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# 3,4-Dihydroxybenzaldehyde thiosemicarbazone

**Kong Wai Tan,[a] Yang Farina,[b] Chew Hee Ng,[c]* Mohd Jamil Maah[a] and Seik Weng Ng[a]**

[a]Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia, [b]School of Chemical Science and Food Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Malaysia, and [c]Faculty of Engineering and Science, Universiti Tunku Abdul Rahman, 53300 Kuala Lumpur, Malaysia
Correspondence e-mail: seikweng@um.edu.my

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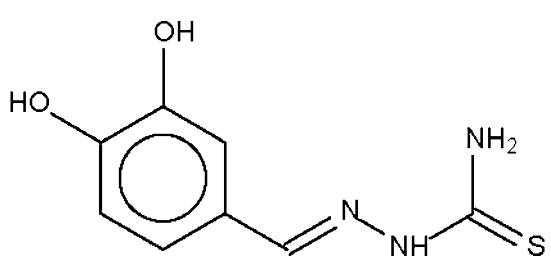
Key indicators: single-crystal X-ray study; $T$ = 100 K; mean $\sigma$(C–C) = 0.005 Å; $R$ factor = 0.061; $wR$ factor = 0.190; data-to-parameter ratio = 15.9.

The asymmetric unit of the title compound, $C_8H_9N_3O_2S$, contains three independent molecules which are stacked approximately over each other. In the crystal structure, centrosymmetric pairs of molecules are formed through intermolecular hydroxy–hydroxy O—H···O and hydroxy–sulfur O—H···S hydrogen bonds which are, in turn, linked into a two-dimensional network by N—H···O(hydroxy) hydrogen bonds.

## Related literature

For the structure of 3,4-dihydroxybenzaldehyde 4-phenylthiosemicarbazone, see: Swesi *et al.* (2006). For some metal complexes of the ligand, see: Zhu *et al.* (1991, 1997).




## Experimental

*Crystal data*

$C_8H_9N_3O_2S$
$M_r$ = 211.24
Triclinic, $P\bar{1}$
$a$ = 10.657 (2) Å
$b$ = 11.794 (2) Å
$c$ = 12.356 (2) Å
$\alpha$ = 111.657 (2)°
$\beta$ = 104.082 (2)°
$\gamma$ = 90.929 (2)°
$V$ = 1390.2 (4) Å$^3$
$Z$ = 6
Mo $K\alpha$ radiation
$\mu$ = 0.33 mm$^{-1}$
$T$ = 100 (2) K
0.20 × 0.18 × 0.04 mm

*Data collection*

Bruker SMART APEX diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min}$ = 0.938, $T_{max}$ = 0.987
8792 measured reflections
6298 independent reflections
3727 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.028

*Refinement*

$R[F^2 > 2\sigma(F^2)]$ = 0.061
$wR(F^2)$ = 0.189
$S$ = 1.01
6298 reflections
397 parameters
6 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.51 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.40 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O1—H1o···O6$^{i}$ | 0.84 (1) | 2.07 (3) | 2.784 (3) | 143 (4) |
| O2—H2o···S1$^{ii}$ | 0.84 (1) | 2.47 (1) | 3.300 (2) | 171 (4) |
| N1—H1n2···O5$^{iii}$ | 0.88 | 2.00 | 2.856 (4) | 163 |
| O3—H3o···O4$^{i}$ | 0.84 (1) | 2.11 (4) | 2.732 (3) | 130 (4) |
| O4—H4o···S2$^{ii}$ | 0.84 (1) | 2.38 (1) | 3.219 (2) | 174 (4) |
| N4—H4n2···O3$^{iii}$ | 0.88 | 2.05 | 2.900 (4) | 162 |
| O5—H5o···O2$^{i}$ | 0.84 (1) | 2.16 (4) | 2.742 (3) | 127 (4) |
| O6—H6o···S3$^{ii}$ | 0.84 (1) | 2.40 (1) | 3.244 (2) | 177 (4) |
| N7—H7n2···O1$^{iii}$ | 0.88 | 2.13 | 2.981 (4) | 161 |

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

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *publCIF* (Westrip, 2008).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2626).

