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1-(3,5-Dinitrobenzoyl)-3,3-dipropylthiourea

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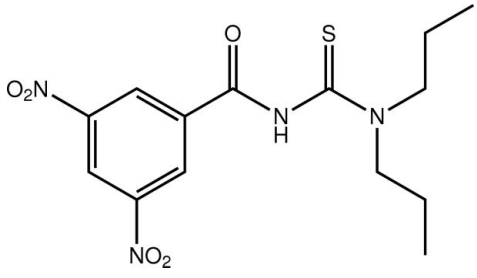
Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.004 Å; R factor = 0.055; wR factor = 0.154; data-to-parameter ratio = 16.4.

The title thiourea derivative, $C_{14}H_{18}N_4O_5S$, features two substantial twists between its component fragments: the dihedral angle between the SN_2C (thiourea) and ONC_2 (amide) residues is 48.89 (7)° and that between the benzene ring and the amide residue is 30.27 (7)°. In the crystal, molecules are linked by bifurcated N—H···(O,S) hydrogen bonds, generating [001] supramolecular chains.

Related literature

For the biological activity of thiourea derivatives, see: Venkatachalam *et al.*, (2004); Saeed *et al.* (2011). For related thiourea structures, see: Gunasekaran *et al.* (2010); Saeed *et al.* (2010); Dzulkifli *et al.* (2011).



Experimental

Crystal data

$C_{14}H_{18}N_4O_5S$
M_r = 354.38
Monoclinic, $P2_1/c$
a = 7.9406 (4) Å
b = 21.2839 (10) Å
c = 9.5967 (4) Å
β = 94.379 (4)°
V = 1617.17 (13) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.23 mm^{-1}
T = 295 K
0.30 × 0.20 × 0.10 mm

Data collection

Agilent SuperNova Dual diffractometer with an Atlas detector
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2010)
T_{min} = 0.933, T_{max} = 0.977
8055 measured reflections
3614 independent reflections
2878 reflections with $I > 2\sigma(I)$
R_{int} = 0.027

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.154
S = 1.02
3614 reflections
221 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 1.04 e Å^{-3}
$\Delta\rho_{min}$ = −0.46 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···O1^{i}	0.87 (1)	2.53 (2)	3.264 (3)	142 (2)
N2—H2···S1^{i}	0.87 (1)	2.69 (2)	3.436 (2)	144 (2)

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

Data collection: *CrysAlis PRO* (Agilent, 2010); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 2006); 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: HB5845).

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1-(3,5-Dinitrobenzoyl)-3,3-dipropylthiourea

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S1. Comment

The biological potential of thiourea derivatives (Venkatachalam *et al.*, 2004; Saeed *et al.*, 2011) motivates structural studies of these compounds (Gunasekaran *et al.* 2010; Saeed *et al.* 2010; Dzulkifli *et al.*, 2011). Herein, the crystal and molecular structure of the title thiourea derivative, (I), is described.

The molecular structure of (I), Fig. 1, shows a significant twist around the central atoms as seen in the value of the dihedral angle formed between the least-squares planes through the S1,N1,N2,C7 (thiourea) and O1,N2,C8,C9 (amide) atoms of 48.89 (7) °. Further, the benzene ring is twisted out of the plane of the carbonyl residue as indicated by the O1—C8—C9—C10 torsion angle of 147.1 (2) °. With respect to the S1,N1,N2,C7 plane, the n-propyl groups lie to either side. Whereas the O2-nitro group is co-planar with the benzene ring to which it is bonded, the O2—N3—C11—C10 torsion angle = -4.2 (3) °, the O4-nitro group is slightly twisted out of the plane as seen in the value of the O4—N4—C13—C12 torsion angle of -9.3 (3) °.

The crystal packing is dominated by N—H···O,*S* hydrogen bonds as the N1—H H atoms is bifurcated, Table 1. These result in the formation of six-membered {···H···OCNCS} synthons and linear supramolecular chains along the *c* direction, Fig. 2.

