

(E)-3-(2-{2-[1-(3-Hydroxyphenyl)ethylidene]hydrazinyl}-1,3-thiazol-4-yl)-2H-chromen-2-one

Afsheen Arshad,^a Hasnah Osman,^{a‡} Chan Kit Lam,^b Madhukar Hemamalini^c and Hoong-Kun Fun^{c*§}

^aSchool of Chemical Sciences, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, ^bSchool of Pharmaceutical Sciences, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, and ^cX-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia
Correspondence e-mail: hkfun@usm.my

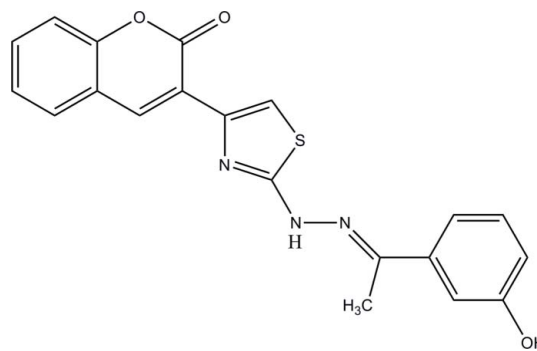
Received 30 March 2011; accepted 1 April 2011

Key indicators: single-crystal X-ray study; *T* = 100 K; mean $\sigma(C-C)$ = 0.002 Å; disorder in main residue; *R* factor = 0.041; *wR* factor = 0.105; data-to-parameter ratio = 19.9.

In the title compound, C₂₀H₁₅N₃O₃S, the thiazole ring is approximately planar, with a maximum deviation of 0.003 (1) Å, and makes dihedral angles of 7.44 (6) and 1.88 (6)° with the hydroxy-substituted phenyl ring and the pyran ring, respectively. The hydroxyl group is disordered over two sets of sites, with an occupancy ratio of 0.567 (3):0.433 (3). In the crystal, the major disorder component molecules are connected *via* bifurcated (three-centre) O—H...O and C—H...O hydrogen bonds, generating *R*₂¹(6) motifs and resulting in supramolecular chains along the *a* axis. In the minor occupancy component, however, molecules are connected *via* C—H...O hydrogen bonds, forming supramolecular chains along the *b* axis. Furthermore, the crystal structure is stabilized by π - π interactions between the thiazole rings [centroid-centroid distance = 3.5476 (7) Å].

Related literature

For details of coumarin derivatives, see: Raghu *et al.* (2009); Gursoy & Karali (2003); Chimenti *et al.* (2010); Kamal *et al.* (2009); Kalkhambkar *et al.* (2007). For graph-set notation, see: Bernstein *et al.* (1995). For the stability of the temperature controller used in the data collection, see: Cosier & Glazer (1986). For the synthesis of (E)-2-(1-(3-hydroxyphenyl)ethylidene)hydrazinecarbothioamide, see: Greenbaum *et al.* (2004) and for that of 3-[ω -bromoacetyl coumarin, see: Nadeem *et al.* (2009).



Experimental

Crystal data

C₂₀H₁₅N₃O₃S
M_r = 377.41
Monoclinic, *P*2₁/*c*
a = 9.1569 (1) Å
b = 9.9070 (2) Å
c = 18.7478 (3) Å
 β = 92.040 (1)°

V = 1699.67 (5) Å³
Z = 4
Mo *K* α radiation
 μ = 0.22 mm⁻¹
T = 100 K
0.34 × 0.32 × 0.10 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
*T*_{min} = 0.929, *T*_{max} = 0.979

29914 measured reflections
5400 independent reflections
4641 reflections with *I* > 2 σ (*I*)
*R*_{int} = 0.030

Refinement

R[*F*² > 2 σ (*F*²)] = 0.041
wR(*F*²) = 0.105
S = 1.07
5400 reflections
271 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{max}$ = 0.39 e Å⁻³
 $\Delta\rho_{min}$ = -0.30 e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O3—H1O <i>A</i> ...O2 ⁱ	0.89 (4)	1.89 (4)	2.7693 (19)	171 (4)
C19—H19 <i>A</i> ...O2 ⁱ	0.93	2.59	3.3020 (17)	133

Symmetry code: (i) *x* + 1, *y* - 1, *z*.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

AA, HO, CKL thank the Malaysian Government and Universiti Sains Malaysia (USM) for a grant [1001/PKimia/811133] to conduct this work. AA also thanks USM for a fellowship. HKF and MH thank the Malaysian Government and USM for the Research University Grant No. 1001/PFIZIK/811160. MH also thanks USM for a post-doctoral research fellowship.

