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1-(2,3,4-Trihydroxybenzylidene)thiosemicarbazide

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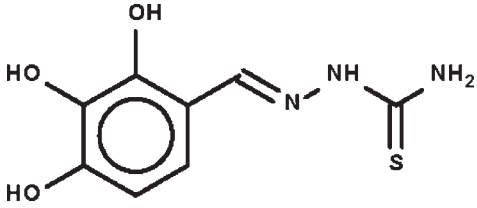
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.003 Å; R factor = 0.042; wR factor = 0.114; data-to-parameter ratio = 13.2.

In the title molecule, $C_8H_9N_3O_3S$, the thiosemicarbazide ═N—NH—C(═S)—NH— fragment is twist a different degree of twist in the three independent molecules [dihedral angles = 7.6 (1), 11.6 (1) and 20.7 (1)°]. Intramolecular O—H···N and O—H···O hydrogen bonds occur. In the crystal, the hydroxy and amino groups are hydrogen-bond donors and the O—H···O, O—H···S and N—H···O hydrogen bonds generate a layer motif.

Related literature

For the crystal structures of 2,4-dihydroxybenzaldehyde thiosemicarbazone and 3,4-dihydroxybenzaldehyde thiosemicarbazone, see: Swesi *et al.* (2006); Tan *et al.* (2008).



Experimental

Crystal data

$C_8H_9N_3O_3S$
M_r = 227.24
Triclinic, $P\overline{1}$
a = 10.3121 (10) Å
b = 11.8797 (12) Å
c = 12.4037 (12) Å
α = 68.969 (1)°
β = 87.487 (1)°
γ = 77.161 (1)°
V = 1381.8 (2) Å^3
Z = 6
Mo $K\alpha$ radiation
μ = 0.34 mm^{-1}
T = 100 K
0.35 × 0.10 × 0.02 mm

Data collection

Bruker SMART APEX diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.890, T_{max} = 0.993
13248 measured reflections
6327 independent reflections
4487 reflections with $I > 2\sigma(I)$
R_{int} = 0.033

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.114
S = 1.02
6327 reflections
478 parameters
18 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.38 e Å^{-3}
$\Delta\rho_{min}$ = −0.37 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···N1	0.84 (1)	1.94 (2)	2.682 (2)	147 (3)
O2—H2···O3^{i}	0.83 (1)	2.17 (2)	2.773 (2)	129 (3)
O3—H3···S1^{ii}	0.83 (1)	2.36 (1)	3.184 (2)	173 (3)
O4—H4···N4	0.84 (1)	1.96 (2)	2.666 (2)	141 (3)
O5—H5···O6	0.83 (1)	2.24 (3)	2.730 (2)	118 (3)
O6—H6···S2^{ii}	0.84 (1)	2.45 (1)	3.276 (2)	172 (2)
O7—H7···N7	0.83 (1)	1.97 (2)	2.710 (2)	148 (3)
O8—H8···O9	0.84 (1)	2.24 (3)	2.697 (2)	114 (2)
O9—H9···S3^{iii}	0.84 (1)	2.40 (1)	3.237 (2)	174 (2)
N3—H31···O2^{iv}	0.85 (1)	2.09 (1)	2.902 (2)	159 (3)
N6—H61···O8^{v}	0.86 (1)	2.01 (1)	2.847 (2)	164 (2)
N9—H91···O5^{vi}	0.86 (1)	2.11 (2)	2.896 (2)	153 (2)

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

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: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PK2242).

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supporting information

Acta Cryst. (2010). E**66**, o1278 [https://doi.org/10.1107/S1600536810015850]

1-(2,3,4-Trihydroxybenzylidene)thiosemicarbazide

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S1. Experimental

2,3,4-Trihydroxybenzaldehyde (1.54 g, 10 mmol) and thiosemicarbazide (0.91 g, 1 mmol) were heated in ethanol (20 ml). The cool solution was set aside for the growth of crystals.

S2. Refinement

Carbon-bound H-atoms were placed in calculated positions (C—H 0.95 to 0.98 Å) and were included in the refinement in the riding model approximation, with U(H) set to 1.2 or 1.5U(C_{Me}).