S2. Experimental

A solution of 3,5-dinitrobenzoyl chloride (0.01 mol) in anhydrous acetone (75 ml) and 3% tetrabutylammonium bromide (TBAB) as a phase-transfer catalyst (PTC) in anhydrous acetone was added drop-wise to a suspension of dry potassium thiocyanate (0.01 mol) in acetone (50 ml) and the reaction mixture was refluxed for 50 min. After cooling to room temperature, a solution of dipropyl amine (0.01 mol) in anhydrous acetone (25 ml) was added drop-wise and the resulting mixture refluxed for 3 h. Hydrochloric acid (0.1 N, 300 ml) was added and the solution was filtered. The solid product was washed with water and purified by re-crystallization from ethyl acetate to yield light-yellow prisms of (I). Yield: 1.29 g (82%); *M*.pt. 407–408 K. IR (KBr, cm^{-1}): 3173 *v*(NH), 1690 *v*(C═O), 1536 *v*(benzene ring), 1180 *v*(C═S). Anal. Calcd. for $C_{14}H_{18}N_4O_5S$: C, 47.45; H, 5.12; N, 15.81; S, 9.05%. Found: C, 47.53; H, 5.17; N, 15.75; S, 9.03%.

S3. Refinement

Carbon-bound H-atoms were placed in calculated positions [C—H 0.93–0.97 Å, U_{iso}(H) 1.2–1.5U_{eq}(C)] and were included in the refinement in the riding model approximation. The amino H-atoms were located in a difference Fourier map, and were refined with a distance restraint of N—H 0.88±0.01 Å; the U_{iso} values were refined. The maximum and minimum residual electron density peaks of 1.04 and 0.46 e $Å^{-3}$, respectively, were located 1.05 Å and 0.33 Å from the C2 and H2a atoms, respectively.

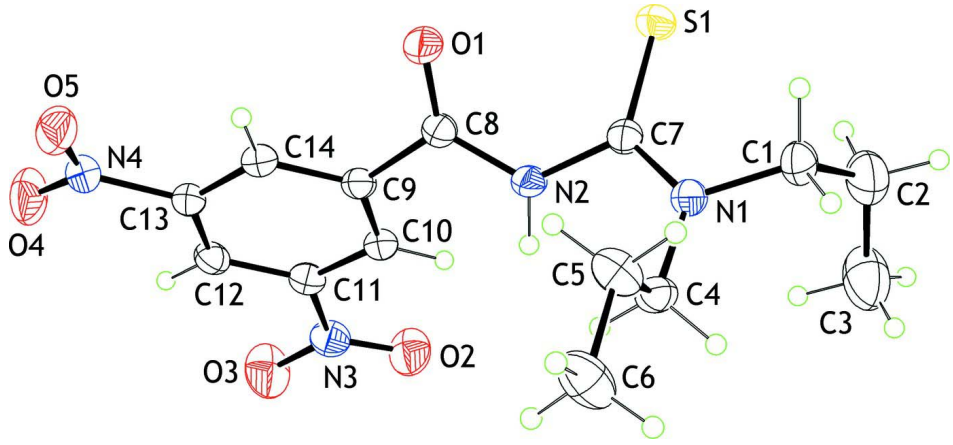

Figure 1

The molecular structure of (I) showing displacement ellipsoids at the 35% probability level.

