

(–)-(S)-N,N′-Bis[1-(1-naphthyl)ethyl]-oxalamide

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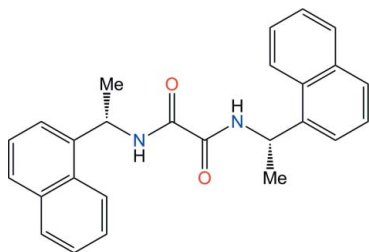
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.008$ Å; R factor = 0.043; wR factor = 0.138; data-to-parameter ratio = 8.6.

The title molecule, $\text{C}_{26}\text{H}_{24}\text{N}_2\text{O}_2$, displays C_2 symmetry, with the molecule located on a twofold axis perpendicular to the plane of the oxalamide unit $-\text{NH}-\text{CO}-\text{CO}-\text{NH}-$. The oxalamide core deviates from planarity, as reflected by the $\text{O}=\text{C}-\text{C}=\text{O}$ and $\text{N}-\text{C}-\text{C}-\text{N}$ torsion angles of 164.3 (5) and 163.2 (5)°, respectively. The naphthyl groups are oriented toward the same face of the oxalamide mean plane and make a dihedral angle of 43.76 (8)°. This conformation is suitable for the formation of intermolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds, giving noncentrosymmetric dimers incorporating $R_2^2(10)$ ring motifs. These nonbonding interactions propagate along the 6_1 screw axis normal to the molecular twofold axis, resulting in a single-stranded right-handed helix parallel to $[001]$. In the crystal, Δ helices are arranged side-by-side and interact through $\pi-\pi$ contacts between naphthyl groups. The shortest centroid-centroid separation between interacting benzene rings is 3.623 (4) Å.

Related literature

For crystal structures of closely related oxalamides, see: Štefanić *et al.* (2003); Zhang *et al.* (2006); Lee & Wang (2007); Lee (2010). For general references on dicarboxamides and oxalamides, and their synthesis under solvent-free conditions, see: Bernès *et al.* (2008); Montero-Vázquez *et al.* (2008); Jeon *et al.* (2005); Noyori (2005). For helicity assignment in enantiomorphic space groups, see: Ha & Allewell (1997).



Experimental

Crystal data

$\text{C}_{26}\text{H}_{24}\text{N}_2\text{O}_2$
 $M_r = 396.47$
 Hexagonal, $P6_122$
 $a = 11.4489$ (11) Å
 $c = 28.350$ (4) Å
 $V = 3218.2$ (7) Å³
 $Z = 6$
 Mo $K\alpha$ radiation
 $\mu = 0.08$ mm⁻¹
 $T = 298$ K
 $0.40 \times 0.22 \times 0.20$ mm

Data collection

Siemens P4 diffractometer
 5314 measured reflections
 1208 independent reflections
 730 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.057$
 3 standard reflections every 97 reflections
 intensity decay: 1%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.138$
 $S = 1.11$
 1208 reflections
 141 parameters
 1 restraint
 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.12$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.14$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N2}-\text{H2}\cdots\text{O1}^i$	0.91 (1)	2.06 (2)	2.931 (3)	161 (3)

Symmetry code: (i) $y, -x + y, z - \frac{1}{6}$.

Data collection: XSCANS (Siemens, 1996); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: Mercury (Macrae *et al.*, 2006); software used to prepare material for publication: SHELXL97.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: JH2225).

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supplementary materials

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(-)-(S)-N,N'-Bis[1-(1-naphthyl)ethyl]oxalamide

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Comment

Earlier, we have focused our attention on dicarboxamides (Bernès *et al.*, 2008), mostly due to their versatile and interesting properties. In continuation of this work, we synthesized the title chiral compound, under the solvent-free approach, because the reactions occur under mild conditions and usually require easier workup procedures and simpler equipment. Likewise, reducing the use of organic solvents and minimizing the formation of waste are worth-considering points to keep in mind by using this protocol (Jeon *et al.*, 2005; Noyori, 2005).