‡ Additional correspondence author, e-mail: ohasnah@usm.my.

§ Thomson Reuters ResearcherID: A-3561-2009.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WN2428).

References

- Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Bruker (2009). *APEX2, SAINT and SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Chimenti, F., Bizzarri, B., Bolasco, A., Secci, D., Chimenti, P., Granese, A., Carradori, S., D'Ascenzio, M., Scaltrito, M. M. & Sisto, F. (2010). *J. Heterocycl. Chem.* **47**, 1269–1274.
- Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.
- Greenbaum, D. C., Mackey, Z., Hansell, E., Doyle, P., Gut, J., Caffrey, C. R., Lehrman, J., Rosenthal, P. J., McKerrow, J. H. & Chibale, K. (2004). *J. Med. Chem.* **47**, 3212–3219.
- Gursoy, A. & Karali, N. (2003). *Turk. J. Chem.* **27**, 545–552.
- Kalkhambkar, R., Kulkarni, G., Shivkumar, H. & Rao, R. (2007). *Eur. J. Med. Chem.* **42**, 1272–1276.
- Kamal, A., Adil, S., Tamboli, J., Siddardha, B. & Murthy, U. (2009). *Lett. Drug Des. Discov.* **6**, 201–209.
- Nadeem, S., Faiz, M. A. & Khan, S. A. (2009). *Acta Pol. Pharm. Drug Res.* **66**, 161–167.
- Raghu, M., Nagaraj, A. & Sanjeeva, R. C. (2009). *J. Heterocycl. Chem.* **46**, 261–267.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.

supplementary materials

Acta Cryst. (2011). E67, o1072-o1073 [doi:10.1107/S1600536811012189]

(*E*)-3-(2-{2-[1-(3-Hydroxyphenyl)ethylidene]hydrazinyl}-1,3-thiazol-4-yl)-2*H*-chromen-2-one

A. Arshad, H. Osman, C. K. Lam, M. Hemamalini and H.-K. Fun

Comment

Coumarin derivatives containing the thiazolyl unit exhibit promising antimicrobial activities against different microbial strains (Raghu *et al.*, 2009), including *Mycobacterium tuberculosis* (Gursoy *et al.*, 2003) and *Helicobacter pylori* (Chimenti *et al.*, 2010). These types of compounds are also reported to be good anticancer (Kamal *et al.*, 2009), analgesic and anti-inflammatory agents (Kalkhambkar *et al.*, 2007). The title compound is a new derivative of coumarin with the thiazole ring. We present here its crystal structure.

In the molecular structure of the compound, (Fig.1), the thiazole (S1/N1/C10–C12) ring is approximately planar, with a maximum deviation of 0.003 (1) Å for atom C11. The central thiazole (S1/N1/C10–C12) ring makes dihedral angles of 7.44 (6)° and 1.88 (6)° with the hydroxyl- substituted phenyl (C14–C19) ring and the pyran (O1/C1,C2/C7–C9) ring, respectively. The hydroxyl group is disordered over two sites, with an occupancy ratio 0.567 (3):0.433 (3).

In the crystal packing (Fig. 2), the major component molecules are connected via bifurcated O3—H10A···O2 and C19—H19A···O2 hydrogen bonds, generating $R^1_2(6)$ motifs, (Bernstein *et al.*, 1995), resulting in supramolecular chains along the *a*-axis. In the minor component, however, molecules are connected via C19—H19A···O2 hydrogen bonds, forming one-dimensional supramolecular chains along the *b*-axis (Fig. 3). Furthermore, the crystal structure is stabilized by $\pi\cdots\pi$ interactions between the thiazole (S1/N1/C10–C12) rings [centroid-centroid distance = 3.5476 (7) Å; -x, -y, 1-z].

