Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Ethyl 2-[3-(4-nitrobenzoyl)thioureido]-benzoate

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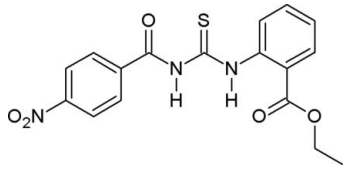
Received 11 March 2010; accepted 24 March 2010

Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.005 Å; R factor = 0.059; wR factor = 0.171; data-to-parameter ratio = 17.9.

In the title compound, $C_{17}H_{15}N_3O_5S$, the nitro and thioureido groups are twisted by 7.2 (7) and 21.4 (2)°, respectively, from the nitrobenzene ring plane whereas the thioureido and the ethyl ester group make dihedral angles of 43.0 (1) and 18.0 (2)°, respectively, with the benzene rings to which they are attached. Intramolecular N—H···O hydrogen-bonding interactions are observed. In the crystal, intermolecular N—H···O hydrogen bonds connect the molecules into chains running along the *a* axis.

Related literature

For general background to the chemistry of thiourea derivatives, see: Ugur *et al.* (2006). For related compounds with antitubercular properties, see: Huebner *et al.* (1953) and for other biological activities of thiourea compounds, see: Glasser & Doughty (1964). For related structures, see: Saeed *et al.* (2008*a*,*b*). For the cytotoxicity of anticancer drugs to normal cells in cancer therapy, see: Saeed *et al.* (2010). For the herbicidal activity of thiourea derivatives, see: Zheng *et al.* (2004).



Experimental

Crystal data

$C_{17}H_{15}N_3O_5S$
M_r = 373.38
Orthorhombic, *Pbca*
a = 9.0698 (13) Å
b = 15.778 (2) Å
c = 24.889 (4) Å
V = 3561.7 (9) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.22 mm^{-1}
T = 295 K
0.36 × 0.25 × 0.03 mm

Data collection

Bruker SMART 1000 CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.927, T_{max} = 0.994
23121 measured reflections
4362 independent reflections
2877 reflections with $I > 2\sigma(I)$
R_{int} = 0.032

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.171
S = 1.07
4362 reflections
244 parameters
6 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.63 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2*N*···O3^{i}	0.80 (4)	2.12 (4)	2.903 (3)	165 (3)
N3—H3*N*···O3	0.91 (3)	1.91 (3)	2.664 (3)	139 (3)
N3—H3*N*···O4	0.91 (3)	2.15 (3)	2.721 (3)	120 (2)

Symmetry code: (i) $x+\frac{1}{2}, y, -z+\frac{1}{2}$.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 2006); data reduction: *SAINT* and *CrystalStructure* (Rigaku/MSC and Rigaku, 2006); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

The authors are grateful to Allama Iqbal Open University, Islamabad, and The Hong Kong Polytechnic University for providing laboratory and analytical facilities.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SI2248).

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supporting information

Acta Cryst. (2010). E**66**, o980 [doi:10.1107/S1600536810011116]