The amino and hydroxy H-atoms were located in a difference Fourier map, and were refined with distance restraints of N–H 0.86 (1) and O–H 0.84 (1) Å; their temperature factors were freely refined.

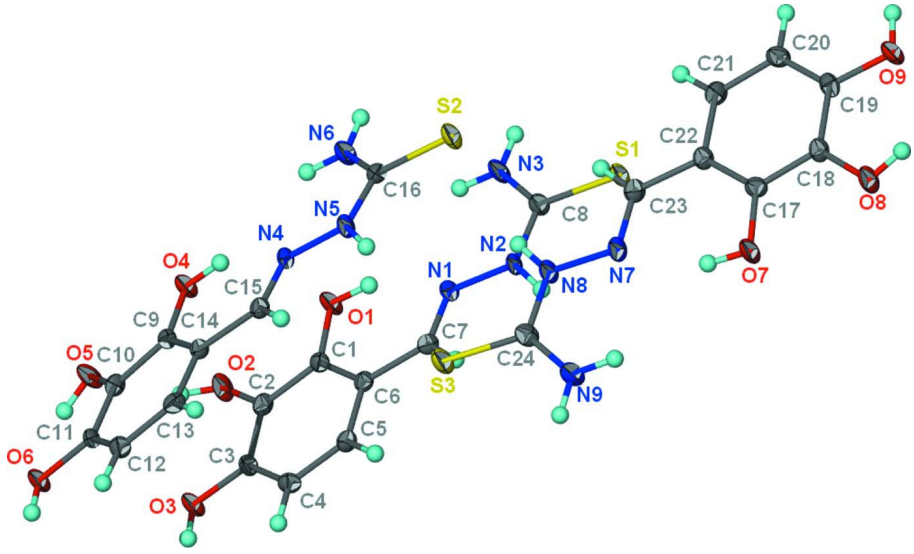

Figure 1

Thermal ellipsoid plot (Barbour, 2001) of the three independent molecules of $C_8H_9N_3O_3S$ at the 70% probability level; hydrogen atoms are drawn as spheres of arbitrary radius.

1-(2,3,4-Trihydroxybenzylidene)thiosemicarbazide

Crystal data

$C_8H_9N_3O_3S$
M_r = 227.24
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 10.3121 (10) Å
b = 11.8797 (12) Å
c = 12.4037 (12) Å
α = 68.969 (1)°
β = 87.487 (1)°
γ = 77.161 (1)°

V = 1381.8 (2) Å^3
Z = 6
F(000) = 708
D_x = 1.639 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2924 reflections
θ = 2.6–28.1°
μ = 0.34 mm^{-1}
T = 100 K
Plate, pale brown
0.35 × 0.10 × 0.02 mm

Data collection

Bruker SMART APEX diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.890, T_{max} = 0.993
13248 measured reflections
6327 independent reflections
4487 reflections with $I > 2\sigma(I)$
R_{int} = 0.033
θ_{max} = 27.5°, θ_{min} = 1.8°
h = −13→12
k = −15→15
l = −16→16

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.114
S = 1.02
6327 reflections
478 parameters
18 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0572P)^2 + 0.0368P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.38 e Å^{-3}
$\Delta\rho_{min}$ = −0.37 e Å^{-3}

