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# (5,7-Dimethyl-2-oxo-2*H*-chromen-4-yl)-methyl diethyldithiocarbamate

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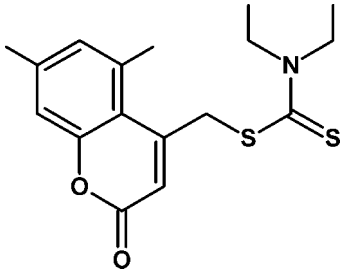
Key indicators: single-crystal X-ray study; $T$ = 293 K; mean $\sigma$(C–C) = 0.004 Å; $R$ factor = 0.051; $wR$ factor = 0.135; data-to-parameter ratio = 14.9.

In the title compound, $C_{17}H_{21}NO_2S_2$, the coumarin ring system is nearly planar, with a maximum deviation of 0.080 (2) Å from the mean plane. An intramolecular C—H···S hydrogen bond occurs. The crystal structure features C—H···S hydrogen bonds and weak $\pi$–$\pi$ interactions with a centroid–centroid distance of 3.679 (1) Å.

## Related literature

For biological applications of coumarins and dithiocarbamates, see: Smith *et al.* (1998); Nawrot-Modraka *et al.* (2006); Basanagouda *et al.* (2009); Kalkhambkar *et al.* (2007); El-Shorbagi (2000); Ronconi *et al.* (2006); Cvek & Dvorak (2007). For a related structure, see: Kumar *et al.* (2012). For the synthesis of the title compound, see: Shastri *et al.* (2004).




## Experimental

### Crystal data

$C_{17}H_{21}NO_2S_2$
$M_r$ = 335.47
Monoclinic, $P2_1/n$
$a$ = 7.8570 (2) Å
$b$ = 23.7745 (5) Å
$c$ = 9.7684 (2) Å
$\beta$ = 109.483 (1)°
$V$ = 1720.22 (7) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.32 mm$^{-1}$
$T$ = 293 K
0.24 × 0.20 × 0.12 mm

### Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: $\psi$ scan (*SADABS*; Sheldrick, 2007)
$T_{min}$ = 0.770, $T_{max}$ = 1.000
14939 measured reflections
3033 independent reflections
2803 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.020

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.135
$S$ = 1.04
3033 reflections
204 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.90 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.73 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C8—H8···S2$^{i}$ | 0.93 | 2.86 | 3.751 (2) | 161 |
| C16—H16*C*···S1 | 0.96 | 2.53 | 3.282 (3) | 135 |

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

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); 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: WN2474).

## References

Basanagouda, M., Kulkarni, M. V., Sharma, D., Gupta, V. K., Pranesha, Sandhyarani, P. & Rasal, V. P. (2009). *J. Chem. Sci.* **121**, 485–495.
Bruker (2001). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Cvek, B. & Dvorak, Z. T. (2007). *Curr. Pharm. Des.* **13**, 3155–3167.
El-Shorbagi, A. N. (2000). *Arch. Pharm.* **33**, 281–284.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Kalkhambkar, R. G., Kulkarni, G. M. & Lee, C.-S. (2007). *X-ray Struct. Anal. Online*, **23**, 31–32.
Kumar, K. M., Kour, D., Kapoor, K., Mahabaleshwaraiah, N. M., Kotresh, O., Gupta, V. K. & Kant, R. (2012). *Acta Cryst.* E**68**, o878–o879.
Nawrot-Modraka, J., Nawrot, E. & Graczik, J. (2006). *Eur. J. Med. Chem.* **41**, 1301–1309.
Ronconi, L., Marzano, C., Zanello, P., Corsini, M., Miolo, G., Macca, C., Trevisan, A. & Fregona, D. (2006). *J. Med. Chem.* **49**, 1648–1657.
Shastri, L. A., Ghate, M. D. & Kulkarni, M. V. (2004). *Indian J. Chem. Sect. B*, **43**, 2416–2422.
Sheldrick, G. M. (2007). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Smith, R. H., Jorgen, W. H., Tirado, R. J. & Lamb, M. L. (1998). *J. Med. Chem.* **41**, 5272–5286.

