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N-Carbamothioylamino-7-oxabicyclo-[2.2.1]hept-5-ene-2,3-dicarboximide

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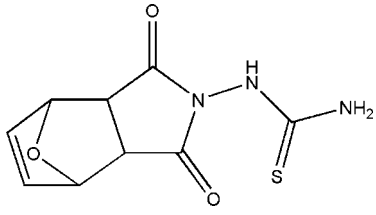
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.003 Å; R factor = 0.029; wR factor = 0.071; data-to-parameter ratio = 12.4.

The title compound, $C_9H_9N_3O_3S$, comprises a racemic mixture of chiral molecules containing four stereogenic centres. The cyclohexane ring tends towards a boat conformation, while the tetrahydrofuran ring and the dihydrofuran ring adopt envelope conformations. The dihedral angle between the thiosemicarbazide fragment and the fused-ring system is 77.20 (10)°. The crystal structure is stabilized by two intermolecular N—H···O hydrogen bonds.

Related literature

For the use of 7-oxa-bicyclo[2,2,1]hept-5-ene-2,3-dicarboxylic anhydride in clinical practice, see: Deng & Hu (2007). For the pharmacological activity of its derivatives, see: Hart *et al.* (2004). For bond lengths and angles in related structures, see: Goh *et al.* (2008).



Experimental

Crystal data

$C_9H_9N_3O_3S$ M_r = 239.25
Orthorhombic, $P2_12_12_1$
a = 8.3978 (8) Å
b = 8.9032 (9) Å
c = 13.5930 (14) Å
V = 1016.31 (18) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.31 mm^{-1}
T = 298 K
0.45 × 0.43 × 0.40 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
T_{min} = 0.872, T_{max} = 0.885
5015 measured reflections
1791 independent reflections
1632 reflections with $I > 2\sigma(I)$
R_{int} = 0.023

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.071
S = 1.07
1791 reflections
145 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.14 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}
Absolute structure: Flack (1983), 728 Friedel pairs
Flack parameter: 0.01 (9)

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···O3^{i}	0.86	1.96	2.809 (2)	167
N3—H3B···O1^{ii}	0.86	2.14	2.958 (2)	160

Symmetry codes: (i) $x+\frac{1}{2}, -y+\frac{1}{2}, -z+1$; (ii) $-x+\frac{3}{2}, -y+1, z+\frac{1}{2}$.

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

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BX2331).

References

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supplementary materials

Acta Cryst. (2010). E**66**, o3327 [**doi:10.1107/S160053681004835X**]

N-Carbamothioylamino-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide

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Comment

7-Oxa-bicyclo[2,2,1]hept-5-ene-2,3-dicarboxylic anhydride has been widely employed in clinical practice, as it is less toxic and much easier to be synthesized [Deng *et al.*, 2007]. Its derivatives are also pharmacologically active [Hart *et al.*, 2004]. We report here the crystal structure of the title compound, (I) which comprises a racemic mixture of chiral molecules containing four stereogenic centres. The cyclohexane ring tends towards a boat conformation, the tetrahydrofuran ring and the dihydrofuran ring adopt envelope conformations (Fig. 1). The bond lengths and bond angles are normal range and comparable to those in the similar compound [Goh, *et al.*, 2008] as representative example. The dihedral angle between the thiosemicarbazide fragment and fused-ring system is 77.20 (10)°. The crystal structure is stabilized by two intermolecular N—H···O and one intramolecular N—H···N hydrogen bonds (Table 1, Fig. 2).

Experimental

A mixture of *exo*-7-oxa-bicyclo[2,2,1]hept-5-ene-2,3-dicarboxylic anhydride (0.332 g, 2 mmol) and thiocarbanide (0.182 g, 2 mmol) in methanol (5 ml) was stirred for 5 h at room temperature, and then refluxed for 1 h. After cooling the precipitate was filtered and dried, the title compound was obtained. The crude product of 20 mg was dissolved in methanol of 10 ml. The solution was filtered to remove impurities, and then the filtrate was left for crystallization at room temperature. The single-crystal suitable for X-ray determination was obtained by evaporation from the methanol solution after 5 d.

Refinement

H atoms were initially located from difference maps and then refined in a riding model with C—H = 0.93–0.96 Å and U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(methyl C).

Figures

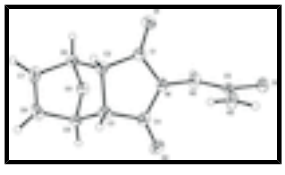

Fig. 1. The molecular structure of (I), with the atom-numbering scheme. Displacement ellipsoide are drawn at 30% probability level.