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

	x	y	z	U_{iso}*/U_{eq}
S1	0.04483 (6)	0.85739 (5)	0.67520 (4)	0.01600 (14)
S2	0.39952 (6)	0.72567 (5)	0.55744 (5)	0.01715 (14)
S3	0.32855 (6)	1.02438 (5)	0.19484 (5)	0.01889 (15)
O1	0.02467 (17)	0.58729 (14)	0.32793 (12)	0.0171 (4)
H1	0.030 (3)	0.622 (2)	0.3749 (19)	0.033 (8)*
O2	−0.01767 (17)	0.52286 (14)	0.14650 (13)	0.0185 (4)
H2	0.023 (3)	0.489 (3)	0.103 (2)	0.048 (10)*
O3	0.00587 (16)	0.67307 (14)	−0.07208 (12)	0.0165 (3)
H3	0.019 (3)	0.725 (2)	−0.1352 (14)	0.031 (8)*
O4	0.30904 (16)	0.48727 (14)	0.20588 (12)	0.0159 (3)
H4	0.325 (3)	0.514 (3)	0.257 (2)	0.054 (10)*
O5	0.23954 (17)	0.43594 (14)	0.02850 (13)	0.0180 (4)
H5	0.218 (3)	0.438 (3)	−0.0364 (14)	0.063 (11)*
O6	0.30786 (16)	0.55735 (14)	−0.19098 (13)	0.0166 (3)
H6	0.326 (3)	0.607 (2)	−0.2539 (13)	0.030 (8)*
O7	0.27294 (17)	1.30858 (14)	0.54062 (13)	0.0184 (4)
H7	0.287 (3)	1.270 (2)	0.496 (2)	0.038 (9)*
O8	0.27623 (17)	1.38726 (14)	0.71552 (13)	0.0182 (4)
H8	0.284 (3)	1.399 (3)	0.7771 (16)	0.051 (10)*

O9	0.28539 (16)	1.23273 (14)	0.93746 (12)	0.0168 (3)
H9	0.294 (3)	1.1754 (17)	1.0024 (12)	0.025 (7)*
N1	0.05073 (18)	0.77060 (16)	0.39755 (14)	0.0124 (4)
N2	0.05168 (19)	0.83290 (16)	0.47275 (15)	0.0131 (4)
H21	0.045 (2)	0.9116 (10)	0.445 (2)	0.024 (7)*
N3	0.0408 (2)	0.65715 (17)	0.62610 (16)	0.0194 (4)
H31	0.033 (3)	0.620 (2)	0.6981 (10)	0.036 (8)*
H32	0.038 (2)	0.6192 (19)	0.5797 (17)	0.018 (7)*
N4	0.39153 (18)	0.64797 (15)	0.27613 (15)	0.0126 (4)
N5	0.40933 (19)	0.70383 (17)	0.35334 (15)	0.0135 (4)
H51	0.425 (3)	0.7772 (14)	0.324 (2)	0.045 (9)*
N6	0.3389 (2)	0.54900 (17)	0.49721 (16)	0.0177 (4)
H61	0.325 (2)	0.510 (2)	0.5681 (10)	0.020 (7)*