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## supplementary materials

*Acta Cryst.* (2008). E**64**, o1073 [ **doi:10.1107/S160053680801386X** ]

### 3,4-Dihydroxybenzaldehyde thiosemicarbazone

**K. W. Tan, Y. Farina, C. H. Ng, M. J. Maah and S. W. Ng**

#### Comment

A previous study of Schiff bases derived by condensing substituted benzaldehydes with 4-phenylthiosemicarbazides describes the 3,4-dihydroxybenzaldehyde derivative, which crystallizes as a hemihydrate. The compound features extensive hydrogen bonds (Swesi *et al.*, 2006). The condensation product of the reaction between thiosemicarbazide and 3,4-dihydroxybenzaldehyde has an amino $-NH_2$ group in place of the phenyl group. In the crystal structure, a molecule is linked to an adjacent molecule by a hydrogen bond [$O$–$H_{3\text{-hydroxy}}\cdots O_{4\text{-hydroxy}}$]; it is linked to another adjacent molecule by another hydrogen bond [$O$–$H_{4\text{-hydroxy}}\cdots S$]. The structure is consolidated into a two-dimensional network motif by a $N_{\text{terminal}}$–$H\cdots O_{4\text{-hydroxy}}$ hydrogen bond. The asymmetric unit features three molecules that are approximately stacked over each other (Fig. 1).

#### Experimental

Thiosemicarbazide (0.09 g, 1 mmol) and 2,4-dihydroxybenzaldehyde (0.14 g, 1 mmol) were heated in an ethanol/water mixture (20/5 ml) for 3 h. Slow evaporation of the solvent yielded yellow crystals.

#### Refinement

Carbon-bound H-atoms were placed in calculated positions (C—H 0.95 Å) and were included in the refinement in the riding model approximation, with $U$(H) set to 1.2 $U$(C). The amino H-atoms were similarly treated (N–H 0.88 Å). The hydroxy H-atoms were located in a difference Fourier map, and were refined with a distance retraint of O–H 0.85±0.01 Å; their temperature factors were tied by a factor of 1.5.

#### Figures

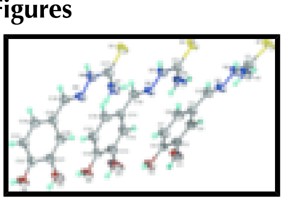


Fig. 1. Thermal ellipsoid (Barbour, 2001) plot of the three independent molecules of $C_{14}H_{13}N_3O_2S$ at the 70% probability level. Hydrogen atoms are drawn as spheres of arbitrary radii.

#### 3,4-Dihydroxybenzaldehyde thiosemicarbazone

*Crystal data*

| | |
|---|---|
| $C_8H_9N_3O_2S$ | $Z = 6$ |
| $M_r = 211.24$ | $F_{000} = 660$ |
| Triclinic, $P\overline{1}$ | $D_x = 1.514$ Mg m$^{-3}$ |

| | |
|---|---|
| Hall symbol: -P 1 | Mo $K\alpha$ radiation<br>$\lambda$ = 0.71073 Å |
| $a$ = 10.657 (2) Å | Cell parameters from 1478 reflections |
| $b$ = 11.794 (2) Å | $\theta$ = 2.7–27.8° |
| $c$ = 12.356 (2) Å | $\mu$ = 0.33 mm$^{-1}$ |
| $\alpha$ = 111.657 (2)° | $T$ = 100 (2) K |
| $\beta$ = 104.082 (2)° | Block, yellow |
| $\gamma$ = 90.929 (2)° | 0.20 × 0.18 × 0.04 mm |
| $V$ = 1390.2 (4) Å$^3$ | |

*Data collection*

| | |
|---|---|
| Bruker SMART APEX diffractometer | 6298 independent reflections |
| Radiation source: fine-focus sealed tube | 3727 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite | $R_{int}$ = 0.028 |
| $T$ = 100(2) K | $\theta_{max}$ = 27.5° |
| ω scans | $\theta_{min}$ = 1.8° |
| Absorption correction: multi-scan (SADABS; Sheldrick, 1996) | $h = -13 \rightarrow 13$ |
| $T_{min}$ = 0.938, $T_{max}$ = 0.987 | $k = -15 \rightarrow 9$ |
| 8792 measured reflections | $l = -14 \rightarrow 16$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)]$ = 0.061 | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2)$ = 0.189 | $w = 1/[\sigma^2(F_o^2) + (0.1004P)^2]$<br>where $P = (F_o^2 + 2F_c^2)/3$ |
| $S$ = 1.01 | $(\Delta/\sigma)_{max}$ = 0.001 |
| 6298 reflections | $\Delta\rho_{max}$ = 0.51 e Å$^{-3}$ |
| 397 parameters | $\Delta\rho_{min}$ = −0.39 e Å$^{-3}$ |
| 6 restraints | Extinction correction: none |
| Primary atom site location: structure-invariant direct methods | |