# supplementary materials

*Acta Cryst.* (2012). E**68**, o1657 [doi:10.1107/S1600536812019757]

## (5,7-Dimethyl-2-oxo-2*H*-chromen-4-yl)methyl diethyldithiocarbamate

**K. Mahesh Kumar, H. C. Devarajegowda, S Jeyaseelan, N. M. Mahabaleshwaraiah and O. Kotresh**

### Comment

Coumarins constitute a class of compounds which are found widely in nature and possess diverse biological activities. Over recent decades, medicinal chemists have paid great attention to the isolation, screening and structural modifications of new coumarins. They have been found to exhibit a wide range of applications in cancer, the HIV drug development arena (Smith *et al.,* 1998), anti-tumor, anti-bacterial and cytotoxic activity (Nawrot-Modraka *et al.,* 2006). In 4-substituted coumarins, the groups attached at the C-4 methylene carbon been shown to influence their solid state conformations, as observed in 4-aryloxymethyl (Basanagouda *et al.,* 2009) and 4-arylaminomethyl coumarins (Kalkhambkar *et al.,* 2007).

Dithiocarbamates have shown wide applications as pesticides,fungicides in agriculture (El-Shorbagi, 2000), potent anticancer agents (Ronconi *et al.,* 2006), organic intermediates, rubber additives, additives of polluted water and vulcanizing agents (Cvek & Dvorak, 2007).

In view of the above observations,we proposed that 4-substituted coumarins bearing the dithiocarbamate (DTC)group should display some interesting biological activity and the title compound was screened for fungicidal, bacterial and DNA cleavage properties.The crystal structure of a coumarin derivative linked to the DTC group has been reported (Kumar *et al.,* 2012).

The title compound is one of a series of dithiocarbamate coumarins with potential as possible anti-microbial agents. For these reasons, in continuation of our interest in the crystal structures of coumarin derivatives, we report here its crystal structure.

The asymmetric unit of 5,7-dimethyl-2-oxo-2*H*-chromen-4-yl)methyl diethyldithiocarbamate is shown in Fig. 1.The coumarin ring system (O3/C6–C14) is nearly planar, with a maximum deviation from the mean plane of 0.080 (2) Å for atom C12.

In the crystal structure (Fig. 2), the molecules are connected *via* weak intramolecular C8—H8···S2 and intermolecular C16—H16C···S1 hydrogen bonds (Table 1). Furthermore, the crystal structure features $\pi$-$\pi$ stacking interactions between the pyran ring (O3/C10–C14; centroid *Cg1*) and the benzene ring (C6–C11; centroid *Cg2*), with a *Cg1*···*Cg2* distance of 3.679 (1) Å.

### Experimental

All the chemicals were of analytical reagent grade and were used directly without further purification. 4-Bromomethyl coumarin required for the synthesis of the target molecule was synthesized according to an already reported procedure involving Pechmann cyclization of phenols with 4-bromoethyl acetoacetate (Shastri *et al.,* 2004) and sodium diethyl-dithiocarbamate purchased from Sigma- Aldrich.

A mixture of 2.6 g (0.01 mol) of 5,7-dimethyl-4-bromomethylcoumarin and 1.71 g (0.01 mol) of sodium diethyldithiocarbamate in 30 ml dry alcohol was stirred for 24 h at room temperature (the reaction was monitored by TLC). The solvent was evaporated and the resulting solid was extracted twice with a dichloromethane-$H_2O$ mixture. The organic layer was dried over anhydrous $CaCl_2$ and evaporation of the organic solvent gave the title compound. The compound was recrystallized from an ethanol-chloroform mixture. Colour: Colourless. Yield: 91%. M.P.: 409 K.

## Refinement

All H atoms were positioned geometrically [$Csp^2$—H = 0.93 Å, C(methylene)—H = 0.97 Å and C(methyl)—H = 0.96 Å] and refined using a riding model with $U_{iso}$(H) = 1.5$U_{eq}$(C) for methyl H and $U_{iso}$(H) = 1.2$U_{eq}$(C) for other H.

## Computing details

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT* (Bruker, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008).