H62	0.334 (2)	0.515 (2)	0.4482 (16)	0.019 (7)*
N7	0.30054 (19)	1.11133 (16)	0.47366 (15)	0.0153 (4)
N8	0.3167 (2)	1.04604 (17)	0.39915 (15)	0.0163 (4)
H81	0.337 (2)	0.9667 (9)	0.425 (2)	0.019 (7)*
N9	0.2893 (2)	1.22846 (17)	0.24562 (16)	0.0200 (4)
H91	0.284 (2)	1.270 (2)	0.1728 (9)	0.024 (7)*
H92	0.278 (3)	1.265 (2)	0.2949 (18)	0.034 (8)*
C1	0.0359 (2)	0.66793 (19)	0.21952 (17)	0.0121 (4)
C2	0.0183 (2)	0.63384 (18)	0.12652 (18)	0.0129 (4)
C3	0.0300 (2)	0.71265 (19)	0.01372 (17)	0.0123 (4)
C4	0.0646 (2)	0.82510 (19)	−0.00648 (18)	0.0139 (5)
H4A	0.0770	0.8772	−0.0829	0.017*
C5	0.0806 (2)	0.85971 (19)	0.08633 (17)	0.0129 (4)
H5A	0.1033	0.9368	0.0726	0.015*
C6	0.0645 (2)	0.78427 (19)	0.19995 (17)	0.0117 (4)
C7	0.0709 (2)	0.83158 (19)	0.29141 (17)	0.0123 (4)
H7A	0.0908	0.9106	0.2726	0.015*
C8	0.0451 (2)	0.77519 (19)	0.58732 (18)	0.0136 (5)
C9	0.3408 (2)	0.55759 (19)	0.09885 (17)	0.0125 (4)
C10	0.3076 (2)	0.52858 (18)	0.00573 (18)	0.0129 (4)
C11	0.3422 (2)	0.59381 (19)	−0.10491 (17)	0.0120 (4)
C12	0.4069 (2)	0.68949 (19)	−0.12458 (18)	0.0138 (5)
H12	0.4322	0.7323	−0.2002	0.017*
C13	0.4343 (2)	0.72205 (19)	−0.03270 (18)	0.0135 (4)
H13	0.4767	0.7889	−0.0463	0.016*
C14	0.4006 (2)	0.65829 (19)	0.07964 (17)	0.0119 (4)
C15	0.4214 (2)	0.70176 (19)	0.17123 (18)	0.0126 (4)
H15	0.4584	0.7725	0.1532	0.015*
C16	0.3804 (2)	0.65349 (19)	0.46518 (18)	0.0130 (4)
C17	0.2798 (2)	1.22282 (19)	0.64927 (18)	0.0135 (4)
C18	0.2795 (2)	1.26454 (19)	0.74128 (18)	0.0134 (5)
C19	0.2838 (2)	1.1822 (2)	0.85449 (18)	0.0134 (4)
C20	0.2863 (2)	1.0579 (2)	0.87772 (18)	0.0152 (5)
H20	0.2871	1.0021	0.9551	0.018*
C21	0.2877 (2)	1.0171 (2)	0.78646 (18)	0.0153 (5)