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)*

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| S1 | 0.84547 (10) | 0.94314 (8) | 0.21803 (8) | 0.0401 (3) |
| S2 | 0.45653 (10) | 0.85179 (8) | 0.31556 (7) | 0.0359 (2) |
| S3 | 0.10237 (10) | 0.74686 (8) | 0.41416 (8) | 0.0390 (3) |
| O1 | 0.7414 (3) | 0.5896 (2) | 0.7057 (2) | 0.0440 (7) |
| H1O | 0.750 (4) | 0.566 (4) | 0.763 (3) | 0.066* |
| O2 | 0.7519 (2) | 0.7405 (2) | 0.9368 (2) | 0.0333 (6) |

| | | | | |
|---|---|---|---|---|
| H2O | 0.769 (4) | 0.797 (3) | 1.0057 (17) | 0.050* |
| O3 | 0.4715 (4) | 0.5066 (2) | 0.8312 (2) | 0.0615 (9) |
| H3O | 0.476 (5) | 0.496 (5) | 0.895 (3) | 0.092* |
| O4 | 0.4659 (3) | 0.6536 (2) | 1.05646 (19) | 0.0359 (6) |
| H4O | 0.464 (4) | 0.710 (3) | 1.122 (2) | 0.054* |
| O5 | 0.2270 (3) | 0.4329 (2) | 0.9629 (2) | 0.0441 (7) |
| H5O | 0.232 (4) | 0.426 (4) | 1.029 (2) | 0.066* |
| O6 | 0.1658 (3) | 0.5600 (2) | 1.1704 (2) | 0.0370 (6) |
| H6O | 0.152 (4) | 0.609 (3) | 1.235 (2) | 0.056* |
| N1 | 0.7685 (3) | 0.7537 (3) | 0.2628 (2) | 0.0407 (8) |
| H1N1 | 0.7486 | 0.7210 | 0.3109 | 0.049* |
| H1N2 | 0.7622 | 0.7072 | 0.1868 | 0.049* |
| N2 | 0.8145 (3) | 0.9368 (2) | 0.4209 (2) | 0.0328 (7) |
| H2N | 0.8332 | 1.0172 | 0.4520 | 0.039* |
| N3 | 0.7922 (3) | 0.8755 (2) | 0.4912 (2) | 0.0316 (6) |
| N4 | 0.4570 (3) | 0.6598 (3) | 0.3786 (3) | 0.0438 (8) |
| H4N1 | 0.4531 | 0.6259 | 0.4305 | 0.053* |
| H4N2 | 0.4637 | 0.6141 | 0.3061 | 0.053* |
| N5 | 0.4424 (3) | 0.8421 (2) | 0.5209 (2) | 0.0294 (6) |
| H5N | 0.4379 | 0.9218 | 0.5460 | 0.035* |
| N6 | 0.4390 (3) | 0.7808 (2) | 0.5960 (2) | 0.0282 (6) |
| N7 | 0.1429 (3) | 0.5636 (3) | 0.4892 (3) | 0.0470 (9) |
| H7N1 | 0.1457 | 0.5309 | 0.5431 | 0.056* |
| H7N2 | 0.1607 | 0.5210 | 0.4205 | 0.056* |
| N8 | 0.0866 (3) | 0.7341 (3) | 0.6182 (2) | 0.0334 (7) |
| H8N | 0.0617 | 0.8082 | 0.6370 | 0.040* |
| N9 | 0.1000 (3) | 0.6760 (2) | 0.6982 (2) | 0.0299 (6) |
| C1 | 0.8075 (3) | 0.8720 (3) | 0.3043 (3) | 0.0300 (7) |
| C2 | 0.7942 (3) | 0.9415 (3) | 0.5994 (3) | 0.0306 (7) |
| H2 | 0.8072 | 1.0284 | 0.6258 | 0.037* |
| C3 | 0.7772 (3) | 0.8876 (3) | 0.6840 (3) | 0.0279 (7) |
| C4 | 0.7636 (3) | 0.7614 (3) | 0.6542 (3) | 0.0296 (7) |
| H4 | 0.7605 | 0.7070 | 0.5743 | 0.035* |
| C5 | 0.7545 (3) | 0.7147 (3) | 0.7389 (3) | 0.0293 (7) |
| C6 | 0.7597 (3) | 0.7934 (3) | 0.8565 (3) | 0.0257 (7) |
| C7 | 0.7714 (3) | 0.9180 (3) | 0.8871 (3) | 0.0319 (8) |
| H7C | 0.7737 | 0.9719 | 0.9670 | 0.038* |
| C8 | 0.7799 (3) | 0.9652 (3) | 0.8013 (3) | 0.0327 (8) |
| H8 | 0.7875 | 1.0516 | 0.8228 | 0.039* |
| C9 | 0.4526 (3) | 0.7787 (3) | 0.4095 (3) | 0.0273 (7) |
| C10 | 0.4204 (3) | 0.8443 (3) | 0.6983 (3) | 0.0288 (7) |
| H10 | 0.4054 | 0.9277 | 0.7164 | 0.035* |
| C11 | 0.4218 (3) | 0.7917 (3) | 0.7876 (3) | 0.0252 (7) |
| C12 | 0.4409 (3) | 0.6698 (3) | 0.7657 (3) | 0.0298 (7) |
| H12 | 0.4459 | 0.6164 | 0.6879 | 0.036* |
| C13 | 0.4526 (3) | 0.6261 (3) | 0.8557 (3) | 0.0321 (8) |
| C14 | 0.4480 (3) | 0.7039 (3) | 0.9711 (3) | 0.0257 (7) |
| C15 | 0.4243 (3) | 0.8234 (3) | 0.9921 (3) | 0.0316 (8) |
| H15 | 0.4172 | 0.8760 | 1.0694 | 0.038* |