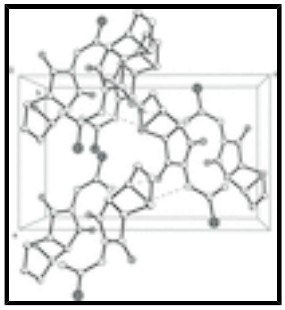

Fig. 2. The crystal packing of (I), viewed along *b* axis. Dashed lines indicate hydrogen bonds.

_N_-Carbamothioylamino-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide

Crystal data

$C_9H_9N_3O_3S$	$F(000) = 496$
$M_r = 239.25$	$D_x = 1.564$ Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: P 2ac 2ab	Cell parameters from 2624 reflections
$a = 8.3978$ (8) Å	$\theta = 2.7$–$26.3°$
$b = 8.9032$ (9) Å	$\mu = 0.31$ mm^{-1}
$c = 13.5930$ (14) Å	$T = 298$ K
$V = 1016.31$ (18) Å^3	Block, light yellow
$Z = 4$	0.45 × 0.43 × 0.40 mm

Data collection

Bruker SMART CCD area-detector diffractometer	1791 independent reflections
Radiation source: fine-focus sealed tube	1632 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.023$
phi and ω scans	$\theta_{max} = 25.0°$, $\theta_{min} = 2.7°$
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)	$h = -9\rightarrow9$
$T_{min} = 0.872$, $T_{max} = 0.885$	$k = -10\rightarrow10$
5015 measured reflections	$l = -16\rightarrow11$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.029$	H-atom parameters constrained
$wR(F^2) = 0.071$	$w = 1/[\sigma^2(F_o^2) + (0.0346P)^2 + 0.1693P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{max} < 0.001$
1791 reflections	$\Delta\rho_{max} = 0.14$ e Å^{-3}
145 parameters	$\Delta\rho_{min} = -0.16$ e Å^{-3}

0 restraints

Primary atom site location: structure-invariant direct methods

Absolute structure: Flack (1983), 728 Friedel pairs

Flack parameter: 0.01 (9)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'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 $F^2 > \sigma(F^2)$ 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	0.97059 (7)	0.24096 (7)	0.78384 (4)	0.04347 (17)
N1	0.5849 (2)	0.39754 (19)	0.65892 (11)	0.0314 (4)
N2	0.7287 (2)	0.3264 (2)	0.67804 (13)	0.0407 (5)
H2	0.7712	0.2722	0.6327	0.049*
N3	0.7384 (2)	0.4298 (2)	0.83195 (13)	0.0447 (5)
H3A	0.6516	0.4766	0.8184	0.054*
H3B	0.7826	0.4413	0.8885	0.054*
O1	0.68615 (19)	0.5596 (2)	0.54443 (11)	0.0466 (4)
O2	0.4254 (2)	0.22814 (19)	0.73858 (12)	0.0529 (5)
O3	0.32651 (18)	0.33700 (17)	0.48808 (10)	0.0362 (4)
C1	0.5731 (3)	0.5099 (2)	0.58861 (14)	0.0321 (5)
C2	0.4001 (2)	0.5466 (2)	0.57606 (14)	0.0306 (5)
H2A	0.3754	0.6517	0.5911	0.037*
C3	0.3110 (2)	0.4351 (2)	0.64312 (15)	0.0322 (5)
H3	0.2452	0.4855	0.6927	0.039*
C4	0.4385 (3)	0.3383 (2)	0.68800 (14)	0.0334 (5)
C5	0.8043 (3)	0.3395 (2)	0.76542 (14)	0.0298 (5)
C6	0.3396 (3)	0.4970 (3)	0.47264 (15)	0.0357 (5)
H6	0.4065	0.5276	0.4171	0.043*
C7	0.1677 (3)	0.5434 (3)	0.46640 (18)	0.0457 (6)
H7	0.1252	0.6207	0.4287	0.055*
C8	0.0896 (3)	0.4521 (3)	0.52523 (17)	0.0450 (6)
H8	−0.0191	0.4531	0.5382	0.054*
C9	0.2106 (3)	0.3459 (3)	0.56743 (15)	0.0368 (5)
H9	0.1687	0.2495	0.5906	0.044*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0357 (3)	0.0469 (3)	0.0479 (3)	0.0058 (3)	−0.0064 (3)	0.0046 (3)