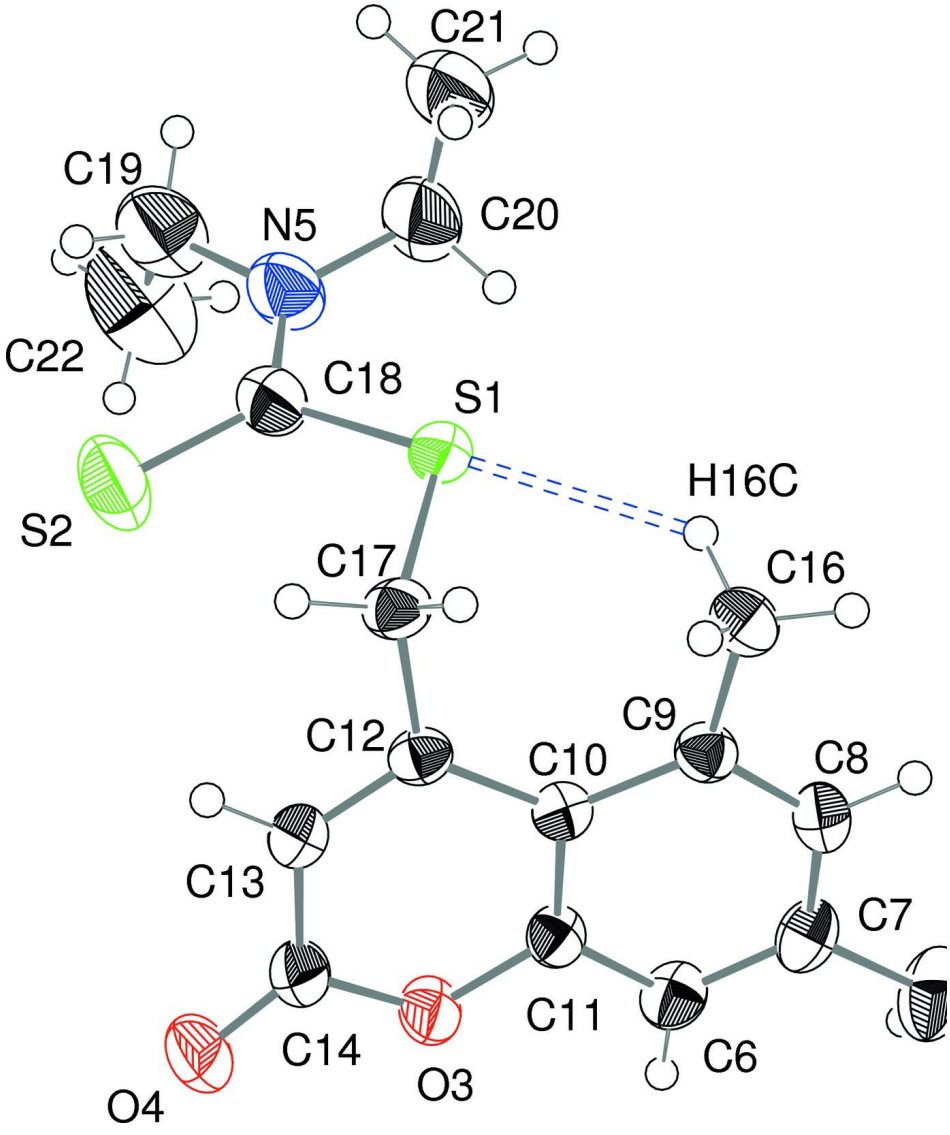


**Figure 1**

The molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are shown as spheres of arbitrary radius. The dashed line indicates the intramolecular hydrogen bond.