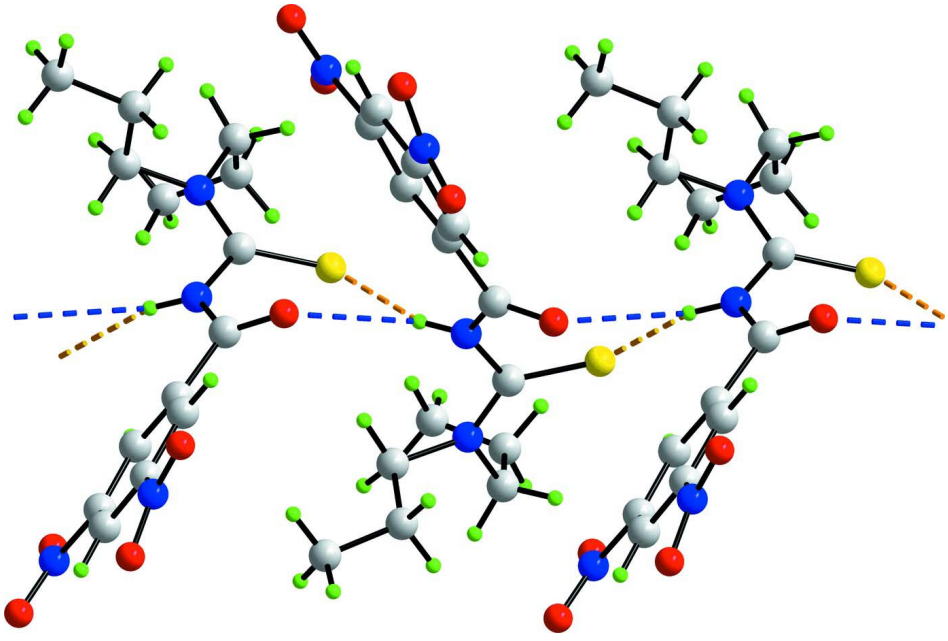

Figure 2

Supramolecular chain aligned along the *c* axis in (I) mediated by N—H···O, S hydrogen bonding shown as blue and orange dashed lines, respectively.

1-(3,5-Dinitrobenzoyl)-3,3-dipropylthiourea

Crystal data

$C_{14}H_{18}N_4O_5S$
$M_r = 354.38$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 7.9406\ (4)$ Å
$b = 21.2839\ (10)$ Å
$c = 9.5967\ (4)$ Å
$\beta = 94.379\ (4)°$
$V = 1617.17\ (13)$ Å^3
$Z = 4$
$F(000) = 744$
$D_x = 1.456$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3443 reflections
$\theta = 2.3–29.3°$
$\mu = 0.23$ mm^{-1}

T = 295 K
Prism, light yellow

0.30 × 0.20 × 0.10 mm

Data collection

Agilent SuperNova Dual diffractometer with an Atlas detector
Radiation source: SuperNova (Mo) X-ray Source
Mirror monochromator
Detector resolution: 10.4041 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2010)

T_{min} = 0.933, T_{max} = 0.977
8055 measured reflections
3614 independent reflections
2878 reflections with $I > 2\sigma(I)$
R_{int} = 0.027
θ_{max} = 27.5°, θ_{min} = 2.3°
h = −10→10
k = −27→26
l = −12→10

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.154
S = 1.02
3614 reflections
221 parameters
1 restraint
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
$w = 1/[\sigma^2(F_o^2) + (0.0697P)^2 + 1.1729P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.04 e Å^{-3}
$\Delta\rho_{min}$ = −0.46 e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}
S1	0.37257 (8)	0.21276 (3)	0.24866 (6)	0.0405 (2)
O1	0.7561 (2)	0.24758 (9)	0.29218 (19)	0.0505 (5)
O2	0.5844 (3)	0.44242 (11)	0.7375 (2)	0.0621 (6)
O3	0.8149 (3)	0.49393 (11)	0.7748 (3)	0.0761 (7)
O4	1.2906 (3)	0.44304 (11)	0.5156 (3)	0.0711 (7)
O5	1.3052 (3)	0.35161 (11)	0.4221 (2)	0.0623 (6)
N1	0.4129 (2)	0.15013 (9)	0.4887 (2)	0.0334 (4)
N2	0.5882 (3)	0.23606 (9)	0.4730 (2)	0.0343 (4)
H2	0.581 (3)	0.2455 (12)	0.5607 (13)	0.044 (7)*
N3	0.7311 (3)	0.45149 (10)	0.7190 (2)	0.0451 (5)
N4	1.2306 (3)	0.39224 (11)	0.4807 (2)	0.0440 (5)
C1	0.2706 (3)	0.10939 (12)	0.4387 (3)	0.0433 (6)
H1A	0.2787	0.0701	0.4899	0.052*
H1B	0.2802	0.0999	0.3408	0.052*
C2	0.0973 (4)	0.1384 (2)	0.4550 (4)	0.0746 (10)
H2A	0.0819	0.1733	0.3903	0.089*
H2B	0.0117	0.1073	0.4280	0.089*
C3	0.0687 (5)	0.1608 (2)	0.5930 (5)	0.0882 (13)
H3A	−0.0414	0.1795	0.5919	0.132*
H3B	0.1528	0.1915	0.6217	0.132*
H3C	0.0757	0.1262	0.6574	0.132*
C4	0.5096 (3)	0.12842 (12)	0.6168 (2)	0.0396 (6)