Experimental

(*E*)-2-(1-(3-Hydroxyphenyl)ethylidene)hydrazinecarbothioamide (Greenbaum *et al.*, 2004) and 3-[ω -bromoacetyl coumarin] (Nadeem *et al.*, 2009) were synthesized as reported in the literature. The title compound was prepared by treating (*E*)-2-(1-(3-hydroxyphenyl)ethylidene)hydrazinecarbothioamide (2.5 mmol) with 3- ω -bromoacetylcoumarin (2.5 mmol) in a chloroform-ethanol (2:1) mixture. The reaction mixture was refluxed for 2–3 hours at 60°C to yield dense yellow precipitates. The precipitates were filtered and boiled with water containing sodium acetate. The title compound was recrystallized as golden crystals from ethanol:chloroform (3:1).

Refinement

Atoms H1N2, H10A, H10B and H11 were located in a difference Fourier map and refined freely [N—H = 0.85 (2) Å; O—H = 0.80 (5) and 0.89 (4) Å; C—H = 0.965 (17) Å]. The remaining H atoms were positioned geometrically [C—H = 0.93 Å for aromatic C and C—H = 0.96 Å for methyl C] and were refined using a riding model, with $U_{\text{iso}}(\text{H}) = kU_{\text{eq}}(\text{C})$, where $k = 1.2$ for aromatic C and 1.5 for methyl C. A rotating group model was applied to the methyl groups. The hydroxyl group is disordered over two sites, with an occupancy ratio 0.567 (3):0.433 (3).

Figures

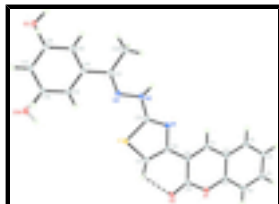


Fig. 1. The asymmetric unit of the title compound, showing 30% probability displacement ellipsoids. The open bonds represent the minor disordered components.

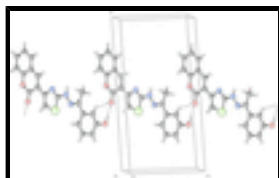


Fig. 2. The crystal packing of the title compound, involving the major disorder components of the molecules. Dashed lines indicate hydrogen bonds.

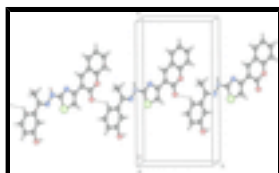


Fig. 3. The crystal packing of the title compound, involving the minor disorder components of the molecules. Dashed lines indicate hydrogen bonds.

(E)-3-(2-{2-[1-(3-Hydroxyphenyl)ethylidene]hydrazinyl}-1,3-thiazol-4-yl)-2H-chromen-2-one

Crystal data

$C_{20}H_{15}N_3O_3S$

$M_r = 377.41$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 9.1569$ (1) Å

$b = 9.9070$ (2) Å

$c = 18.7478$ (3) Å

$\beta = 92.040$ (1)°

$V = 1699.67$ (5) Å³

$Z = 4$

$F(000) = 784$

$D_x = 1.475$ Mg m⁻³

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

Cell parameters from 9987 reflections

$\theta = 3.0$ – 30.8 °

$\mu = 0.22$ mm⁻¹

$T = 100$ K

Plate, yellow

$0.34 \times 0.32 \times 0.10$ mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer

Radiation source: fine-focus sealed tube graphite

φ and ω scans

Absorption correction: multi-scan (SADABS; Bruker, 2009)

$T_{\min} = 0.929$, $T_{\max} = 0.979$

29914 measured reflections

5400 independent reflections

4641 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.030$

$\theta_{\max} = 31.0$ °, $\theta_{\min} = 2.2$ °

$h = -12 \rightarrow 13$

$k = -13 \rightarrow 14$

$l = -27 \rightarrow 27$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.041$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.105$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.07$	$w = 1/[\sigma^2(F_o^2) + (0.0429P)^2 + 0.8634P]$
5400 reflections	where $P = (F_o^2 + 2F_c^2)/3$
271 parameters	$(\Delta/\sigma)_{\max} < 0.001$
0 restraints	$\Delta\rho_{\max} = 0.39 \text{ e } \text{\AA}^{-3}$
	$\Delta\rho_{\min} = -0.30 \text{ e } \text{\AA}^{-3}$

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cryosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1) K.