| | | | | |
|---|---|---|---|---|
| C16 | 0.4107 (3) | 0.8671 (3) | 0.9006 (3) | 0.0304 (7) |
| H16 | 0.3936 | 0.9495 | 0.9153 | 0.036* |
| C17 | 0.1122 (3) | 0.6761 (3) | 0.5111 (3) | 0.0306 (7) |
| C18 | 0.0760 (3) | 0.7363 (3) | 0.7984 (3) | 0.0286 (7) |
| H18 | 0.0465 | 0.8147 | 0.8120 | 0.034* |
| C19 | 0.0928 (3) | 0.6872 (3) | 0.8926 (3) | 0.0264 (7) |
| C20 | 0.1458 (3) | 0.5772 (3) | 0.8812 (3) | 0.0288 (7) |
| H20 | 0.1662 | 0.5295 | 0.8081 | 0.035* |
| C21 | 0.1686 (3) | 0.5376 (3) | 0.9745 (3) | 0.0291 (7) |
| C22 | 0.1375 (3) | 0.6051 (3) | 1.0814 (3) | 0.0270 (7) |
| C23 | 0.0804 (3) | 0.7116 (3) | 1.0922 (3) | 0.0295 (7) |
| H23 | 0.0556 | 0.7566 | 1.1637 | 0.035* |
| C24 | 0.0594 (3) | 0.7524 (3) | 0.9982 (3) | 0.0300 (7) |
| H24 | 0.0214 | 0.8264 | 1.0064 | 0.036* |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| S1 | 0.0718 (7) | 0.0287 (5) | 0.0288 (5) | 0.0104 (4) | 0.0234 (4) | 0.0146 (4) |
| S2 | 0.0636 (6) | 0.0242 (4) | 0.0253 (4) | 0.0079 (4) | 0.0172 (4) | 0.0123 (4) |
| S3 | 0.0631 (6) | 0.0330 (5) | 0.0286 (5) | 0.0124 (4) | 0.0187 (4) | 0.0164 (4) |
| O1 | 0.083 (2) | 0.0205 (12) | 0.0354 (14) | 0.0112 (13) | 0.0242 (14) | 0.0123 (11) |
| O2 | 0.0527 (15) | 0.0269 (13) | 0.0263 (12) | 0.0067 (11) | 0.0144 (11) | 0.0144 (10) |
| O3 | 0.137 (3) | 0.0278 (15) | 0.0344 (15) | 0.0361 (17) | 0.0385 (18) | 0.0173 (13) |
| O4 | 0.0637 (17) | 0.0257 (13) | 0.0238 (12) | 0.0131 (12) | 0.0166 (12) | 0.0123 (10) |
| O5 | 0.083 (2) | 0.0266 (13) | 0.0343 (14) | 0.0200 (13) | 0.0278 (14) | 0.0167 (12) |
| O6 | 0.0633 (17) | 0.0276 (13) | 0.0252 (12) | 0.0146 (12) | 0.0162 (12) | 0.0127 (11) |
| N1 | 0.075 (2) | 0.0255 (16) | 0.0245 (15) | 0.0053 (15) | 0.0198 (15) | 0.0091 (13) |
| N2 | 0.0565 (19) | 0.0214 (14) | 0.0249 (14) | 0.0070 (13) | 0.0161 (13) | 0.0105 (12) |
| N3 | 0.0492 (18) | 0.0255 (15) | 0.0270 (14) | 0.0069 (13) | 0.0133 (13) | 0.0156 (12) |
| N4 | 0.085 (3) | 0.0232 (16) | 0.0285 (16) | 0.0122 (16) | 0.0230 (16) | 0.0106 (13) |
| N5 | 0.0500 (18) | 0.0194 (13) | 0.0235 (14) | 0.0081 (12) | 0.0140 (12) | 0.0107 (11) |
| N6 | 0.0444 (17) | 0.0221 (14) | 0.0230 (13) | 0.0032 (12) | 0.0105 (12) | 0.0131 (11) |
| N7 | 0.088 (3) | 0.0285 (17) | 0.0371 (17) | 0.0156 (17) | 0.0319 (17) | 0.0165 (14) |
| N8 | 0.0529 (19) | 0.0271 (15) | 0.0302 (15) | 0.0141 (13) | 0.0172 (13) | 0.0179 (13) |
| N9 | 0.0426 (17) | 0.0239 (14) | 0.0293 (14) | 0.0056 (12) | 0.0133 (12) | 0.0147 (12) |
| C1 | 0.043 (2) | 0.0262 (17) | 0.0261 (17) | 0.0123 (15) | 0.0121 (15) | 0.0143 (15) |
| C2 | 0.044 (2) | 0.0221 (16) | 0.0274 (17) | 0.0042 (15) | 0.0093 (15) | 0.0119 (14) |
| C3 | 0.0387 (19) | 0.0247 (17) | 0.0249 (16) | 0.0075 (14) | 0.0106 (14) | 0.0134 (14) |
| C4 | 0.042 (2) | 0.0221 (16) | 0.0261 (17) | 0.0081 (14) | 0.0122 (14) | 0.0087 (14) |
| C5 | 0.0412 (19) | 0.0190 (16) | 0.0316 (17) | 0.0082 (14) | 0.0128 (15) | 0.0119 (14) |
| C6 | 0.0326 (18) | 0.0267 (17) | 0.0235 (16) | 0.0092 (14) | 0.0116 (13) | 0.0132 (14) |
| C7 | 0.050 (2) | 0.0246 (17) | 0.0223 (16) | 0.0063 (15) | 0.0118 (15) | 0.0086 (14) |