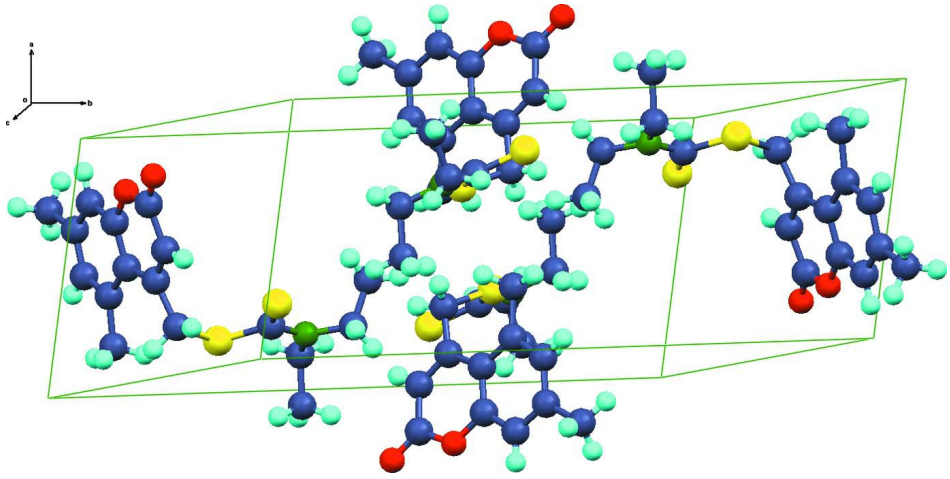

**Figure 2**

The packing of the molecules in the crystal structure.

### (5,7-Dimethyl-2-oxo-2*H*-chromen-4-yl)methyl diethyldithiocarbamate

*Crystal data*

$C_{17}H_{21}NO_2S_2$
$M_r = 335.47$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 7.8570$ (2) Å
$b = 23.7745$ (5) Å
$c = 9.7684$ (2) Å
$\beta = 109.483$ (1)°
$V = 1720.22$ (7) Å$^3$
$Z = 4$
$F(000) = 712$
$D_x = 1.295$ Mg m$^{-3}$
Melting point: 409 K
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3033 reflections
$\theta = 1.7$–25.0°
$\mu = 0.32$ mm$^{-1}$
$T = 293$ K
Plate, colourless
0.24 × 0.20 × 0.12 mm

*Data collection*

Bruker SMART CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\omega$ and $\varphi$ scans
Absorption correction: $\psi$ scan (*SADABS*; Sheldrick, 2007)
$T_{min} = 0.770$, $T_{max} = 1.000$
14939 measured reflections
3033 independent reflections
2803 reflections with $I > 2\sigma(I)$
$R_{int} = 0.020$
$\theta_{max} = 25.0°$, $\theta_{min} = 1.7°$
$h = -9 \rightarrow 9$
$k = -26 \rightarrow 28$
$l = -11 \rightarrow 11$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.135$
$S = 1.04$
3033 reflections
204 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0643P)^2 + 1.5942P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.90$ e Å$^{-3}$
$\Delta\rho_{min} = -0.73$ e Å$^{-3}$

Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^{*}=kFc[1+0.001xFc^{2}\lambda^{3}/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0052 (14)

*Special details*

**Experimental**. IR (KBr) 670 c $m^{-1}$ (C—S), 1204 c $m^{-1}$ (C=S), 1047 c $m^{-1}$ (C—O), 823 c $m^{-1}$ (C—N),1279 c $m^{-1}$ (C—O—C), 1716 c $m^{-1}$ (C=O).GCMS data m/e = 335. 1H NMR (400 MHz, $CDCl_3$, $\delta$, p.p.m.): 1.58 (d Ethylene-6H, $CH_3$), 2.46 (s,3*H*, $CH_3$), 2.71 (s,3*H*, $CH_3$), 3.88 (s,2*H*, Ethylene-$CH_2$), 4.21 (s,2*H*, Ethylene-$CH_2$), 4.50 (s 2H, Methylene-$CH_2$), 6.53 (s,1*H*, Ar—H), 6.92 (s,1*H*, Ar—H), 7.03 (s,1*H*, Ar—H).