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s 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 $F^2 > 2\sigma(F^2)$ 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
S1	0.17023 (3)	0.06980 (3)	0.402397 (16)	0.02037 (8)	
O1	-0.19100 (10)	0.47170 (9)	0.56457 (5)	0.01965 (18)	
O2	-0.14551 (11)	0.40120 (11)	0.45684 (5)	0.0273 (2)	
O3	0.75724 (18)	-0.54395 (18)	0.31831 (9)	0.0234 (5)	0.567 (3)
H1OA	0.797 (4)	-0.556 (4)	0.362 (2)	0.040 (10)*	0.567 (3)
O3A	0.4193 (3)	-0.2752 (3)	0.18640 (12)	0.0273 (7)	0.433 (3)
H1OB	0.363 (5)	-0.216 (5)	0.196 (2)	0.028 (11)*	0.433 (3)
N1	0.15618 (11)	0.10211 (11)	0.53942 (6)	0.0183 (2)	
N2	0.31472 (13)	-0.07177 (12)	0.50380 (6)	0.0227 (2)	
N3	0.36764 (12)	-0.13166 (12)	0.44404 (6)	0.0202 (2)	
C1	-0.00034 (13)	0.28351 (13)	0.62488 (7)	0.0184 (2)	
H1A	0.0626	0.2198	0.6456	0.022*	
C2	-0.07700 (13)	0.37365 (13)	0.67004 (7)	0.0184 (2)	
C3	-0.06263 (14)	0.37246 (14)	0.74487 (7)	0.0228 (3)	
H3A	-0.0011	0.3101	0.7677	0.027*	

supplementary materials

C4	-0.13980 (14)	0.46385 (14)	0.78482 (7)	0.0231 (3)	
H4A	-0.1304	0.4625	0.8344	0.028*	
C5	-0.23196 (14)	0.55839 (14)	0.75060 (7)	0.0214 (2)	
H5A	-0.2831	0.6198	0.7778	0.026*	
C6	-0.24800 (14)	0.56170 (13)	0.67707 (7)	0.0203 (2)	
H6A	-0.3089	0.6248	0.6544	0.024*	
C7	-0.17091 (13)	0.46850 (13)	0.63785 (6)	0.0175 (2)	
C8	-0.11845 (13)	0.38669 (13)	0.52030 (7)	0.0187 (2)	
C9	-0.01694 (13)	0.28851 (12)	0.55271 (6)	0.0167 (2)	
C10	0.06365 (13)	0.19757 (12)	0.50645 (6)	0.0169 (2)	
C11	0.05871 (14)	0.19493 (13)	0.43358 (7)	0.0194 (2)	
C12	0.21703 (13)	0.03050 (13)	0.49064 (7)	0.0183 (2)	
C13	0.45893 (13)	-0.23030 (13)	0.45086 (7)	0.0186 (2)	
C14	0.50587 (13)	-0.28993 (12)	0.38266 (7)	0.0179 (2)	
C15	0.43761 (13)	-0.25098 (13)	0.31754 (7)	0.0189 (2)	
H15A	0.3632	-0.1871	0.3171	0.023*	
C16	0.48063 (14)	-0.30725 (13)	0.25395 (7)	0.0210 (2)	
H16A	0.4359	-0.2796	0.2111	0.025*	0.567 (3)
C17	0.58993 (15)	-0.40455 (14)	0.25351 (7)	0.0232 (3)	
H17A	0.6179	-0.4426	0.2108	0.028*	
C18	0.65664 (14)	-0.44400 (14)	0.31770 (8)	0.0232 (3)	
H18A	0.7292	-0.5097	0.3178	0.028*	0.433 (3)
C19	0.61671 (14)	-0.38669 (13)	0.38209 (7)	0.0210 (2)	
H19A	0.6639	-0.4129	0.4246	0.025*	
C20	0.51371 (16)	-0.28472 (15)	0.52150 (7)	0.0262 (3)	
H20A	0.5374	-0.2111	0.5531	0.039*	
H20B	0.5995	-0.3383	0.5148	0.039*	
H20C	0.4394	-0.3396	0.5418	0.039*	
H1N2	0.338 (2)	-0.090 (2)	0.5468 (11)	0.038 (5)*	
H11	0.0039 (18)	0.2534 (18)	0.4013 (9)	0.029 (4)*	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.02210 (15)	0.02380 (16)	0.01531 (14)	0.00190 (11)	0.00199 (11)	-0.00074 (11)
O1	0.0222 (4)	0.0196 (4)	0.0170 (4)	0.0039 (3)	-0.0006 (3)	0.0017 (3)
O2	0.0337 (5)	0.0307 (5)	0.0174 (4)	0.0105 (4)	-0.0017 (4)	0.0032 (4)
O3	0.0226 (8)	0.0261 (9)	0.0213 (9)	0.0086 (6)	0.0010 (6)	-0.0031 (7)
O3A	0.0396 (14)	0.0249 (13)	0.0179 (11)	0.0025 (10)	0.0077 (9)	-0.0001 (9)
N1	0.0189 (5)	0.0191 (5)	0.0171 (5)	0.0013 (4)	0.0016 (4)	0.0008 (4)
N2	0.0244 (5)	0.0262 (6)	0.0176 (5)	0.0070 (4)	0.0024 (4)	0.0001 (4)
N3	0.0191 (5)	0.0224 (5)	0.0192 (5)	0.0025 (4)	0.0032 (4)	-0.0006 (4)
C1	0.0187 (5)	0.0186 (6)	0.0178 (5)	0.0025 (4)	-0.0005 (4)	0.0002 (4)
C2	0.0178 (5)	0.0197 (6)	0.0176 (5)	0.0012 (4)	-0.0006 (4)	-0.0014 (4)
C3	0.0225 (6)	0.0271 (7)	0.0186 (6)	0.0057 (5)	-0.0026 (5)	-0.0014 (5)
C4	0.0223 (6)	0.0289 (7)	0.0179 (6)	0.0029 (5)	-0.0013 (5)	-0.0045 (5)
C5	0.0193 (6)	0.0213 (6)	0.0236 (6)	0.0009 (5)	0.0018 (5)	-0.0048 (5)
C6	0.0186 (5)	0.0182 (6)	0.0240 (6)	0.0015 (4)	0.0000 (5)	-0.0001 (5)