Ethyl 2-[3-(4-nitrobenzoyl)thioureido]benzoate

Sohail Saeed, Naghmana Rashid and Wing-Tak Wong

S1. Comment

Industrial production and the use of transition elements can cause environmental pollution. However, some of these metals are present in trace amounts as essential elements for biological systems and also play an important role in bioinorganic chemistry. In order to understand the role of these metal ions in biological systems, structural studies of the biological compounds and their metal complexes are extremely important. Compounds containing carbonyl and thio-carbonyl groups occupy an important position among organic reagents as potential donor ligands for transition metal ions (Ugur *et al.*, 2006). Thioureas are also known to exhibit a wide range of biological activities including antiviral, antibacterial, anticancer (Saeed *et al.*, 2010), antifungal, antitubercular, antithyroidal, herbicidal and insecticidal activities (Huebner *et al.*, 1953) and as agrochemicals (Saeed *et al.*, 2008a). An example is furnished by 1- benzoyl-3-(4,5-disubstituted-pyrimidine-2-yl)- thioureas, which have excellent herbicidal activity (Zheng *et al.*, 2004). Thioureas are also well known chelating agents for transition metals and the complexes also show varied biological activities (Glasser & Doughty, 1964). Thioureas and substituted thioureas are also known as epoxy resin curing agents (Saeed *et al.*, 2008b). We became interested in the synthesis of N-aroyl, *N*′-arylthioureas as intermediates towards some new novel heterocycles and for the systematic study of their bioactive complexes and their function as epoxy resin curing agents. Here we present the structure of the title compound (I). The molecule is not planar. The nitro group is slightly twisted (7.2 (7)°) from the benzene ring plane of C1—C6. The thioureido group is 21.4 (1)° from the benzene ring plane of C1—C6 and 43.0 (1)° from the benzene ring plane of C9—C14. The ethyl ester group is twisted 18.0 (2)° from the benzene ring plane of C9—C14. Both intra- and inter-molecular N—H···O H-bond interactions are observed in the crystal lattice. The intermolecular N2—H2N···O3 H-bonding interactions, connect the molecules into 1-D chains running along the a-axis. There seems to be no significant $\pi\cdots\pi$ nor C—H$\cdots\pi$ interaction in the crystal lattice.

There is no residual solvent accessible void volume in the unit cell.

S2. Experimental

A solution of 4-nitrobenzoyl chloride (0.01 mol) in dry acetone (80 ml) was added dropwise to a suspension of ammonium thiocyanate (0.01 mol) in acetone (50 ml) and the reaction mixture was refluxed for 45 minutes. After cooling to room temperature, a solution of ethyl 2-aminobenzoate (0.01 mol) in acetone (25 ml) was added and the resulting mixture refluxed for 2 h. The reaction mixture was poured into five times its volume of cold water, upon which the thio-urea precipitated. The product was recrystallized from ethyl acetate as intensely yellow crystals.

S3. Refinement

All of the C-bound H atoms are observable from difference Fourier map but are all placed at geometrical positions with C—H = 0.93, 0.96 and 0.97Å for phenyl methyl and methylene H-atoms. All C-bound H-atoms are refined using riding model with U_{iso}(H) = 1.2U_{eq}(Carrier).

The N-bound H atoms are located from a difference Fourier map and refined isotropically. Six restraints are related to the refinement of O2 using isotropic restraints of standard deviation of 0.001 in the anisotropic atom displacement components.

Highest peak is 0.63 at (0.3420, 0.1232, 0.3759) [0.84Å from O2] Deepest hole is -0.32 at (0.3460, 0.0919, 0.4004) [0.36Å from O2]

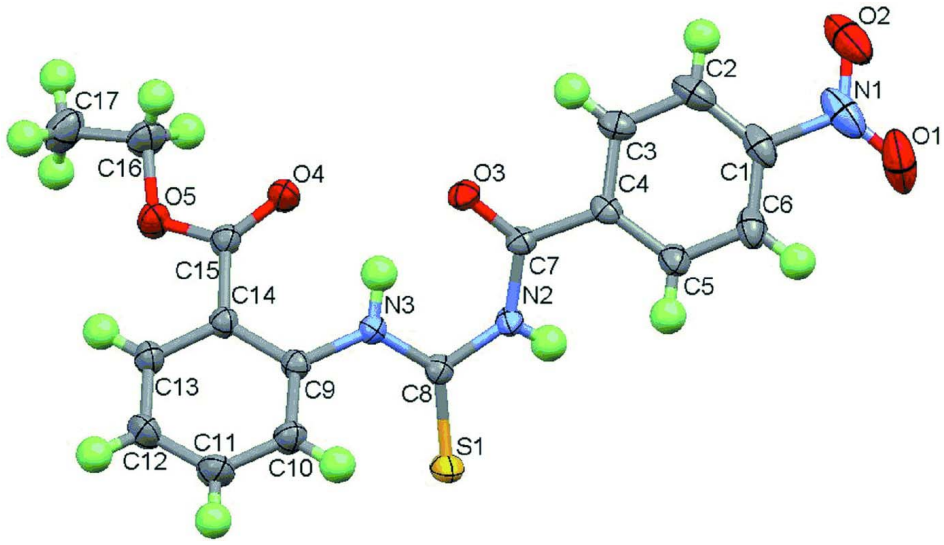

Figure 1

The *ORTEP* plot of the compound was shown at 30% probability thermal ellipsoids with the atom numbering scheme.