**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 ($Å^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| S1 | 0.15831 (9) | 0.15127 (3) | 0.66095 (6) | 0.0434 (2) |
| S2 | 0.25909 (15) | 0.14818 (4) | 0.38884 (10) | 0.0773 (3) |
| O3 | 0.77521 (19) | 0.04484 (8) | 0.88072 (17) | 0.0414 (4) |
| O4 | 0.8065 (3) | 0.01657 (10) | 0.6765 (2) | 0.0610 (6) |
| N5 | 0.1516 (4) | 0.23806 (10) | 0.4975 (3) | 0.0583 (6) |
| C6 | 0.7641 (3) | 0.06546 (11) | 1.1089 (2) | 0.0395 (5) |
| H6 | 0.8887 | 0.0606 | 1.1437 | 0.047* |
| C7 | 0.6727 (3) | 0.07803 (10) | 1.2025 (2) | 0.0401 (5) |
| C8 | 0.4863 (3) | 0.08315 (10) | 1.1453 (2) | 0.0378 (5) |
| H8 | 0.4236 | 0.0902 | 1.2091 | 0.045* |
| C9 | 0.3886 (3) | 0.07847 (9) | 0.9997 (2) | 0.0329 (5) |
| C10 | 0.4826 (3) | 0.06808 (9) | 0.9000 (2) | 0.0294 (5) |
| C11 | 0.6692 (3) | 0.06000 (9) | 0.9621 (2) | 0.0327 (5) |
| C12 | 0.4095 (3) | 0.06440 (9) | 0.7418 (2) | 0.0312 (5) |
| C13 | 0.5170 (3) | 0.04836 (10) | 0.6673 (2) | 0.0380 (5) |
| H13 | 0.4675 | 0.0459 | 0.5668 | 0.046* |
| C14 | 0.7056 (3) | 0.03479 (11) | 0.7350 (3) | 0.0405 (5) |
| C15 | 0.7704 (4) | 0.08551 (15) | 1.3626 (3) | 0.0628 (8) |
| H15A | 0.7936 | 0.0493 | 1.4088 | 0.094* |
| H15B | 0.6971 | 0.1074 | 1.4042 | 0.094* |
| H15C | 0.8827 | 0.1046 | 1.3770 | 0.094* |
| C16 | 0.1861 (3) | 0.08263 (12) | 0.9590 (3) | 0.0465 (6) |
| H16A | 0.1543 | 0.0847 | 1.0456 | 0.070* |
| H16B | 0.1310 | 0.0500 | 0.9041 | 0.070* |
| H16C | 0.1442 | 0.1158 | 0.9016 | 0.070* |
| C17 | 0.2169 (3) | 0.07796 (10) | 0.6516 (2) | 0.0369 (5) |
| H17A | 0.1363 | 0.0548 | 0.6844 | 0.044* |
| H17B | 0.1982 | 0.0683 | 0.5512 | 0.044* |
| C18 | 0.1913 (4) | 0.18349 (11) | 0.5078 (3) | 0.0480 (6) |
| C19 | 0.1622 (6) | 0.27172 (15) | 0.3738 (4) | 0.0795 (11) |
| H19A | 0.1363 | 0.2478 | 0.2887 | 0.095* |