C7	0.0178 (5)	0.0179 (5)	0.0167 (5)	-0.0012 (4)	-0.0004 (4)	0.0001 (4)
C8	0.0195 (5)	0.0176 (5)	0.0190 (6)	0.0007 (4)	0.0010 (4)	0.0011 (4)
C9	0.0167 (5)	0.0159 (5)	0.0174 (5)	-0.0003 (4)	0.0000 (4)	0.0005 (4)
C10	0.0172 (5)	0.0166 (5)	0.0169 (5)	-0.0009 (4)	0.0011 (4)	0.0010 (4)
C11	0.0219 (6)	0.0200 (6)	0.0164 (5)	0.0011 (4)	0.0003 (4)	0.0002 (4)
C12	0.0177 (5)	0.0199 (6)	0.0174 (5)	-0.0007 (4)	0.0014 (4)	0.0009 (4)
C13	0.0169 (5)	0.0194 (6)	0.0197 (6)	-0.0001 (4)	0.0015 (4)	0.0021 (4)
C14	0.0162 (5)	0.0175 (5)	0.0202 (6)	-0.0017 (4)	0.0019 (4)	0.0018 (4)
C15	0.0188 (5)	0.0167 (5)	0.0213 (6)	0.0005 (4)	0.0021 (4)	0.0028 (4)
C16	0.0240 (6)	0.0191 (6)	0.0201 (6)	-0.0022 (5)	0.0024 (5)	0.0026 (5)
C17	0.0266 (6)	0.0200 (6)	0.0234 (6)	-0.0014 (5)	0.0071 (5)	-0.0015 (5)
C18	0.0208 (6)	0.0192 (6)	0.0297 (7)	0.0026 (5)	0.0037 (5)	-0.0004 (5)
C19	0.0183 (5)	0.0204 (6)	0.0244 (6)	0.0011 (4)	0.0002 (5)	0.0016 (5)
C20	0.0286 (7)	0.0286 (7)	0.0213 (6)	0.0041 (5)	-0.0002 (5)	0.0043 (5)