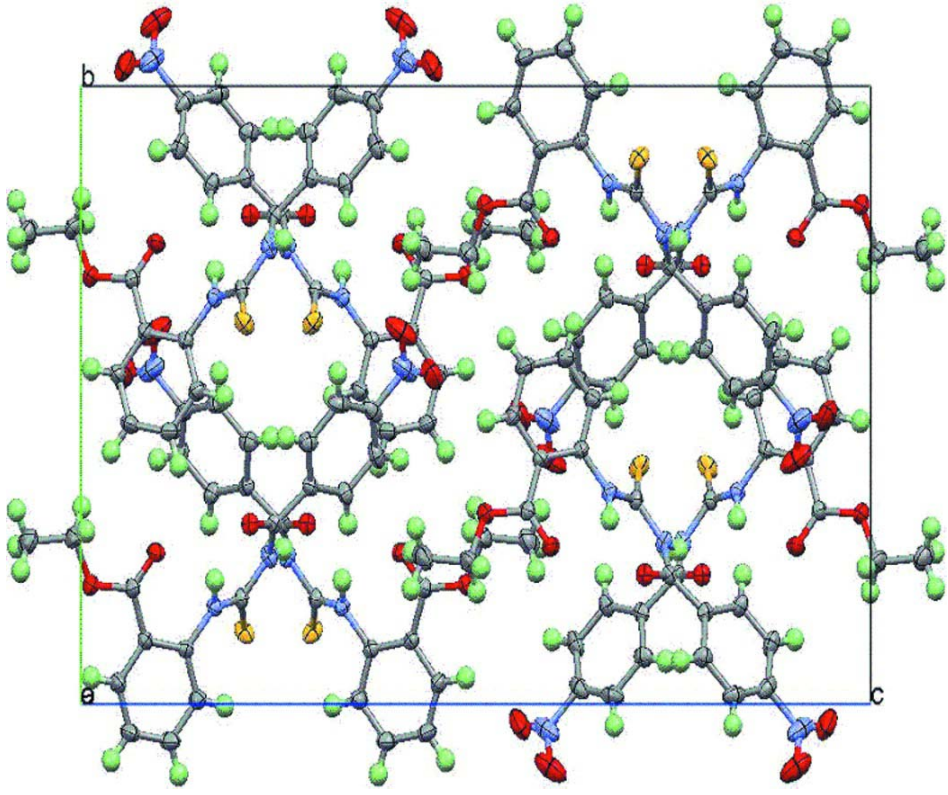

Figure 2

The unit cell packing diagram of the compound was projected down the a-axis and shown at 30% probability thermal ellipsoids.

Ethyl 2-[3-(4-nitrobenzoyl)thioureido]benzoate

Crystal data

$C_{17}H_{15}N_3O_5S$
M_r = 373.38
Orthorhombic, *Pbca*
Hall symbol: -P 2ac 2ab
a = 9.0698 (13) Å
b = 15.778 (2) Å
c = 24.889 (4) Å
V = 3561.7 (9) Å^3
Z = 8
F(000) = 1552

D_x = 1.393 Mg m^{-3}
Melting point: 438 K
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 23121 reflections
θ = 1.6–28.3°
μ = 0.22 mm^{-1}
T = 295 K
Plate, yellow
0.36 × 0.25 × 0.03 mm

Data collection

Bruker SMART 1000 CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scan
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.927, T_{max} = 0.994

23121 measured reflections
4362 independent reflections
2877 reflections with $I > 2\sigma(I)$
R_{int} = 0.032
θ_{max} = 28.3°, θ_{min} = 1.6°
h = −8→11
k = −21→21
l = −33→32