H21a	0.2898	0.9324	0.8020	0.018*
C22	0.2860 (2)	1.09729 (19)	0.67167 (18)	0.0133 (4)
C23	0.2966 (2)	1.0449 (2)	0.58130 (18)	0.0146 (5)
H23	0.3008	0.9590	0.6023	0.018*
C24	0.3104 (2)	1.1070 (2)	0.28385 (18)	0.0149 (5)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0281 (4)	0.0122 (3)	0.0102 (2)	−0.0063 (2)	0.0013 (2)	−0.0060 (2)
S2	0.0270 (4)	0.0164 (3)	0.0125 (3)	−0.0084 (2)	0.0028 (2)	−0.0086 (2)
S3	0.0312 (4)	0.0155 (3)	0.0128 (3)	−0.0074 (2)	0.0010 (2)	−0.0070 (2)
O1	0.0326 (10)	0.0128 (8)	0.0088 (7)	−0.0099 (7)	0.0009 (7)	−0.0042 (6)
O2	0.0340 (11)	0.0120 (8)	0.0157 (8)	−0.0124 (7)	0.0038 (7)	−0.0083 (6)
O3	0.0283 (10)	0.0156 (8)	0.0096 (7)	−0.0104 (7)	0.0011 (7)	−0.0059 (6)
O4	0.0279 (10)	0.0134 (8)	0.0093 (7)	−0.0097 (7)	0.0017 (6)	−0.0046 (6)
O5	0.0321 (10)	0.0160 (8)	0.0105 (7)	−0.0138 (7)	−0.0001 (7)	−0.0052 (6)
O6	0.0286 (10)	0.0147 (8)	0.0097 (7)	−0.0082 (7)	0.0000 (7)	−0.0061 (6)
O7	0.0345 (11)	0.0124 (8)	0.0108 (7)	−0.0075 (7)	0.0019 (7)	−0.0060 (6)
O8	0.0319 (10)	0.0132 (8)	0.0141 (8)	−0.0097 (7)	0.0035 (7)	−0.0079 (6)
O9	0.0257 (10)	0.0178 (8)	0.0099 (7)	−0.0080 (7)	0.0008 (7)	−0.0066 (6)
N1	0.0151 (10)	0.0125 (9)	0.0122 (9)	−0.0039 (7)	−0.0017 (7)	−0.0068 (7)
N2	0.0222 (11)	0.0088 (9)	0.0109 (8)	−0.0041 (8)	−0.0001 (7)	−0.0063 (7)
N3	0.0399 (13)	0.0113 (9)	0.0096 (9)	−0.0090 (9)	−0.0003 (9)	−0.0047 (7)
N4	0.0171 (10)	0.0107 (9)	0.0128 (9)	−0.0025 (7)	−0.0020 (7)	−0.0075 (7)
N5	0.0200 (11)	0.0111 (9)	0.0135 (9)	−0.0057 (8)	0.0003 (7)	−0.0079 (7)
N6	0.0321 (12)	0.0126 (9)	0.0107 (9)	−0.0083 (8)	0.0021 (8)	−0.0049 (8)
N7	0.0226 (11)	0.0114 (9)	0.0154 (9)	−0.0053 (8)	0.0004 (8)	−0.0082 (7)
N8	0.0303 (12)	0.0092 (9)	0.0117 (9)	−0.0059 (8)	0.0005 (8)	−0.0056 (7)
N9	0.0373 (13)	0.0114 (9)	0.0119 (9)	−0.0077 (9)	−0.0011 (9)	−0.0034 (8)
C1	0.0140 (12)	0.0109 (10)	0.0107 (10)	−0.0023 (8)	0.0013 (8)	−0.0035 (8)
C2	0.0151 (12)	0.0091 (10)	0.0156 (10)	−0.0040 (8)	0.0003 (9)	−0.0048 (8)
C3	0.0131 (12)	0.0138 (10)	0.0118 (10)	−0.0033 (9)	0.0002 (8)	−0.0065 (8)
C4	0.0166 (12)	0.0126 (10)	0.0109 (10)	−0.0040 (9)	0.0014 (8)	−0.0018 (8)
C5	0.0161 (12)	0.0087 (10)	0.0146 (10)	−0.0035 (8)	−0.0004 (8)	−0.0044 (8)
C6	0.0117 (11)	0.0104 (10)	0.0137 (10)	−0.0022 (8)	−0.0005 (8)	−0.0051 (8)
C7	0.0132 (12)	0.0102 (10)	0.0143 (10)	−0.0039 (8)	−0.0018 (8)	−0.0044 (8)
C8	0.0165 (12)	0.0136 (10)	0.0121 (10)	−0.0044 (9)	0.0006 (8)	−0.0056 (8)
C9	0.0150 (12)	0.0112 (10)	0.0104 (9)	−0.0009 (8)	0.0011 (8)	−0.0040 (8)
C10	0.0169 (12)	0.0077 (10)	0.0150 (10)	−0.0043 (9)	0.0004 (8)	−0.0042 (8)
C11	0.0161 (12)	0.0107 (10)	0.0109 (10)	−0.0014 (8)	−0.0020 (8)	−0.0064 (8)
C12	0.0165 (12)	0.0125 (10)	0.0124 (10)	−0.0039 (9)	0.0015 (8)	−0.0041 (8)
C13	0.0132 (12)	0.0111 (10)	0.0156 (10)	−0.0022 (8)	−0.0016 (8)	−0.0040 (8)
C14	0.0135 (12)	0.0105 (10)	0.0129 (10)	−0.0018 (8)	−0.0020 (8)	−0.0056 (8)
C15	0.0138 (12)	0.0108 (10)	0.0144 (10)	−0.0021 (8)	−0.0016 (8)	−0.0059 (8)
C16	0.0143 (12)	0.0113 (10)	0.0128 (10)	−0.0006 (9)	−0.0007 (8)	−0.0046 (8)
C17	0.0160 (12)	0.0123 (10)	0.0116 (10)	−0.0041 (9)	0.0001 (8)	−0.0031 (8)
C18	0.0163 (12)	0.0120 (10)	0.0148 (10)	−0.0057 (9)	0.0017 (9)	−0.0067 (8)