Geometric parameters (Å, °)

S1—C11	1.7216 (13)	C5—C6	1.3815 (18)
S1—C12	1.7382 (13)	C5—H5A	0.9300
O1—C8	1.3706 (15)	C6—C7	1.3887 (17)
O1—C7	1.3799 (15)	C6—H6A	0.9300
O2—C8	1.2151 (15)	C8—C9	1.4626 (17)
O3—C18	1.352 (2)	C9—C10	1.4678 (17)
O3—H10A	0.89 (4)	C10—C11	1.3655 (17)
O3A—C16	1.403 (3)	C11—H11	0.965 (17)
O3A—H10B	0.80 (5)	C13—C14	1.4858 (17)
N1—C12	1.2987 (16)	C13—C20	1.4996 (18)
N1—C10	1.3990 (16)	C14—C19	1.3964 (17)
N2—C12	1.3682 (16)	C14—C15	1.4057 (17)
N2—N3	1.3713 (15)	C15—C16	1.3858 (18)
N2—H1N2	0.85 (2)	C15—H15A	0.9300
N3—C13	1.2894 (16)	C16—C17	1.3898 (18)
C1—C9	1.3570 (17)	C16—H16A	0.9300
C1—C2	1.4316 (17)	C17—C18	1.386 (2)
C1—H1A	0.9300	C17—H17A	0.9300
C2—C7	1.3964 (17)	C18—C19	1.3946 (19)
C2—C3	1.4044 (17)	C18—H18A	0.9300
C3—C4	1.3849 (18)	C19—H19A	0.9300
C3—H3A	0.9300	C20—H20A	0.9600
C4—C5	1.4009 (19)	C20—H20B	0.9600
C4—H4A	0.9300	C20—H20C	0.9600
C11—S1—C12	88.13 (6)	C10—C11—S1	110.77 (10)
C8—O1—C7	122.58 (10)	C10—C11—H11	127.8 (10)
C18—O3—H10A	111 (2)	S1—C11—H11	121.4 (10)
C16—O3A—H10B	102 (3)	N1—C12—N2	124.87 (12)
C12—N1—C10	109.05 (10)	N1—C12—S1	116.77 (10)
C12—N2—N3	114.89 (11)	N2—C12—S1	118.36 (9)
C12—N2—H1N2	118.2 (13)	N3—C13—C14	114.99 (11)
N3—N2—H1N2	126.9 (13)	N3—C13—C20	123.73 (12)