H4A	0.4329	0.1098	0.6791	0.047*
H4B	0.5640	0.1641	0.6642	0.047*
C5	0.6417 (4)	0.08077 (13)	0.5847 (3)	0.0510 (7)
H5A	0.7223	0.1002	0.5270	0.061*
H5B	0.5880	0.0464	0.5318	0.061*
C6	0.7351 (4)	0.05486 (15)	0.7163 (4)	0.0659 (9)
H6A	0.8211	0.0262	0.6912	0.099*
H6B	0.6569	0.0332	0.7708	0.099*
H6C	0.7862	0.0888	0.7701	0.099*
C7	0.4603 (3)	0.19711 (10)	0.4084 (2)	0.0313 (5)
C8	0.7150 (3)	0.26338 (11)	0.4063 (2)	0.0339 (5)
C9	0.8066 (3)	0.31654 (10)	0.4830 (2)	0.0320 (5)
C10	0.7262 (3)	0.35735 (11)	0.5703 (2)	0.0337 (5)
H10	0.6152	0.3502	0.5908	0.040*
C11	0.8147 (3)	0.40847 (11)	0.6256 (2)	0.0350 (5)
C12	0.9793 (3)	0.42129 (11)	0.5982 (2)	0.0367 (5)
H12	1.0361	0.4564	0.6352	0.044*
C13	1.0552 (3)	0.37937 (11)	0.5132 (2)	0.0353 (5)
C14	0.9729 (3)	0.32754 (11)	0.4549 (2)	0.0338 (5)
H14	1.0280	0.3004	0.3976	0.041*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0449 (4)	0.0445 (4)	0.0315 (3)	−0.0042 (3)	−0.0021 (2)	0.0030 (2)
O1	0.0508 (11)	0.0646 (12)	0.0378 (10)	−0.0172 (9)	0.0146 (8)	−0.0188 (9)
O2	0.0525 (12)	0.0665 (14)	0.0695 (14)	0.0005 (10)	0.0182 (10)	−0.0207 (11)
O3	0.0734 (15)	0.0652 (14)	0.0909 (17)	−0.0130 (12)	0.0146 (13)	−0.0475 (13)
O4	0.0519 (12)	0.0681 (15)	0.0941 (18)	−0.0262 (11)	0.0118 (12)	−0.0156 (13)
O5	0.0438 (11)	0.0814 (15)	0.0636 (13)	−0.0046 (10)	0.0156 (10)	−0.0176 (12)
N1	0.0346 (10)	0.0325 (10)	0.0331 (10)	−0.0015 (8)	0.0025 (8)	−0.0001 (8)
N2	0.0410 (11)	0.0364 (10)	0.0259 (9)	−0.0079 (8)	0.0048 (8)	−0.0052 (8)
N3	0.0514 (14)	0.0432 (12)	0.0409 (12)	0.0023 (10)	0.0037 (10)	−0.0077 (10)
N4	0.0355 (11)	0.0570 (14)	0.0393 (11)	−0.0067 (10)	0.0005 (9)	0.0007 (10)
C1	0.0423 (14)	0.0389 (13)	0.0486 (14)	−0.0094 (11)	0.0036 (11)	−0.0017 (11)
C2	0.0510 (18)	0.097 (3)	0.076 (2)	−0.0187 (18)	0.0090 (16)	−0.015 (2)
C3	0.059 (2)	0.102 (3)	0.107 (3)	−0.015 (2)	0.022 (2)	−0.040 (3)
C4	0.0476 (14)	0.0394 (13)	0.0317 (12)	−0.0022 (11)	0.0031 (10)	0.0047 (10)
C5	0.0528 (16)	0.0482 (15)	0.0500 (16)	0.0068 (13)	−0.0093 (13)	−0.0058 (12)
C6	0.072 (2)	0.0484 (17)	0.072 (2)	0.0038 (15)	−0.0257 (17)	0.0032 (15)
C7	0.0323 (11)	0.0305 (11)	0.0315 (11)	0.0008 (9)	0.0055 (9)	−0.0042 (9)
C8	0.0363 (12)	0.0348 (12)	0.0308 (11)	−0.0036 (9)	0.0035 (9)	−0.0035 (9)
C9	0.0362 (12)	0.0337 (11)	0.0259 (10)	−0.0029 (9)	0.0015 (9)	0.0012 (9)
C10	0.0353 (12)	0.0372 (12)	0.0285 (11)	−0.0025 (10)	0.0019 (9)	0.0023 (9)
C11	0.0398 (13)	0.0344 (12)	0.0304 (11)	0.0023 (10)	0.0006 (9)	−0.0022 (9)
C12	0.0424 (13)	0.0351 (12)	0.0318 (11)	−0.0063 (10)	−0.0024 (10)	−0.0029 (9)
C13	0.0341 (12)	0.0416 (13)	0.0299 (11)	−0.0042 (10)	0.0002 (9)	0.0037 (9)
C14	0.0364 (12)	0.0363 (12)	0.0290 (11)	0.0003 (10)	0.0040 (9)	−0.0005 (9)

