7—C8	1.395 (4)
O4—C19A	1.457 (10)	C8—C9	1.396 (4)
O4—C19B	1.487 (12)	C9—C10	1.375 (4)

## supplementary materials

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C19A—C20A	1.480 (9)	C9—H9	0.9300
C19A—H19A	0.9700	C10—C11	1.395 (4)
C19A—H19B	0.9700	C11—C12	1.366 (4)
C20A—H20A	0.9600	C11—H11	0.9300
C20A—H20B	0.9600	C12—H12	0.9300
C20A—H20C	0.9600	C13—C14	1.361 (4)
C19B—C20B	1.506 (10)	C13—H13	0.9300
C19B—H19C	0.9700	C14—C15	1.452 (4)
C19B—H19D	0.9700	C14—C18	1.473 (4)
C6—S1—C7	102.90 (15)	C6—C2—C1	124.7 (3)
C15—O2—C16A	111.4 (4)	C3—C2—C1	118.7 (3)
C15—O2—C16B	129.4 (11)	C4—C3—C2	120.2 (3)
C16A—O2—C16B	28.4 (8)	C4—C3—H3	119.9
C17A—C16A—O2	105.8 (5)	C2—C3—H3	119.9
C17A—C16A—H16A	110.6	C3—C4—C5	118.0 (4)
O2—C16A—H16A	110.6	C3—C4—H4	121.0
C17A—C16A—H16B	110.6	C5—C4—H4	121.0
O2—C16A—H16B	110.6	N1—C5—C4	124.3 (4)
H16A—C16A—H16B	108.7	N1—C5—H5	117.9
O2—C16B—C17B	87.8 (14)	C4—C5—H5	117.9
O2—C16B—H16C	114.0	N1—C6—C2	124.6 (3)
C17B—C16B—H16C	114.0	N1—C6—S1	110.9 (3)
O2—C16B—H16D	114.0	C2—C6—S1	124.5 (2)
C17B—C16B—H16D	114.0	C12—C7—C8	119.4 (3)
H16C—C16B—H16D	111.2	C12—C7—S1	115.9 (2)
C16B—C17B—H17D	109.5	C8—C7—S1	124.7 (2)
C16B—C17B—H17E	109.5	C7—C8—C9	119.0 (3)
H17D—C17B—H17E	109.5	C7—C8—C1	124.0 (3)
C16B—C17B—H17F	109.5	C9—C8—C1	117.0 (3)
H17D—C17B—H17F	109.5	C10—C9—C8	121.2 (3)
H17E—C17B—H17F	109.5	C10—C9—H9	119.4
C18—O4—C19A	118.9 (6)	C8—C9—H9	119.4
C18—O4—C19B	113.3 (6)	C9—C10—C11	119.3 (3)
C19A—O4—C19B	15.6 (11)	C9—C10—N2	122.1 (3)
O4—C19A—C20A	102.0 (8)	C11—C10—N2	118.6 (3)
O4—C19A—H19A	111.4	C12—C11—C10	120.2 (3)
C20A—C19A—H19A	111.4	C12—C11—H11	119.9
O4—C19A—H19B	111.4	C10—C11—H11	119.9
C20A—C19A—H19B	111.4	C11—C12—C7	120.9 (3)
H19A—C19A—H19B	109.2	C11—C12—H12	119.5
O4—C19B—C20B	107.4 (10)	C7—C12—H12	119.5
O4—C19B—H19C	110.2	N2—C13—C14	127.9 (3)
C20B—C19B—H19C	110.2	N2—C13—H13	116.1
O4—C19B—H19D	110.2	C14—C13—H13	116.1
C20B—C19B—H19D	110.2	C13—C14—C15	119.7 (3)
H19C—C19B—H19D	108.5	C13—C14—C18	114.3 (3)
C5—N1—C6	116.3 (3)	C15—C14—C18	125.9 (3)
C13—N2—C10	125.3 (3)	O3—C15—O2	121.9 (3)
C13—N2—H2	117.4	O3—C15—C14	123.4 (3)