supplementary materials

C13—N3—N2	119.58 (11)	C14—C13—C20	121.27 (11)
C9—C1—C2	121.80 (11)	C19—C14—C15	118.86 (12)
C9—C1—H1A	119.1	C19—C14—C13	120.81 (11)
C2—C1—H1A	119.1	C15—C14—C13	120.33 (11)
C7—C2—C3	118.15 (11)	C16—C15—C14	120.36 (12)
C7—C2—C1	118.13 (11)	C16—C15—H15A	119.8
C3—C2—C1	123.71 (12)	C14—C15—H15A	119.8
C4—C3—C2	120.22 (12)	C15—C16—C17	120.73 (12)
C4—C3—H3A	119.9	C15—C16—O3A	124.63 (15)
C2—C3—H3A	119.9	C17—C16—O3A	114.63 (15)
C3—C4—C5	120.00 (12)	C15—C16—H16A	119.6
C3—C4—H4A	120.0	C17—C16—H16A	119.6
C5—C4—H4A	120.0	O3A—C16—H16A	5.1
C6—C5—C4	120.91 (12)	C18—C17—C16	119.04 (12)
C6—C5—H5A	119.5	C18—C17—H17A	120.5
C4—C5—H5A	119.5	C16—C17—H17A	120.5
C5—C6—C7	118.34 (12)	O3—C18—C17	119.52 (14)
C5—C6—H6A	120.8	O3—C18—C19	119.37 (14)
C7—C6—H6A	120.8	C17—C18—C19	121.04 (12)
O1—C7—C6	117.37 (11)	O3—C18—H18A	2.7
O1—C7—C2	120.27 (11)	C17—C18—H18A	119.5
C6—C7—C2	122.37 (12)	C19—C18—H18A	119.5
O2—C8—O1	115.71 (11)	C18—C19—C14	119.94 (12)
O2—C8—C9	126.15 (12)	C18—C19—H19A	120.0
O1—C8—C9	118.14 (11)	C14—C19—H19A	120.0
C1—C9—C8	119.05 (11)	C13—C20—H20A	109.5
C1—C9—C10	121.73 (11)	C13—C20—H20B	109.5
C8—C9—C10	119.22 (11)	H20A—C20—H20B	109.5
C11—C10—N1	115.28 (11)	C13—C20—H20C	109.5
C11—C10—C9	127.12 (11)	H20A—C20—H20C	109.5
N1—C10—C9	117.59 (10)	H20B—C20—H20C	109.5
C12—N2—N3—C13	-179.10 (12)	C8—C9—C10—N1	-177.98 (11)
C9—C1—C2—C7	0.02 (19)	N1—C10—C11—S1	0.55 (14)
C9—C1—C2—C3	-179.70 (13)	C9—C10—C11—S1	-179.34 (10)
C7—C2—C3—C4	-0.2 (2)	C12—S1—C11—C10	-0.43 (10)
C1—C2—C3—C4	179.48 (13)	C10—N1—C12—N2	179.60 (12)
C2—C3—C4—C5	-0.4 (2)	C10—N1—C12—S1	0.00 (14)
C3—C4—C5—C6	0.3 (2)	N3—N2—C12—N1	-178.57 (12)
C4—C5—C6—C7	0.28 (19)	N3—N2—C12—S1	1.03 (15)
C8—O1—C7—C6	178.55 (11)	C11—S1—C12—N1	0.26 (11)
C8—O1—C7—C2	-1.91 (17)	C11—S1—C12—N2	-179.37 (11)
C5—C6—C7—O1	178.62 (11)	N2—N3—C13—C14	178.40 (11)
C5—C6—C7—C2	-0.91 (19)	N2—N3—C13—C20	-0.57 (19)
C3—C2—C7—O1	-178.63 (11)	N3—C13—C14—C19	172.60 (12)
C1—C2—C7—O1	1.64 (18)	C20—C13—C14—C19	-8.40 (18)
C3—C2—C7—C6	0.89 (19)	N3—C13—C14—C15	-8.30 (17)
C1—C2—C7—C6	-178.84 (12)	C20—C13—C14—C15	170.69 (12)
C7—O1—C8—O2	-179.37 (11)	C19—C14—C15—C16	-0.43 (18)
C7—O1—C8—C9	0.49 (17)	C13—C14—C15—C16	-179.54 (11)

C2—C1—C9—C8	-1.41 (18)	C14—C15—C16—C17	1.10 (19)
C2—C1—C9—C10	178.93 (11)	C14—C15—C16—O3A	179.92 (16)
O2—C8—C9—C1	-178.99 (13)	C15—C16—C17—C18	-0.56 (19)
O1—C8—C9—C1	1.17 (17)	O3A—C16—C17—C18	-179.49 (15)
O2—C8—C9—C10	0.7 (2)	C16—C17—C18—O3	176.29 (14)
O1—C8—C9—C10	-179.16 (11)	C16—C17—C18—C19	-0.7 (2)
C12—N1—C10—C11	-0.35 (15)	O3—C18—C19—C14	-175.63 (14)
C12—N1—C10—C9	179.55 (11)	C17—C18—C19—C14	1.3 (2)
C1—C9—C10—C11	-178.43 (13)	C15—C14—C19—C18	-0.76 (18)
C8—C9—C10—C11	1.90 (19)	C13—C14—C19—C18	178.35 (12)
C1—C9—C10—N1	1.68 (17)		

Hydrogen-bond geometry (\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>
O3—H10A \cdots O2 ⁱ	0.89 (4)	1.89 (4)	2.7693 (19)	171 (4)
C19—H19A \cdots O2 ⁱ	0.93	2.59	3.3020 (17)	133

Symmetry codes: (i) $x+1, y-1, z$.