| | | | | |
|---|---|---|---|---|
| H19B | 0.0718 | 0.3012 | 0.3524 | 0.095* |
| C20 | 0.0865 (5) | 0.26865 (13) | 0.6014 (4) | 0.0666 (9) |
| H20A | 0.1272 | 0.3074 | 0.6075 | 0.080* |
| H20B | 0.1384 | 0.2519 | 0.6968 | 0.080* |
| C21 | −0.1163 (5) | 0.26762 (16) | 0.5582 (4) | 0.0793 (10) |
| H21A | −0.1682 | 0.2849 | 0.4647 | 0.119* |
| H21B | −0.1529 | 0.2879 | 0.6286 | 0.119* |
| H21C | −0.1570 | 0.2294 | 0.5538 | 0.119* |
| C22 | 0.3417 (7) | 0.29714 (19) | 0.4049 (7) | 0.1145 (17) |
| H22A | 0.3700 | 0.3194 | 0.4917 | 0.172* |
| H22B | 0.3420 | 0.3206 | 0.3251 | 0.172* |
| H22C | 0.4303 | 0.2680 | 0.4184 | 0.172* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| S1 | 0.0513 (4) | 0.0436 (4) | 0.0340 (3) | 0.0154 (3) | 0.0127 (3) | 0.0011 (2) |
| S2 | 0.1254 (8) | 0.0562 (5) | 0.0777 (6) | 0.0240 (5) | 0.0703 (6) | 0.0081 (4) |
| O3 | 0.0260 (8) | 0.0627 (11) | 0.0369 (9) | 0.0014 (7) | 0.0124 (6) | 0.0009 (8) |
| O4 | 0.0491 (11) | 0.0906 (16) | 0.0508 (11) | 0.0181 (10) | 0.0267 (9) | −0.0012 (10) |
| N5 | 0.0738 (16) | 0.0432 (13) | 0.0683 (16) | 0.0112 (11) | 0.0373 (13) | 0.0056 (11) |
| C6 | 0.0270 (11) | 0.0512 (14) | 0.0360 (12) | −0.0054 (10) | 0.0046 (9) | 0.0016 (10) |
| C7 | 0.0441 (13) | 0.0425 (13) | 0.0300 (11) | −0.0084 (10) | 0.0074 (10) | −0.0005 (9) |
| C8 | 0.0424 (13) | 0.0403 (13) | 0.0351 (12) | −0.0017 (10) | 0.0188 (10) | −0.0017 (9) |
| C9 | 0.0311 (11) | 0.0325 (11) | 0.0361 (12) | 0.0004 (9) | 0.0126 (9) | 0.0013 (9) |
| C10 | 0.0270 (10) | 0.0287 (10) | 0.0318 (11) | −0.0028 (8) | 0.0090 (9) | 0.0004 (8) |
| C11 | 0.0279 (11) | 0.0383 (12) | 0.0331 (11) | −0.0031 (9) | 0.0117 (9) | 0.0024 (9) |
| C12 | 0.0303 (11) | 0.0283 (10) | 0.0320 (11) | −0.0002 (8) | 0.0065 (9) | 0.0002 (8) |
| C13 | 0.0389 (12) | 0.0439 (13) | 0.0294 (11) | 0.0050 (10) | 0.0091 (9) | 0.0002 (9) |
| C14 | 0.0389 (12) | 0.0498 (14) | 0.0366 (12) | 0.0040 (11) | 0.0177 (10) | 0.0036 (10) |
| C15 | 0.0609 (18) | 0.087 (2) | 0.0334 (14) | −0.0135 (16) | 0.0061 (12) | −0.0067 (14) |
| C16 | 0.0348 (13) | 0.0618 (16) | 0.0475 (14) | 0.0073 (11) | 0.0199 (11) | 0.0059 (12) |
| C17 | 0.0332 (12) | 0.0381 (12) | 0.0338 (12) | 0.0033 (9) | 0.0035 (9) | −0.0026 (9) |
| C18 | 0.0528 (15) | 0.0451 (14) | 0.0500 (15) | 0.0078 (11) | 0.0224 (12) | 0.0020 (11) |
| C19 | 0.104 (3) | 0.0531 (18) | 0.101 (3) | 0.0124 (18) | 0.060 (2) | 0.0154 (18) |
| C20 | 0.097 (2) | 0.0421 (15) | 0.069 (2) | 0.0145 (15) | 0.0382 (18) | −0.0025 (14) |
| C21 | 0.094 (3) | 0.072 (2) | 0.086 (2) | 0.0324 (19) | 0.049 (2) | 0.0158 (19) |
| C22 | 0.132 (4) | 0.079 (3) | 0.165 (5) | −0.026 (3) | 0.093 (4) | −0.017 (3) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| S1—C18 | 1.775 (3) | C13—C14 | 1.443 (3) |
| S1—C17 | 1.813 (2) | C13—H13 | 0.9300 |
| S2—C18 | 1.659 (3) | C15—H15A | 0.9600 |
| O3—C14 | 1.365 (3) | C15—H15B | 0.9600 |
| O3—C11 | 1.377 (3) | C15—H15C | 0.9600 |
| O4—C14 | 1.202 (3) | C16—H16A | 0.9600 |
| N5—C18 | 1.330 (4) | C16—H16B | 0.9600 |
| N5—C20 | 1.472 (4) | C16—H16C | 0.9600 |
| N5—C19 | 1.474 (4) | C17—H17A | 0.9700 |

| | | | |
|---|---|---|---|
| C6—C7 | 1.371 (3) | C17—H17B | 0.9700 |
| C6—C11 | 1.384 (3) | C19—C22 | 1.469 (6) |
| C6—H6 | 0.9300 | C19—H19A | 0.9700 |
| C7—C8 | 1.388 (3) | C19—H19B | 0.9700 |
| C7—C15 | 1.505 (3) | C20—C21 | 1.506 (5) |
| C8—C9 | 1.377 (3) | C20—H20A | 0.9700 |
| C8—H8 | 0.9300 | C20—H20B | 0.9700 |
| C9—C10 | 1.426 (3) | C21—H21A | 0.9600 |
| C9—C16 | 1.510 (3) | C21—H21B | 0.9600 |
| C10—C11 | 1.400 (3) | C21—H21C | 0.9600 |
| C10—C12 | 1.461 (3) | C22—H22A | 0.9600 |
| C12—C13 | 1.341 (3) | C22—H22B | 0.9600 |
| C12—C17 | 1.510 (3) | C22—H22C | 0.9600 |