C19	0.0118 (12)	0.0181 (11)	0.0134 (10)	−0.0050 (9)	0.0033 (8)	−0.0085 (9)
C20	0.0179 (13)	0.0149 (11)	0.0112 (10)	−0.0045 (9)	0.0011 (9)	−0.0025 (8)
C21	0.0202 (13)	0.0102 (10)	0.0161 (11)	−0.0048 (9)	0.0007 (9)	−0.0044 (8)
C22	0.0148 (12)	0.0125 (10)	0.0145 (10)	−0.0045 (9)	0.0005 (8)	−0.0063 (8)
C23	0.0171 (12)	0.0123 (10)	0.0165 (11)	−0.0046 (9)	−0.0007 (9)	−0.0066 (9)
C24	0.0174 (12)	0.0155 (11)	0.0136 (10)	−0.0068 (9)	0.0002 (9)	−0.0052 (9)

Geometric parameters (Å, º)

S1—C8	1.704 (2)	N7—N8	1.388 (2)
S2—C16	1.698 (2)	N8—C24	1.348 (3)
S3—C24	1.702 (2)	N8—H81	0.858 (10)
O1—C1	1.360 (2)	N9—C24	1.316 (3)
O1—H1	0.836 (10)	N9—H91	0.857 (10)
O2—C2	1.383 (2)	N9—H92	0.861 (10)
O2—H2	0.834 (10)	C1—C2	1.383 (3)
O3—C3	1.360 (2)	C1—C6	1.411 (3)
O3—H3	0.833 (10)	C2—C3	1.394 (3)
O4—C9	1.362 (2)	C3—C4	1.392 (3)
O4—H4	0.835 (10)	C4—C5	1.381 (3)
O5—C10	1.374 (2)	C4—H4A	0.9500
O5—H5	0.831 (10)	C5—C6	1.399 (3)
O6—C11	1.373 (2)	C5—H5A	0.9500
O6—H6	0.835 (10)	C6—C7	1.445 (3)
O7—C17	1.360 (2)	C7—H7A	0.9500
O7—H7	0.830 (10)	C9—C10	1.394 (3)
O8—C18	1.369 (2)	C9—C14	1.406 (3)
O8—H8	0.837 (10)	C10—C11	1.389 (3)
O9—C19	1.367 (2)	C11—C12	1.385 (3)
O9—H9	0.840 (10)	C12—C13	1.386 (3)
N1—C7	1.288 (3)	C12—H12	0.9500
N1—N2	1.385 (2)	C13—C14	1.398 (3)
N2—C8	1.344 (3)	C13—H13	0.9500
N2—H21	0.860 (10)	C14—C15	1.447 (3)
N3—C8	1.320 (3)	C15—H15	0.9500
N3—H31	0.851 (10)	C17—C18	1.398 (3)
N3—H32	0.853 (10)	C17—C22	1.402 (3)
N4—C15	1.285 (3)	C18—C19	1.390 (3)
N4—N5	1.385 (2)	C19—C20	1.394 (3)
N5—C16	1.349 (3)	C20—C21	1.380 (3)
N5—H51	0.865 (10)	C20—H20	0.9500
N6—C16	1.323 (3)	C21—C22	1.399 (3)
N6—H61	0.858 (10)	C21—H21a	0.9500
N6—H62	0.849 (10)	C22—C23	1.454 (3)
N7—C23	1.288 (3)	C23—H23	0.9500
C1—O1—H1	108.4 (19)	N3—C8—N2	118.19 (19)
C2—O2—H2	110 (2)	N3—C8—S1	123.33 (16)