N1	0.0315 (9)	0.0367 (10)	0.0261 (8)	0.0045 (8)	−0.0032 (8)	−0.0030 (8)
N2	0.0382 (10)	0.0540 (12)	0.0299 (10)	0.0176 (9)	−0.0048 (8)	−0.0105 (8)
N3	0.0447 (11)	0.0553 (12)	0.0342 (10)	0.0059 (10)	−0.0116 (9)	−0.0121 (9)
O1	0.0357 (9)	0.0642 (12)	0.0399 (9)	−0.0093 (8)	0.0035 (8)	0.0077 (8)
O2	0.0607 (10)	0.0508 (10)	0.0472 (9)	−0.0104 (9)	−0.0100 (8)	0.0191 (9)
O3	0.0405 (8)	0.0351 (8)	0.0330 (8)	0.0003 (7)	−0.0017 (7)	−0.0079 (7)
C1	0.0368 (12)	0.0350 (11)	0.0245 (10)	−0.0046 (10)	−0.0007 (9)	−0.0048 (9)
C2	0.0333 (11)	0.0257 (11)	0.0329 (11)	0.0010 (9)	−0.0030 (10)	−0.0008 (9)
C3	0.0324 (11)	0.0354 (12)	0.0287 (10)	0.0009 (9)	0.0042 (9)	−0.0030 (9)
C4	0.0411 (13)	0.0348 (12)	0.0243 (10)	−0.0023 (10)	−0.0010 (9)	−0.0046 (9)
C5	0.0330 (11)	0.0283 (10)	0.0282 (11)	−0.0068 (9)	0.0014 (9)	0.0015 (9)
C6	0.0360 (11)	0.0411 (13)	0.0300 (11)	−0.0061 (11)	−0.0019 (9)	0.0050 (10)
C7	0.0449 (14)	0.0464 (15)	0.0459 (13)	0.0038 (12)	−0.0185 (12)	0.0023 (11)
C8	0.0292 (11)	0.0590 (17)	0.0469 (13)	−0.0001 (11)	−0.0064 (11)	−0.0078 (12)
C9	0.0352 (12)	0.0405 (12)	0.0345 (12)	−0.0095 (10)	0.0001 (10)	0.0027 (10)

Geometric parameters (Å, °)

S1—C5	1.668 (2)	C2—C3	1.542 (3)
N1—C1	1.387 (3)	C2—C6	1.558 (3)
N1—N2	1.388 (2)	C2—H2A	0.9800
N1—C4	1.395 (3)	C3—C4	1.504 (3)
N2—C5	1.352 (3)	C3—C9	1.549 (3)
N2—H2	0.8600	C3—H3	0.9800
N3—C5	1.331 (3)	C6—C7	1.505 (3)
N3—H3A	0.8600	C6—H6	0.9800
N3—H3B	0.8600	C7—C8	1.315 (3)
O1—C1	1.207 (2)	C7—H7	0.9300
O2—C4	1.203 (2)	C8—C9	1.502 (3)
O3—C6	1.444 (3)	C8—H8	0.9300
O3—C9	1.455 (3)	C9—H9	0.9800
C1—C2	1.499 (3)		
C1—N1—N2	121.34 (18)	O2—C4—N1	123.4 (2)
C1—N1—C4	113.89 (17)	O2—C4—C3	129.3 (2)
N2—N1—C4	122.77 (17)	N1—C4—C3	107.21 (16)
C5—N2—N1	122.28 (18)	N3—C5—N2	116.96 (19)
C5—N2—H2	118.9	N3—C5—S1	124.34 (16)
N1—N2—H2	118.9	N2—C5—S1	118.69 (16)
C5—N3—H3A	120.0	O3—C6—C7	101.85 (18)
C5—N3—H3B	120.0	O3—C6—C2	99.98 (16)
H3A—N3—H3B	120.0	C7—C6—C2	106.61 (17)
C6—O3—C9	96.03 (15)	O3—C6—H6	115.5
O1—C1—N1	123.4 (2)	C7—C6—H6	115.5
O1—C1—C2	128.8 (2)	C2—C6—H6	115.5
N1—C1—C2	107.75 (17)	C8—C7—C6	105.9 (2)
C1—C2—C3	105.23 (17)	C8—C7—H7	127.0
C1—C2—C6	110.89 (17)	C6—C7—H7	127.0
C3—C2—C6	101.12 (16)	C7—C8—C9	106.5 (2)
C1—C2—H2A	112.9	C7—C8—H8	126.7