Fig. 1

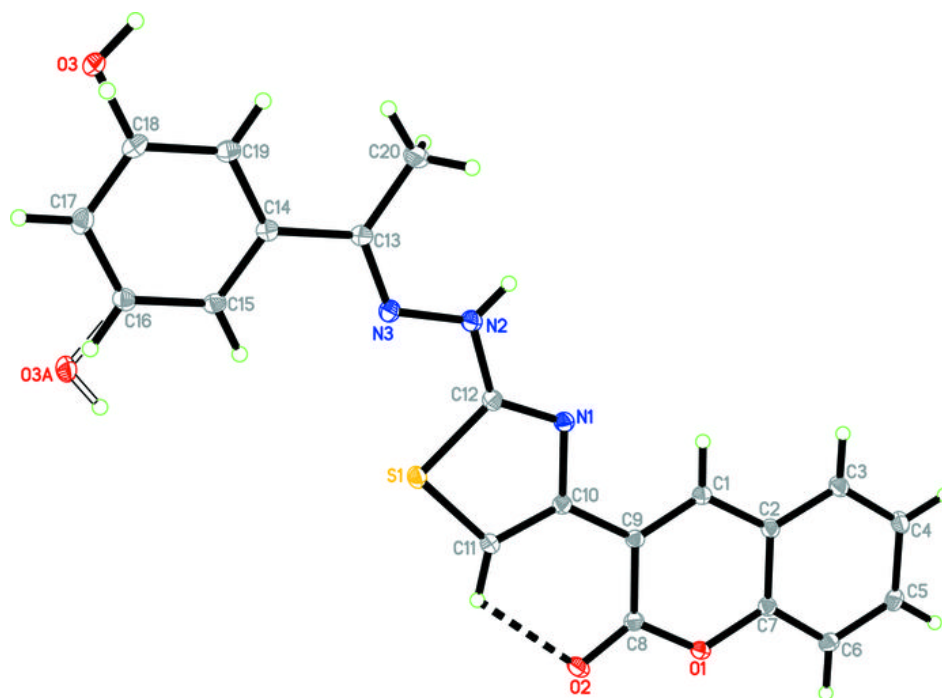


Fig. 2

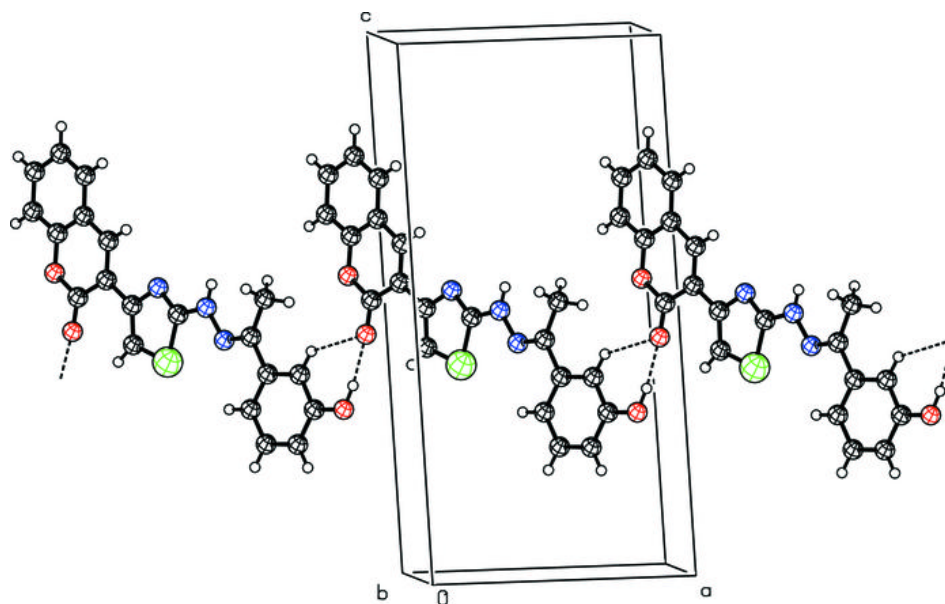


Fig. 3