Geometric parameters (Å, º)

S1—C7	1.668 (2)	C3—H3B	0.9600
O1—C8	1.214 (3)	C3—H3C	0.9600
O2—N3	1.207 (3)	C4—C5	1.508 (4)
O3—N3	1.221 (3)	C4—H4A	0.9700
O4—N4	1.218 (3)	C4—H4B	0.9700
O5—N4	1.211 (3)	C5—C6	1.519 (4)
N1—C7	1.334 (3)	C5—H5A	0.9700
N1—C4	1.473 (3)	C5—H5B	0.9700
N1—C1	1.475 (3)	C6—H6A	0.9600
N2—C8	1.364 (3)	C6—H6B	0.9600
N2—C7	1.417 (3)	C6—H6C	0.9600
N2—H2	0.871 (10)	C8—C9	1.507 (3)
N3—C11	1.474 (3)	C9—C14	1.388 (3)
N4—C13	1.476 (3)	C9—C10	1.394 (3)
C1—C2	1.527 (4)	C10—C11	1.379 (3)
C1—H1A	0.9700	C10—H10	0.9300
C1—H1B	0.9700	C11—C12	1.380 (3)
C2—C3	1.441 (5)	C12—C13	1.378 (3)
C2—H2A	0.9700	C12—H12	0.9300
C2—H2B	0.9700	C13—C14	1.379 (3)
C3—H3A	0.9600	C14—H14	0.9300
C7—N1—C4	124.44 (19)	C4—C5—C6	112.2 (2)
C7—N1—C1	119.7 (2)	C4—C5—H5A	109.2
C4—N1—C1	115.12 (19)	C6—C5—H5A	109.2
C8—N2—C7	125.03 (19)	C4—C5—H5B	109.2
C8—N2—H2	117.3 (18)	C6—C5—H5B	109.2
C7—N2—H2	117.5 (18)	H5A—C5—H5B	107.9
O2—N3—O3	123.6 (2)	C5—C6—H6A	109.5
O2—N3—C11	118.3 (2)	C5—C6—H6B	109.5
O3—N3—C11	118.1 (2)	H6A—C6—H6B	109.5
O5—N4—O4	124.5 (2)	C5—C6—H6C	109.5
O5—N4—C13	117.9 (2)	H6A—C6—H6C	109.5
O4—N4—C13	117.5 (2)	H6B—C6—H6C	109.5
N1—C1—C2	113.7 (2)	N1—C7—N2	114.2 (2)
N1—C1—H1A	108.8	N1—C7—S1	124.35 (18)
C2—C1—H1A	108.8	N2—C7—S1	121.38 (17)
N1—C1—H1B	108.8	O1—C8—N2	124.3 (2)
C2—C1—H1B	108.8	O1—C8—C9	119.7 (2)
H1A—C1—H1B	107.7	N2—C8—C9	115.93 (19)
C3—C2—C1	115.8 (3)	C14—C9—C10	119.9 (2)
C3—C2—H2A	108.3	C14—C9—C8	117.6 (2)
C1—C2—H2A	108.3	C10—C9—C8	122.3 (2)
C3—C2—H2B	108.3	C11—C10—C9	118.6 (2)
C1—C2—H2B	108.3	C11—C10—H10	120.7
H2A—C2—H2B	107.4	C9—C10—H10	120.7