C3—C2—H2A	112.9	C9—C8—H8	126.7
C6—C2—H2A	112.9	O3—C9—C8	101.75 (17)
C4—C3—C2	105.28 (17)	O3—C9—C3	99.01 (15)
C4—C3—C9	111.29 (18)	C8—C9—C3	107.42 (18)
C2—C3—C9	101.62 (16)	O3—C9—H9	115.5
C4—C3—H3	112.6	C8—C9—H9	115.5
C2—C3—H3	112.6	C3—C9—H9	115.5
C9—C3—H3	112.6		
C1—N1—N2—C5	114.5 (2)	C9—C3—C4—N1	115.12 (18)
C4—N1—N2—C5	−82.6 (3)	N1—N2—C5—N3	−3.0 (3)
N2—N1—C1—O1	−4.8 (3)	N1—N2—C5—S1	176.11 (16)
C4—N1—C1—O1	−169.10 (19)	C9—O3—C6—C7	−49.14 (18)
N2—N1—C1—C2	171.97 (16)	C9—O3—C6—C2	60.34 (17)
C4—N1—C1—C2	7.6 (2)	C1—C2—C6—O3	76.2 (2)
O1—C1—C2—C3	173.2 (2)	C3—C2—C6—O3	−34.98 (19)
N1—C1—C2—C3	−3.4 (2)	C1—C2—C6—C7	−178.11 (19)
O1—C1—C2—C6	64.6 (3)	C3—C2—C6—C7	70.7 (2)
N1—C1—C2—C6	−111.89 (18)	O3—C6—C7—C8	32.6 (2)
C1—C2—C3—C4	−1.5 (2)	C2—C6—C7—C8	−71.7 (2)
C6—C2—C3—C4	113.97 (17)	C6—C7—C8—C9	−1.1 (2)
C1—C2—C3—C9	−117.64 (18)	C6—O3—C9—C8	48.43 (18)
C6—C2—C3—C9	−2.2 (2)	C6—O3—C9—C3	−61.60 (17)
C1—N1—C4—O2	170.38 (19)	C7—C8—C9—O3	−30.6 (2)
N2—N1—C4—O2	6.3 (3)	C7—C8—C9—C3	72.9 (2)
C1—N1—C4—C3	−8.6 (2)	C4—C3—C9—O3	−73.4 (2)
N2—N1—C4—C3	−172.69 (17)	C2—C3—C9—O3	38.29 (19)
C2—C3—C4—O2	−173.1 (2)	C4—C3—C9—C8	−178.77 (18)
C9—C3—C4—O2	−63.8 (3)	C2—C3—C9—C8	−67.1 (2)
C2—C3—C4—N1	5.8 (2)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O3^{i}	0.86	1.96	2.809 (2)	167
N3—H3B···O1^{ii}	0.86	2.14	2.958 (2)	160
N3—H3A···N1	0.86	2.35	2.697 (2)	105

Symmetry codes: (i) *x*+1/2, −*y*+1/2, −*z*+1; (ii) −*x*+3/2, −*y*+1, *z*+1/2.

Fig. 1

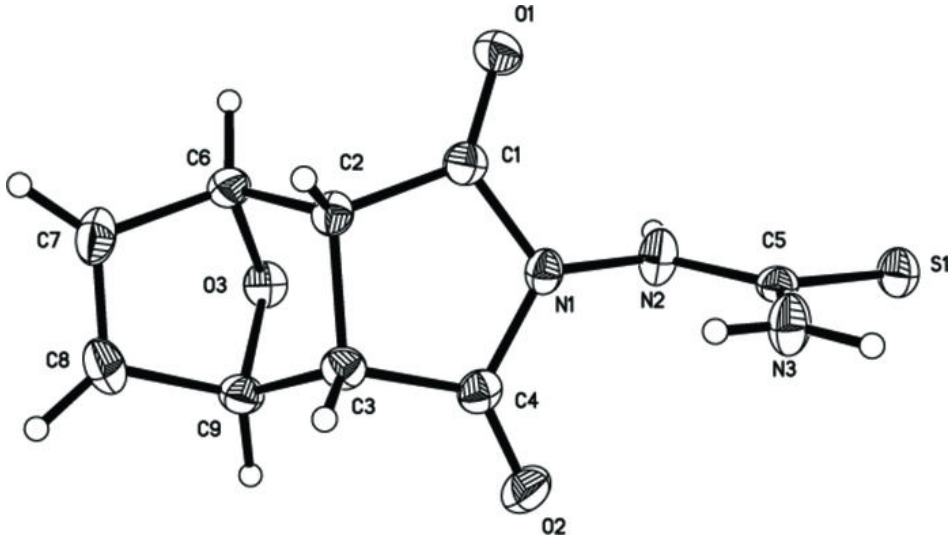

Fig. 2