C3—O3—H3	108.4 (19)	N2—C8—S1	118.47 (16)
C9—O4—H4	112 (2)	O4—C9—C10	117.13 (19)
C10—O5—H5	104 (2)	O4—C9—C14	122.83 (19)
C11—O6—H6	107.5 (19)	C10—C9—C14	120.01 (19)
C17—O7—H7	106 (2)	O5—C10—C11	122.75 (19)
C18—O8—H8	109 (2)	O5—C10—C9	117.48 (19)
C19—O9—H9	108.1 (18)	C11—C10—C9	119.76 (19)
C7—N1—N2	114.97 (17)	O6—C11—C12	123.38 (19)
C8—N2—N1	120.71 (17)	O6—C11—C10	115.75 (19)
C8—N2—H21	119.4 (17)	C12—C11—C10	120.87 (19)
N1—N2—H21	119.2 (17)	C13—C12—C11	119.3 (2)
C8—N3—H31	119.2 (19)	C13—C12—H12	120.3
C8—N3—H32	121.1 (16)	C11—C12—H12	120.3
H31—N3—H32	119 (2)	C12—C13—C14	121.2 (2)
C15—N4—N5	116.06 (18)	C12—C13—H13	119.4
C16—N5—N4	119.95 (18)	C14—C13—H13	119.4
C16—N5—H51	122.7 (19)	C13—C14—C9	118.70 (19)
N4—N5—H51	116.4 (19)	C13—C14—C15	119.20 (19)
C16—N6—H61	121.8 (17)	C9—C14—C15	122.01 (19)
C16—N6—H62	119.6 (17)	N4—C15—C14	122.3 (2)
H61—N6—H62	118 (2)	N4—C15—H15	118.9
C23—N7—N8	114.78 (18)	C14—C15—H15	118.9
C24—N8—N7	120.06 (18)	N6—C16—N5	117.59 (19)
C24—N8—H81	118.3 (16)	N6—C16—S2	123.38 (16)
N7—N8—H81	121.4 (16)	N5—C16—S2	119.03 (16)
C24—N9—H91	120.2 (17)	O7—C17—C18	117.13 (19)
C24—N9—H92	118.8 (18)	O7—C17—C22	123.12 (19)
H91—N9—H92	121 (2)	C18—C17—C22	119.74 (19)
O1—C1—C2	118.45 (19)	O8—C18—C19	122.09 (19)
O1—C1—C6	121.89 (18)	O8—C18—C17	117.80 (18)
C2—C1—C6	119.65 (19)	C19—C18—C17	120.11 (19)
O2—C2—C1	119.04 (18)	O9—C19—C18	115.08 (19)
O2—C2—C3	120.19 (18)	O9—C19—C20	124.29 (19)
C1—C2—C3	120.69 (19)	C18—C19—C20	120.6 (2)
O3—C3—C4	123.43 (18)	C21—C20—C19	118.9 (2)
O3—C3—C2	116.36 (18)	C21—C20—H20	120.5
C4—C3—C2	120.20 (19)	C19—C20—H20	120.5
C5—C4—C3	119.01 (19)	C20—C21—C22	121.8 (2)
C5—C4—H4A	120.5	C20—C21—H21a	119.1
C3—C4—H4A	120.5	C22—C21—H21a	119.1
C4—C5—C6	121.78 (19)	C21—C22—C17	118.79 (19)
C4—C5—H5A	119.1	C21—C22—C23	118.05 (19)
C6—C5—H5A	119.1	C17—C22—C23	123.11 (19)
C5—C6—C1	118.54 (19)	N7—C23—C22	122.12 (19)
C5—C6—C7	118.53 (19)	N7—C23—H23	118.9
C1—C6—C7	122.85 (19)	C22—C23—H23	118.9
N1—C7—C6	122.49 (19)	N9—C24—N8	118.0 (2)
N1—C7—H7A	118.8	N9—C24—S3	123.12 (17)