C10—N2—H2	117.4	O2—C15—C14	114.6 (4)
O1—C1—C8	121.0 (3)	O5—C18—O4	123.0 (4)
O1—C1—C2	120.4 (3)	O5—C18—C14	124.4 (4)
C8—C1—C2	118.5 (3)	O4—C18—C14	112.5 (3)
C6—C2—C3	116.6 (3)		
C15—O2—C16A—C17A	164.6 (6)	O1—C1—C8—C9	5.8 (4)
C16B—O2—C16A—C17A	-60.2 (19)	C2—C1—C8—C9	-172.7 (2)
C15—O2—C16B—C17B	101.0 (17)	C7—C8—C9—C10	1.2 (4)
C16A—O2—C16B—C17B	42.9 (14)	C1—C8—C9—C10	-179.5 (3)
C18—O4—C19A—C20A	-118.4 (9)	C8—C9—C10—C11	-1.1 (4)
C19B—O4—C19A—C20A	-46 (3)	C8—C9—C10—N2	179.5 (3)
C18—O4—C19B—C20B	-166.4 (9)	C13—N2—C10—C9	-16.8 (5)
C19A—O4—C19B—C20B	79 (3)	C13—N2—C10—C11	163.8 (3)
O1—C1—C2—C6	174.9 (3)	C9—C10—C11—C12	0.0 (4)
C8—C1—C2—C6	-6.5 (4)	N2—C10—C11—C12	179.4 (3)
O1—C1—C2—C3	-5.4 (4)	C10—C11—C12—C7	1.0 (4)
C8—C1—C2—C3	173.2 (3)	C8—C7—C12—C11	-0.9 (4)
C6—C2—C3—C4	0.4 (5)	S1—C7—C12—C11	179.2 (2)
C1—C2—C3—C4	-179.3 (3)	C10—N2—C13—C14	-179.4 (3)
C2—C3—C4—C5	-0.9 (5)	N2—C13—C14—C15	-4.2 (5)
C6—N1—C5—C4	0.9 (5)	N2—C13—C14—C18	172.5 (3)
C3—C4—C5—N1	0.2 (6)	C16A—O2—C15—O3	2.2 (6)
C5—N1—C6—C2	-1.5 (5)	C16B—O2—C15—O3	-23.5 (11)
C5—N1—C6—S1	179.4 (2)	C16A—O2—C15—C14	178.4 (5)
C3—C2—C6—N1	0.9 (4)	C16B—O2—C15—C14	152.7 (10)
C1—C2—C6—N1	-179.4 (3)	C13—C14—C15—O3	6.0 (5)
C3—C2—C6—S1	179.8 (2)	C18—C14—C15—O3	-170.3 (4)
C1—C2—C6—S1	-0.5 (4)	C13—C14—C15—O2	-170.2 (3)
C7—S1—C6—N1	-174.8 (2)	C18—C14—C15—O2	13.5 (5)
C7—S1—C6—C2	6.2 (3)	C19A—O4—C18—O5	5.6 (8)
C6—S1—C7—C12	173.8 (2)	C19B—O4—C18—O5	-10.6 (8)
C6—S1—C7—C8	-6.1 (3)	C19A—O4—C18—C14	-178.4 (6)
C12—C7—C8—C9	-0.2 (4)	C19B—O4—C18—C14	165.4 (7)
S1—C7—C8—C9	179.7 (2)	C13—C14—C18—O5	29.7 (5)
C12—C7—C8—C1	-179.4 (3)	C15—C14—C18—O5	-153.8 (4)
S1—C7—C8—C1	0.5 (4)	C13—C14—C18—O4	-146.2 (3)
O1—C1—C8—C7	-175.0 (3)	C15—C14—C18—O4	30.3 (5)
C2—C1—C8—C7	6.5 (4)		

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

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
N2—H2 $\cdots$ O3	0.86	2.06	2.683 (3)	129
C11—H11 $\cdots$ O5 <sup>i</sup>	0.93	2.49	3.403 (4)	167
C12—H12 $\cdots$ O1 <sup>i</sup>	0.93	2.45	3.322 (4)	157
C17A—H17C $\cdots$ O3 <sup>ii</sup>	0.96	2.58	3.516 (8)	165
C19A—H19B $\cdots$ O3 <sup>iii</sup>	0.97	2.47	3.231 (11)	135

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

Fig. 1

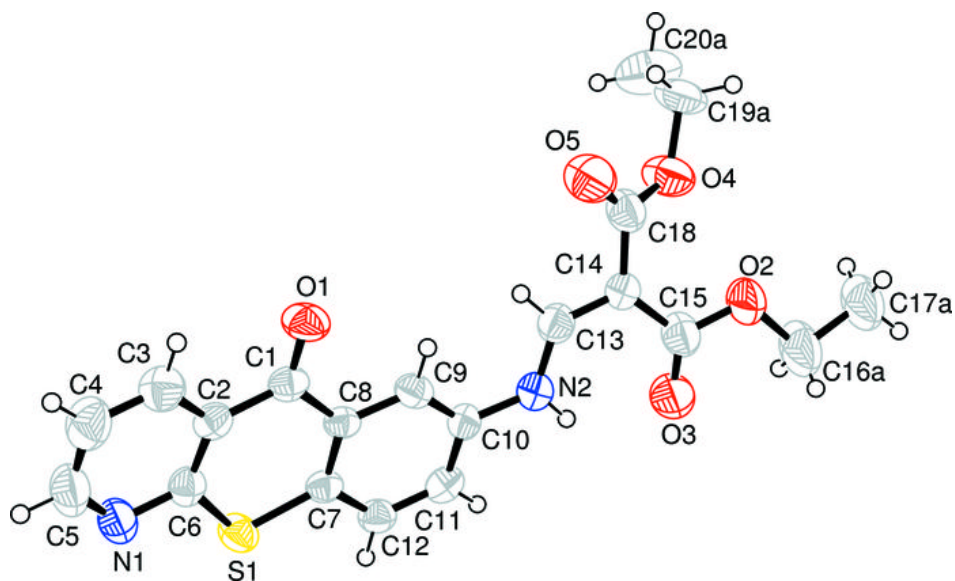


Fig. 2