| C8 | 0.049 (2) | 0.0179 (16) | 0.0316 (18) | 0.0037 (15) | 0.0121 (16) | 0.0094 (14) |
| C9 | 0.0363 (18) | 0.0234 (17) | 0.0245 (16) | 0.0080 (14) | 0.0089 (14) | 0.0111 (14) |
| C10 | 0.0357 (19) | 0.0256 (17) | 0.0293 (17) | 0.0079 (14) | 0.0114 (14) | 0.0137 (14) |
| C11 | 0.0315 (17) | 0.0240 (16) | 0.0250 (16) | 0.0059 (13) | 0.0099 (13) | 0.0133 (14) |
| C12 | 0.046 (2) | 0.0250 (17) | 0.0211 (15) | 0.0092 (15) | 0.0134 (14) | 0.0092 (14) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C13 | 0.050 (2) | 0.0209 (16) | 0.0306 (17) | 0.0120 (15) | 0.0156 (15) | 0.0126 (14) |
| C14 | 0.0371 (18) | 0.0245 (16) | 0.0211 (15) | 0.0062 (14) | 0.0111 (13) | 0.0128 (13) |
| C15 | 0.047 (2) | 0.0236 (17) | 0.0259 (17) | 0.0085 (15) | 0.0163 (15) | 0.0074 (14) |
| C16 | 0.048 (2) | 0.0191 (16) | 0.0296 (17) | 0.0078 (14) | 0.0133 (15) | 0.0132 (14) |
| C17 | 0.0397 (19) | 0.0259 (17) | 0.0288 (17) | 0.0040 (15) | 0.0122 (15) | 0.0116 (15) |
| C18 | 0.0333 (18) | 0.0267 (17) | 0.0289 (17) | 0.0061 (14) | 0.0096 (14) | 0.0131 (14) |
| C19 | 0.0337 (18) | 0.0221 (16) | 0.0242 (16) | 0.0019 (13) | 0.0079 (13) | 0.0098 (13) |
| C20 | 0.042 (2) | 0.0212 (16) | 0.0262 (16) | 0.0048 (14) | 0.0140 (14) | 0.0094 (14) |
| C21 | 0.0408 (19) | 0.0205 (16) | 0.0300 (17) | 0.0070 (14) | 0.0141 (14) | 0.0111 (14) |
| C22 | 0.0361 (18) | 0.0240 (16) | 0.0242 (16) | 0.0036 (14) | 0.0103 (14) | 0.0115 (14) |
| C23 | 0.0405 (19) | 0.0252 (17) | 0.0245 (16) | 0.0092 (15) | 0.0131 (14) | 0.0084 (14) |
| C24 | 0.0375 (19) | 0.0248 (17) | 0.0281 (17) | 0.0067 (14) | 0.0089 (14) | 0.0103 (14) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| S1—C1 | 1.693 (3) | N9—C18 | 1.270 (4) |
| S2—C9 | 1.689 (3) | C2—C3 | 1.453 (4) |
| S3—C17 | 1.680 (3) | C2—H2 | 0.9500 |
| O1—C5 | 1.372 (4) | C3—C4 | 1.391 (4) |
| O1—H1O | 0.837 (10) | C3—C8 | 1.393 (4) |
| O2—C6 | 1.369 (4) | C4—C5 | 1.372 (4) |
| O2—H2O | 0.840 (10) | C4—H4 | 0.9500 |
| O3—C13 | 1.358 (4) | C5—C6 | 1.392 (4) |
| O3—H3O | 0.836 (10) | C6—C7 | 1.371 (4) |
| O4—C14 | 1.367 (4) | C7—C8 | 1.387 (4) |
| O4—H4O | 0.841 (10) | C7—H7C | 0.9500 |
| O5—C21 | 1.368 (4) | C8—H8 | 0.9500 |
| O5—H5O | 0.838 (10) | C10—C11 | 1.450 (4) |
| O6—C22 | 1.364 (4) | C10—H10 | 0.9500 |
| O6—H6O | 0.844 (10) | C11—C16 | 1.385 (4) |
| N1—C1 | 1.316 (4) | C11—C12 | 1.390 (4) |
| N1—H1N1 | 0.8800 | C12—C13 | 1.369 (4) |
| N1—H1N2 | 0.8800 | C12—H12 | 0.9500 |
| N2—C1 | 1.341 (4) | C13—C14 | 1.396 (4) |
| N2—N3 | 1.375 (3) | C14—C15 | 1.375 (4) |
| N2—H2N | 0.8800 | C15—C16 | 1.385 (4) |
| N3—C2 | 1.269 (4) | C15—H15 | 0.9500 |
| N4—C9 | 1.316 (4) | C16—H16 | 0.9500 |
| N4—H4N1 | 0.8800 | C18—C19 | 1.457 (4) |
| N4—H4N2 | 0.8800 | C18—H18 | 0.9500 |
| N5—C9 | 1.335 (4) | C19—C24 | 1.384 (4) |
| N5—N6 | 1.377 (3) | C19—C20 | 1.397 (4) |
| N5—H5N | 0.8800 | C20—C21 | 1.368 (4) |
| N6—C10 | 1.276 (4) | C20—H20 | 0.9500 |
| N7—C17 | 1.316 (4) | C21—C22 | 1.390 (4) |
| N7—H7N1 | 0.8800 | C22—C23 | 1.380 (4) |
| N7—H7N2 | 0.8800 | C23—C24 | 1.386 (4) |
| N8—C17 | 1.344 (4) | C23—H23 | 0.9500 |
| N8—N9 | 1.380 (3) | C24—H24 | 0.9500 |