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.171$
$S = 1.07$
4362 reflections
244 parameters
6 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
$w = 1/[\sigma^2(F_o^2) + (0.0709P)^2 + 2.2491P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.63$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.51557 (9)	0.11637 (5)	0.20685 (4)	0.0587 (3)
O1	0.3603 (6)	0.5330 (3)	0.44429 (14)	0.1331 (16)
O2	0.1862 (4)	0.6034 (2)	0.40527 (18)	0.1245 (13)
O3	0.1165 (2)	0.29106 (13)	0.21392 (8)	0.0476 (5)
O4	0.0879 (3)	0.24551 (13)	0.09489 (9)	0.0641 (6)
O5	0.0925 (3)	0.19226 (14)	0.01211 (9)	0.0662 (7)
N1	0.2655 (5)	0.5415 (2)	0.41024 (19)	0.0936 (13)
N2	0.3396 (2)	0.23826 (15)	0.23814 (10)	0.0428 (5)
N3	0.2463 (3)	0.15722 (15)	0.16898 (9)	0.0414 (5)
C1	0.2484 (4)	0.4741 (2)	0.36882 (15)	0.0648 (9)
C2	0.1512 (4)	0.4866 (2)	0.32689 (17)	0.0690 (10)
H2	0.0937	0.5353	0.3250	0.083*
C3	0.1416 (4)	0.4242 (2)	0.28770 (13)	0.0552 (8)
H3	0.0758	0.4306	0.2593	0.066*
C4	0.2296 (3)	0.35235 (17)	0.29062 (11)	0.0423 (6)
C5	0.3214 (3)	0.3409 (2)	0.33479 (12)	0.0516 (7)
H5	0.3764	0.2914	0.3379	0.062*
C6	0.3312 (4)	0.4026 (2)	0.37399 (13)	0.0630 (9)
H6	0.3932	0.3955	0.4034	0.076*
C7	0.2219 (3)	0.29142 (16)	0.24481 (10)	0.0388 (6)
C8	0.3576 (3)	0.17016 (17)	0.20286 (10)	0.0411 (6)
C9	0.2299 (3)	0.08868 (17)	0.13261 (11)	0.0423 (6)
C10	0.2679 (4)	0.00680 (19)	0.14754 (13)	0.0575 (8)
H10	0.3060	−0.0030	0.1817	0.069*