C2—C3—H3A	109.5	C10—C11—C12	123.0 (2)
C2—C3—H3B	109.5	C10—C11—N3	118.9 (2)
H3A—C3—H3B	109.5	C12—C11—N3	118.1 (2)
C2—C3—H3C	109.5	C13—C12—C11	116.6 (2)
H3A—C3—H3C	109.5	C13—C12—H12	121.7
H3B—C3—H3C	109.5	C11—C12—H12	121.7
N1—C4—C5	111.5 (2)	C12—C13—C14	122.9 (2)
N1—C4—H4A	109.3	C12—C13—N4	117.9 (2)
C5—C4—H4A	109.3	C14—C13—N4	119.2 (2)
N1—C4—H4B	109.3	C13—C14—C9	119.0 (2)
C5—C4—H4B	109.3	C13—C14—H14	120.5
H4A—C4—H4B	108.0	C9—C14—H14	120.5
C7—N1—C1—C2	−79.3 (3)	C8—C9—C10—C11	−173.6 (2)
C4—N1—C1—C2	110.2 (3)	C9—C10—C11—C12	0.2 (3)
N1—C1—C2—C3	−52.9 (4)	C9—C10—C11—N3	−179.4 (2)
C7—N1—C4—C5	−86.1 (3)	O2—N3—C11—C10	−4.2 (3)
C1—N1—C4—C5	83.9 (3)	O3—N3—C11—C10	174.9 (2)
N1—C4—C5—C6	−176.4 (2)	O2—N3—C11—C12	176.2 (2)
C4—N1—C7—N2	−15.8 (3)	O3—N3—C11—C12	−4.8 (4)
C1—N1—C7—N2	174.7 (2)	C10—C11—C12—C13	−1.2 (3)
C4—N1—C7—S1	167.53 (18)	N3—C11—C12—C13	178.5 (2)
C1—N1—C7—S1	−2.0 (3)	C11—C12—C13—C14	1.2 (3)
C8—N2—C7—N1	144.3 (2)	C11—C12—C13—N4	179.3 (2)
C8—N2—C7—S1	−38.9 (3)	O5—N4—C13—C12	170.3 (2)
C7—N2—C8—O1	−16.5 (4)	O4—N4—C13—C12	−9.3 (3)
C7—N2—C8—C9	163.4 (2)	O5—N4—C13—C14	−11.5 (3)
O1—C8—C9—C14	−27.4 (3)	O4—N4—C13—C14	168.9 (2)
N2—C8—C9—C14	152.7 (2)	C12—C13—C14—C9	−0.3 (3)
O1—C8—C9—C10	147.1 (2)	N4—C13—C14—C9	−178.4 (2)
N2—C8—C9—C10	−32.8 (3)	C10—C9—C14—C13	−0.7 (3)
C14—C9—C10—C11	0.7 (3)	C8—C9—C14—C13	173.9 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O1^{i}	0.87 (1)	2.53 (2)	3.264 (3)	142 (2)
N2—H2···S1^{i}	0.87 (1)	2.69 (2)	3.436 (2)	144 (2)

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