| | | | |
|---|---|---|---|
| N8—H8N | 0.8800 | | |
| C5—O1—H1O | 115 (3) | C3—C8—H8 | 119.6 |
| C6—O2—H2O | 107 (3) | N4—C9—N5 | 116.7 (3) |
| C13—O3—H3O | 106 (4) | N4—C9—S2 | 123.5 (2) |
| C14—O4—H4O | 107 (3) | N5—C9—S2 | 119.8 (2) |
| C21—O5—H5O | 103 (3) | N6—C10—C11 | 121.2 (3) |
| C22—O6—H6O | 112 (3) | N6—C10—H10 | 119.4 |
| C1—N1—H1N1 | 120.0 | C11—C10—H10 | 119.4 |
| C1—N1—H1N2 | 120.0 | C16—C11—C12 | 119.0 (3) |
| H1N1—N1—H1N2 | 120.0 | C16—C11—C10 | 118.9 (3) |
| C1—N2—N3 | 118.9 (3) | C12—C11—C10 | 122.0 (3) |
| C1—N2—H2N | 120.5 | C13—C12—C11 | 120.3 (3) |
| N3—N2—H2N | 120.5 | C13—C12—H12 | 119.8 |
| C2—N3—N2 | 116.4 (3) | C11—C12—H12 | 119.8 |
| C9—N4—H4N1 | 120.0 | O3—C13—C12 | 118.8 (3) |
| C9—N4—H4N2 | 120.0 | O3—C13—C14 | 120.7 (3) |
| H4N1—N4—H4N2 | 120.0 | C12—C13—C14 | 120.5 (3) |
| C9—N5—N6 | 118.9 (3) | O4—C14—C15 | 124.2 (3) |
| C9—N5—H5N | 120.6 | O4—C14—C13 | 116.4 (3) |
| N6—N5—H5N | 120.6 | C15—C14—C13 | 119.4 (3) |
| C10—N6—N5 | 116.1 (3) | C14—C15—C16 | 120.0 (3) |
| C17—N7—H7N1 | 120.0 | C14—C15—H15 | 120.0 |
| C17—N7—H7N2 | 120.0 | C16—C15—H15 | 120.0 |
| H7N1—N7—H7N2 | 120.0 | C15—C16—C11 | 120.6 (3) |
| C17—N8—N9 | 119.0 (3) | C15—C16—H16 | 119.7 |
| C17—N8—H8N | 120.5 | C11—C16—H16 | 119.7 |
| N9—N8—H8N | 120.5 | N7—C17—N8 | 115.9 (3) |
| C18—N9—N8 | 115.9 (3) | N7—C17—S3 | 124.0 (3) |
| N1—C1—N2 | 116.6 (3) | N8—C17—S3 | 120.0 (3) |
| N1—C1—S1 | 123.3 (2) | N9—C18—C19 | 121.1 (3) |
| N2—C1—S1 | 120.1 (2) | N9—C18—H18 | 119.5 |
| N3—C2—C3 | 121.7 (3) | C19—C18—H18 | 119.5 |
| N3—C2—H2 | 119.2 | C24—C19—C20 | 118.6 (3) |
| C3—C2—H2 | 119.2 | C24—C19—C18 | 119.6 (3) |
| C4—C3—C8 | 118.5 (3) | C20—C19—C18 | 121.8 (3) |
| C4—C3—C2 | 122.7 (3) | C21—C20—C19 | 120.4 (3) |
| C8—C3—C2 | 118.8 (3) | C21—C20—H20 | 119.8 |
| C5—C4—C3 | 120.7 (3) | C19—C20—H20 | 119.8 |
| C5—C4—H4 | 119.7 | O5—C21—C20 | 119.0 (3) |
| C3—C4—H4 | 119.7 | O5—C21—C22 | 120.3 (3) |
| O1—C5—C4 | 118.7 (3) | C20—C21—C22 | 120.6 (3) |
| O1—C5—C6 | 121.0 (3) | O6—C22—C23 | 123.8 (3) |
| C4—C5—C6 | 120.3 (3) | O6—C22—C21 | 116.6 (3) |
| O2—C6—C7 | 123.0 (3) | C23—C22—C21 | 119.6 (3) |
| O2—C6—C5 | 117.1 (3) | C22—C23—C24 | 119.5 (3) |
| C7—C6—C5 | 119.9 (3) | C22—C23—H23 | 120.2 |
| C6—C7—C8 | 119.8 (3) | C24—C23—H23 | 120.2 |
| C6—C7—H7C | 120.1 | C19—C24—C23 | 121.2 (3) |
| C8—C7—H7C | 120.1 | C19—C24—H24 | 119.4 |