C11	0.2504 (4)	−0.0600 (2)	0.11286 (15)	0.0661 (9)
H11	0.2767	−0.1144	0.1236	0.079*
C12	0.1938 (4)	−0.0466 (2)	0.06204 (15)	0.0659 (9)
H12	0.1837	−0.0916	0.0382	0.079*
C13	0.1526 (4)	0.03375 (19)	0.04696 (13)	0.0552 (8)
H13	0.1138	0.0424	0.0128	0.066*
C14	0.1677 (3)	0.10259 (17)	0.08161 (11)	0.0435 (6)
C15	0.1132 (3)	0.18718 (18)	0.06483 (12)	0.0472 (7)
C16	0.0290 (5)	0.2705 (2)	−0.00865 (15)	0.0782 (11)
H16A	0.0907	0.3184	0.0010	0.094*
H16B	−0.0684	0.2794	0.0064	0.094*
C17	0.0198 (5)	0.2627 (3)	−0.06722 (17)	0.0872 (13)
H17A	−0.0220	0.3135	−0.0820	0.105*
H17B	−0.0414	0.2152	−0.0763	0.105*
H17C	0.1168	0.2543	−0.0817	0.105*
H2N	0.409 (4)	0.2503 (19)	0.2566 (13)	0.047 (9)*
H3N	0.177 (3)	0.200 (2)	0.1694 (12)	0.050 (8)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0427 (4)	0.0648 (5)	0.0686 (5)	0.0143 (3)	−0.0073 (4)	−0.0180 (4)
O1	0.208 (5)	0.116 (3)	0.075 (2)	−0.037 (3)	−0.004 (3)	−0.037 (2)
O2	0.099 (2)	0.104 (2)	0.171 (3)	−0.0053 (18)	0.0240 (19)	−0.073 (2)
O3	0.0353 (10)	0.0564 (12)	0.0511 (11)	0.0026 (8)	−0.0027 (8)	0.0000 (9)
O4	0.0893 (17)	0.0445 (12)	0.0584 (13)	0.0126 (11)	−0.0185 (12)	−0.0062 (10)
O5	0.0994 (19)	0.0516 (13)	0.0476 (12)	0.0076 (12)	−0.0137 (12)	0.0037 (10)
N1	0.094 (3)	0.073 (2)	0.114 (3)	−0.026 (2)	0.042 (2)	−0.039 (2)
N2	0.0302 (11)	0.0540 (14)	0.0442 (13)	0.0015 (10)	−0.0021 (10)	−0.0106 (10)
N3	0.0400 (12)	0.0416 (12)	0.0425 (12)	0.0015 (10)	−0.0035 (10)	−0.0026 (10)
C1	0.065 (2)	0.062 (2)	0.067 (2)	−0.0163 (17)	0.0258 (18)	−0.0232 (17)
C2	0.066 (2)	0.0466 (18)	0.094 (3)	0.0033 (15)	0.027 (2)	−0.0093 (18)
C3	0.0485 (17)	0.0510 (17)	0.0661 (19)	0.0060 (13)	0.0097 (15)	0.0010 (15)
C4	0.0356 (13)	0.0448 (14)	0.0466 (14)	−0.0019 (11)	0.0115 (11)	−0.0026 (12)
C5	0.0468 (16)	0.0601 (18)	0.0479 (16)	0.0042 (13)	0.0045 (13)	−0.0090 (14)
C6	0.058 (2)	0.083 (2)	0.0482 (17)	−0.0072 (18)	0.0094 (15)	−0.0178 (16)
C7	0.0310 (12)	0.0442 (14)	0.0410 (13)	−0.0020 (10)	0.0057 (11)	0.0024 (11)
C8	0.0379 (13)	0.0476 (15)	0.0378 (13)	−0.0009 (11)	0.0031 (11)	−0.0008 (11)
C9	0.0416 (14)	0.0404 (14)	0.0448 (14)	−0.0014 (11)	0.0001 (12)	−0.0015 (11)
C10	0.068 (2)	0.0458 (16)	0.0589 (19)	0.0016 (15)	−0.0138 (16)	0.0046 (14)
C11	0.079 (2)	0.0407 (17)	0.079 (2)	0.0046 (16)	−0.0134 (19)	0.0007 (15)
C12	0.086 (3)	0.0419 (17)	0.070 (2)	0.0032 (16)	−0.0107 (19)	−0.0121 (15)
C13	0.067 (2)	0.0484 (17)	0.0496 (16)	0.0006 (14)	−0.0096 (15)	−0.0070 (13)
C14	0.0460 (15)	0.0416 (14)	0.0429 (14)	−0.0026 (11)	−0.0026 (12)	−0.0010 (11)
C15	0.0489 (16)	0.0447 (16)	0.0481 (16)	−0.0025 (12)	−0.0088 (13)	0.0004 (12)
C16	0.107 (3)	0.059 (2)	0.069 (2)	0.012 (2)	−0.021 (2)	0.0121 (18)
C17	0.103 (3)	0.083 (3)	0.076 (3)	−0.005 (2)	−0.026 (2)	0.021 (2)

Geometric parameters (Å, º)