| | | | |
|---|---|---|---|
| C18—S1—C17 | 105.17 (12) | C9—C16—H16B | 109.5 |
| C14—O3—C11 | 122.57 (17) | H16A—C16—H16B | 109.5 |
| C18—N5—C20 | 123.8 (2) | C9—C16—H16C | 109.5 |
| C18—N5—C19 | 121.0 (2) | H16A—C16—H16C | 109.5 |
| C20—N5—C19 | 115.1 (2) | H16B—C16—H16C | 109.5 |
| C7—C6—C11 | 119.4 (2) | C12—C17—S1 | 113.43 (15) |
| C7—C6—H6 | 120.3 | C12—C17—H17A | 108.9 |
| C11—C6—H6 | 120.3 | S1—C17—H17A | 108.9 |
| C6—C7—C8 | 117.8 (2) | C12—C17—H17B | 108.9 |
| C6—C7—C15 | 121.3 (2) | S1—C17—H17B | 108.9 |
| C8—C7—C15 | 120.8 (2) | H17A—C17—H17B | 107.7 |
| C9—C8—C7 | 124.0 (2) | N5—C18—S2 | 124.2 (2) |
| C9—C8—H8 | 118.0 | N5—C18—S1 | 112.87 (19) |
| C7—C8—H8 | 118.0 | S2—C18—S1 | 122.90 (16) |
| C8—C9—C10 | 118.8 (2) | C22—C19—N5 | 111.5 (4) |
| C8—C9—C16 | 116.2 (2) | C22—C19—H19A | 109.3 |
| C10—C9—C16 | 124.9 (2) | N5—C19—H19A | 109.3 |
| C11—C10—C9 | 115.73 (19) | C22—C19—H19B | 109.3 |
| C11—C10—C12 | 115.79 (19) | N5—C19—H19B | 109.3 |
| C9—C10—C12 | 128.48 (19) | H19A—C19—H19B | 108.0 |
| O3—C11—C6 | 113.68 (19) | N5—C20—C21 | 112.2 (3) |
| O3—C11—C10 | 122.26 (19) | N5—C20—H20A | 109.2 |
| C6—C11—C10 | 124.0 (2) | C21—C20—H20A | 109.2 |
| C13—C12—C10 | 119.62 (19) | N5—C20—H20B | 109.2 |
| C13—C12—C17 | 115.74 (19) | C21—C20—H20B | 109.2 |
| C10—C12—C17 | 124.64 (19) | H20A—C20—H20B | 107.9 |
| C12—C13—C14 | 123.5 (2) | C20—C21—H21A | 109.5 |
| C12—C13—H13 | 118.3 | C20—C21—H21B | 109.5 |
| C14—C13—H13 | 118.3 | H21A—C21—H21B | 109.5 |
| O4—C14—O3 | 117.4 (2) | C20—C21—H21C | 109.5 |
| O4—C14—C13 | 127.0 (2) | H21A—C21—H21C | 109.5 |
| O3—C14—C13 | 115.58 (19) | H21B—C21—H21C | 109.5 |
| C7—C15—H15A | 109.5 | C19—C22—H22A | 109.5 |
| C7—C15—H15B | 109.5 | C19—C22—H22B | 109.5 |
| H15A—C15—H15B | 109.5 | H22A—C22—H22B | 109.5 |

| | | | |
|---|---|---|---|
| C7—C15—H15C | 109.5 | C19—C22—H22C | 109.5 |
| H15A—C15—H15C | 109.5 | H22A—C22—H22C | 109.5 |
| H15B—C15—H15C | 109.5 | H22B—C22—H22C | 109.5 |
| C9—C16—H16A | 109.5 | | |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C8—H8···S2$^{i}$ | 0.93 | 2.86 | 3.751 (2) | 161 |
| C16—H16*C*···S1 | 0.96 | 2.53 | 3.282 (3) | 135 |

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