| | | | |
|---|---|---|---|
| C7—C8—C3 | 120.8 (3) | C23—C24—H24 | 119.4 |
| C7—C8—H8 | 119.6 | | |

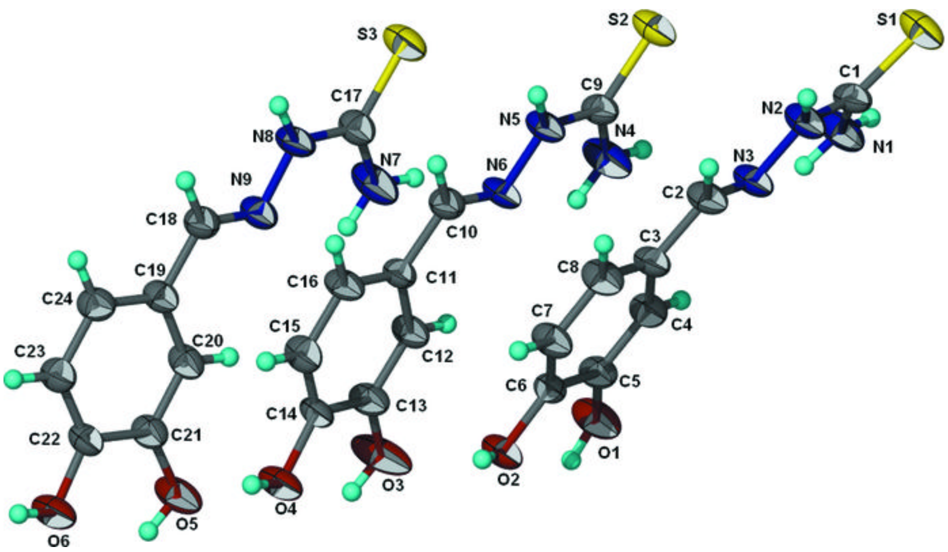
| | | | |
|---|---|---|---|
| C1—N2—N3—C2 | −176.9 (3) | C11—C12—C13—C14 | −1.3 (5) |
| C9—N5—N6—C10 | −175.5 (3) | O3—C13—C14—O4 | 1.2 (5) |
| C17—N8—N9—C18 | 179.2 (3) | C12—C13—C14—O4 | −177.4 (3) |
| N3—N2—C1—N1 | 5.5 (5) | O3—C13—C14—C15 | −177.8 (3) |
| N3—N2—C1—S1 | −175.4 (2) | C12—C13—C14—C15 | 3.7 (5) |
| N2—N3—C2—C3 | −177.5 (3) | O4—C14—C15—C16 | 178.4 (3) |
| N3—C2—C3—C4 | 2.9 (5) | C13—C14—C15—C16 | −2.7 (5) |
| N3—C2—C3—C8 | −179.7 (3) | C14—C15—C16—C11 | −0.5 (5) |
| C8—C3—C4—C5 | −0.8 (5) | C12—C11—C16—C15 | 2.9 (5) |
| C2—C3—C4—C5 | 176.6 (3) | C10—C11—C16—C15 | −173.6 (3) |
| C3—C4—C5—O1 | −179.9 (3) | N9—N8—C17—N7 | 3.0 (5) |
| C3—C4—C5—C6 | −0.4 (5) | N9—N8—C17—S3 | −177.6 (2) |
| O1—C5—C6—O2 | 0.4 (5) | N8—N9—C18—C19 | −177.0 (3) |
| C4—C5—C6—O2 | −179.1 (3) | N9—C18—C19—C24 | −176.7 (3) |
| O1—C5—C6—C7 | −179.3 (3) | N9—C18—C19—C20 | 5.3 (5) |
| C4—C5—C6—C7 | 1.2 (5) | C24—C19—C20—C21 | −2.5 (5) |
| O2—C6—C7—C8 | 179.5 (3) | C18—C19—C20—C21 | 175.5 (3) |
| C5—C6—C7—C8 | −0.9 (5) | C19—C20—C21—O5 | −176.6 (3) |
| C6—C7—C8—C3 | −0.3 (5) | C19—C20—C21—C22 | 1.1 (5) |
| C4—C3—C8—C7 | 1.1 (5) | O5—C21—C22—O6 | −1.2 (5) |