C6—C7—H7A	118.8	N8—C24—S3	118.90 (16)
C7—N1—N2—C8	−173.3 (2)	C11—C12—C13—C14	1.5 (3)
C15—N4—N5—C16	179.99 (19)	C12—C13—C14—C9	1.6 (3)
C23—N7—N8—C24	174.1 (2)	C12—C13—C14—C15	−175.1 (2)
O1—C1—C2—O2	3.8 (3)	O4—C9—C14—C13	177.55 (19)
C6—C1—C2—O2	−176.09 (19)	C10—C9—C14—C13	−4.6 (3)
O1—C1—C2—C3	−179.37 (19)	O4—C9—C14—C15	−5.9 (3)
C6—C1—C2—C3	0.8 (3)	C10—C9—C14—C15	172.0 (2)
O2—C2—C3—O3	−0.7 (3)	N5—N4—C15—C14	−176.27 (18)
C1—C2—C3—O3	−177.53 (19)	C13—C14—C15—N4	179.4 (2)
O2—C2—C3—C4	179.20 (19)	C9—C14—C15—N4	2.9 (3)
C1—C2—C3—C4	2.4 (3)	N4—N5—C16—N6	1.8 (3)
O3—C3—C4—C5	176.8 (2)	N4—N5—C16—S2	−178.53 (15)
C2—C3—C4—C5	−3.1 (3)	O7—C17—C18—O8	−1.8 (3)
C3—C4—C5—C6	0.7 (3)	C22—C17—C18—O8	178.62 (19)
C4—C5—C6—C1	2.4 (3)	O7—C17—C18—C19	178.8 (2)
C4—C5—C6—C7	−174.4 (2)	C22—C17—C18—C19	−0.8 (3)
O1—C1—C6—C5	177.06 (19)	O8—C18—C19—O9	−0.4 (3)
C2—C1—C6—C5	−3.1 (3)	C17—C18—C19—O9	178.91 (19)
O1—C1—C6—C7	−6.3 (3)	O8—C18—C19—C20	179.7 (2)
C2—C1—C6—C7	173.6 (2)	C17—C18—C19—C20	−1.0 (3)
N2—N1—C7—C6	−175.78 (18)	O9—C19—C20—C21	−178.4 (2)
C5—C6—C7—N1	176.6 (2)	C18—C19—C20—C21	1.5 (3)
C1—C6—C7—N1	−0.1 (3)	C19—C20—C21—C22	−0.3 (3)
N1—N2—C8—N3	1.5 (3)	C20—C21—C22—C17	−1.4 (3)
N1—N2—C8—S1	−179.28 (15)	C20—C21—C22—C23	176.0 (2)
O4—C9—C10—O5	3.3 (3)	O7—C17—C22—C21	−177.6 (2)
C14—C9—C10—O5	−174.69 (19)	C18—C17—C22—C21	1.9 (3)
O4—C9—C10—C11	−177.45 (18)	O7—C17—C22—C23	5.2 (4)
C14—C9—C10—C11	4.5 (3)	C18—C17—C22—C23	−175.3 (2)
O5—C10—C11—O6	−2.0 (3)	N8—N7—C23—C22	177.28 (19)
C9—C10—C11—O6	178.77 (19)	C21—C22—C23—N7	−177.5 (2)
O5—C10—C11—C12	177.7 (2)	C17—C22—C23—N7	−0.3 (4)
C9—C10—C11—C12	−1.5 (3)	N7—N8—C24—N9	0.3 (3)
O6—C11—C12—C13	178.2 (2)	N7—N8—C24—S3	−179.20 (16)
C10—C11—C12—C13	−1.6 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···N1	0.84 (1)	1.94 (2)	2.682 (2)	147 (3)
O2—H2···O3^{i}	0.83 (1)	2.17 (2)	2.773 (2)	129 (3)
O3—H3···S1^{ii}	0.83 (1)	2.36 (1)	3.184 (2)	173 (3)
O4—H4···N4	0.84 (1)	1.96 (2)	2.666 (2)	141 (3)
O5—H5···O6	0.83 (1)	2.24 (3)	2.730 (2)	118 (3)
O6—H6···S2^{ii}	0.84 (1)	2.45 (1)	3.276 (2)	172 (2)
O7—H7···N7	0.83 (1)	1.97 (2)	2.710 (2)	148 (3)

O8—H8···O9	0.84 (1)	2.24 (3)	2.697 (2)	114 (2)
O9—H9···S3^{iii}	0.84 (1)	2.40 (1)	3.237 (2)	174 (2)
N3—H31···O2^{iv}	0.85 (1)	2.09 (1)	2.902 (2)	159 (3)
N6—H61···O8^{v}	0.86 (1)	2.01 (1)	2.847 (2)	164 (2)
N9—H91···O5^{vi}	0.86 (1)	2.11 (2)	2.896 (2)	153 (2)

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