S1—C8	1.668 (3)	C4—C7	1.493 (4)
O1—N1	1.215 (6)	C5—C6	1.381 (4)
O2—N1	1.219 (5)	C5—H5	0.9300
O3—C7	1.227 (3)	C6—H6	0.9300
O4—C15	1.208 (3)	C9—C10	1.388 (4)
O5—C15	1.328 (3)	C9—C14	1.406 (4)
O5—C16	1.457 (4)	C10—C11	1.371 (4)
N1—C1	1.489 (5)	C10—H10	0.9300
N2—C7	1.368 (3)	C11—C12	1.381 (5)
N2—C8	1.397 (3)	C11—H11	0.9300
N2—H2N	0.80 (3)	C12—C13	1.373 (5)
N3—C8	1.331 (3)	C12—H12	0.9300
N3—C9	1.418 (3)	C13—C14	1.394 (4)
N3—H3N	0.91 (3)	C13—H13	0.9300
C1—C6	1.361 (5)	C14—C15	1.483 (4)
C1—C2	1.380 (6)	C16—C17	1.465 (6)
C2—C3	1.388 (5)	C16—H16A	0.9700
C2—H2	0.9300	C16—H16B	0.9700
C3—C4	1.388 (4)	C17—H17A	0.9600
C3—H3	0.9300	C17—H17B	0.9600
C4—C5	1.391 (4)	C17—H17C	0.9600
C15—O5—C16	117.2 (3)	C10—C9—C14	119.1 (3)
O1—N1—O2	125.2 (4)	C10—C9—N3	120.9 (3)
O1—N1—C1	118.6 (4)	C14—C9—N3	119.9 (2)
O2—N1—C1	116.1 (5)	C11—C10—C9	121.2 (3)
C7—N2—C8	129.7 (2)	C11—C10—H10	119.4
C7—N2—H2N	113 (2)	C9—C10—H10	119.4
C8—N2—H2N	117 (2)	C10—C11—C12	120.1 (3)
C8—N3—C9	126.9 (2)	C10—C11—H11	119.9
C8—N3—H3N	113.5 (19)	C12—C11—H11	119.9
C9—N3—H3N	119.5 (19)	C13—C12—C11	119.5 (3)
C6—C1—C2	122.8 (3)	C13—C12—H12	120.2
C6—C1—N1	117.9 (4)	C11—C12—H12	120.2
C2—C1—N1	119.2 (4)	C12—C13—C14	121.6 (3)
C1—C2—C3	118.0 (3)	C12—C13—H13	119.2
C1—C2—H2	121.0	C14—C13—H13	119.2
C3—C2—H2	121.0	C13—C14—C9	118.4 (3)
C2—C3—C4	120.4 (3)	C13—C14—C15	119.6 (3)
C2—C3—H3	119.8	C9—C14—C15	121.9 (2)
C4—C3—H3	119.8	O4—C15—O5	122.6 (3)
C3—C4—C5	119.4 (3)	O4—C15—C14	125.1 (3)
C3—C4—C7	117.3 (3)	O5—C15—C14	112.3 (2)
C5—C4—C7	123.2 (2)	O5—C16—C17	107.7 (3)
C6—C5—C4	120.4 (3)	O5—C16—H16A	110.2
C6—C5—H5	119.8	C17—C16—H16A	110.2

C4—C5—H5	119.8	O5—C16—H16B	110.2
C1—C6—C5	118.8 (3)	C17—C16—H16B	110.2
C1—C6—H6	120.6	H16A—C16—H16B	108.5
C5—C6—H6	120.6	C16—C17—H17A	109.5
O3—C7—N2	122.0 (2)	C16—C17—H17B	109.5
O3—C7—C4	121.2 (2)	H17A—C17—H17B	109.5
N2—C7—C4	116.8 (2)	C16—C17—H17C	109.5
N3—C8—N2	115.3 (2)	H17A—C17—H17C	109.5
N3—C8—S1	127.7 (2)	H17B—C17—H17C	109.5
N2—C8—S1	117.0 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*N*···O3^{i}	0.80 (4)	2.12 (4)	2.903 (3)	165 (3)
N3—H3*N*···O3	0.91 (3)	1.91 (3)	2.664 (3)	139 (3)
N3—H3*N*···O4	0.91 (3)	2.15 (3)	2.721 (3)	120 (2)

Symmetry code: (i) $x+1/2, y, -z+1/2$.