| C2—C3—C8—C7 | −176.4 (3) | C20—C21—C22—O6 | −178.8 (3) |
| N6—N5—C9—N4 | 0.9 (5) | O5—C21—C22—C23 | 179.0 (3) |
| N6—N5—C9—S2 | 179.8 (2) | C20—C21—C22—C23 | 1.4 (5) |
| N5—N6—C10—C11 | −176.7 (3) | O6—C22—C23—C24 | 177.8 (3) |
| N6—C10—C11—C16 | 175.3 (3) | C21—C22—C23—C24 | −2.5 (5) |
| N6—C10—C11—C12 | −1.1 (5) | C20—C19—C24—C23 | 1.4 (5) |
| C16—C11—C12—C13 | −2.0 (5) | C18—C19—C24—C23 | −176.6 (3) |
| C10—C11—C12—C13 | 174.4 (3) | C22—C23—C24—C19 | 1.0 (5) |
| C11—C12—C13—O3 | −179.9 (3) | | |

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1—H1o···O6$^{i}$ | 0.84 (1) | 2.07 (3) | 2.784 (3) | 143 (4) |
| O2—H2o···S1$^{ii}$ | 0.84 (1) | 2.47 (1) | 3.300 (2) | 171 (4) |
| N1—H1n2···O5$^{iii}$ | 0.88 | 2.00 | 2.856 (4) | 163 |
| O3—H3o···O4$^{i}$ | 0.84 (1) | 2.11 (4) | 2.732 (3) | 130 (4) |
| O4—H4o···S2$^{ii}$ | 0.84 (1) | 2.38 (1) | 3.219 (2) | 174 (4) |
| N4—H4n2···O3$^{iii}$ | 0.88 | 2.05 | 2.900 (4) | 162 |
| O5—H5o···O2$^{i}$ | 0.84 (1) | 2.16 (4) | 2.742 (3) | 127 (4) |
| O6—H6o···S3$^{ii}$ | 0.84 (1) | 2.40 (1) | 3.244 (2) | 177 (4) |
| N7—H7n2···O1$^{iii}$ | 0.88 | 2.13 | 2.981 (4) | 161 |

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

**Fig. 1**


S3
S2
S1
C17
C9
C1
N8
N5
N4
N2
N7
N3
N1
N9
N6
C2
C18
C10
C3
C19
C16
C11
C8
C24
C4
C7
C20
C15
C23
C12
C5
C6
C13
C14
C22
C21
O1
O3
O2
O4
O5
O6