The title molecule belongs to the oxalamide family, a well studied class of compounds, which are useful in many areas (*e.g.* Montero-Vázquez *et al.*, 2008). The molecule is placed on a twofold axis, passing by the midpoint of the central C1—C1ⁱ bond (symmetry code *i*: $x-y, -y, 1-z$). The twofold axis is perpendicular to the mean plane of the core oxalamide group. In contrast to other oxalamide derivatives (*e.g.* Zhang *et al.*, 2006) the oxalamide group in the title compound is not planar. As a consequence, *trans* angles O1—C1—C1ⁱ—O1ⁱ and N2—C1—C1ⁱ—N2ⁱ deviate significantly from 180°. N atoms are substituted by chiral groups including naphthyl cycles, which make a dihedral angle of 43.76 (8)° (Fig. 1).

The C₂-symmetric molecules are connected in the crystal through N2—H2...O1ⁱⁱ hydrogen bonds (symmetry code *ii*: $y, -x+y, z-1/6$), which generate R₂²(10) ring motifs (Fig. 2). Such motifs have been observed in related chiral (Štefanić *et al.*, 2003) and achiral (Lee & Wang, 2007) oxalamides, but gave different supramolecular structures, depending of the ability of terminal groups to be involved in hydrogen bonds. In the case of the title oxalamide, hydrogen bonds form a supramolecular structure based on a single stranded helix using the screw axis 6₁ as backbone (Fig. 2, inset). The molecular and supramolecular axes are thus perpendicular. Although the space group is enantiomorphic, the helicity of the supramolecular structure can be assigned, since the chirality of the asymmetric unit is known (Ha & Allewell, 1997). The *S* configuration of chiral center C3 affords right-handed helix oriented along [001]. It is worth noting that such chiral supramolecular structures cannot be achieved for centrosymmetric oxalamide derivatives (Zhang *et al.*, 2006; Lee, 2010).

The crystal structure of the title compound is build up on densely packed parallel Δ helix, which interact through π - π contacts involving terminal naphthyl groups. The shortest intermolecular separation between symmetry-related benzene rings is 3.623 (4) Å [*Cg*...*Cg*ⁱⁱⁱ, where *Cg* is the centroid of ring C9...C14 and *iii* is symmetry code: $1-y, 1-x, 5/6-z$]. This contact should however be regarded as a secondary interaction compared to hydrogen bonds forming the one-dimensional supramolecular structure. Although the ring approach is short, constraints induced by molecular conformation reduce the efficiency of such contacts. For instance, π systems involved in π - π contacts are not parallel, making a dihedral angle of 11.7 (2)°.

Experimental

Under solvent-free conditions, a mixture of oxalyl chloride (0.2 g, 1.5 mmol) and (*S*)-(-)-1-(1-naphthyl)ethylamine (0.53 g, 3.0 mmol) in a 1:2 molar ratio were mixed at room temperature, giving a white solid. The crude was recrystallized twice

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from CH_2Cl_2 , affording colorless crystals of the title compound. Yield 96%; m.p. 240–242 °C. Spectroscopic data: $[\alpha]_D^{25} = -10.5$ (c 1, CHCl_3). FT—IR (KBr): 3450 cm^{-1} (NH), 1650 cm^{-1} (CO). ^1H NMR (400 MHz, CDCl_3/TMS): $\delta = 1.5\text{--}1.7$ (d, 6H, CHCH₃), 4.1 (br s, 2H, NH), 5.1 (q, 2H, CHCH₃), 7.3–8.1 (m, 14 H, Ar); ^{13}C NMR (100 MHz, CDCl_3/TMS) $\delta = 23.3$ (CCH₃), 46.9 (CHCH₃), 122.7 (Ar), 125.1 (Ar), 125.6 (Ar), 127.9 (Ar), 128.9 (Ar), 128.4 (Ar), 133.7 (Ar), 138.9 (Ar), 144.3 (Ar), 158.5 (C=O). MS—EI: $m/z = 396$ (M^+).

Refinement

All C-bonded H atoms were placed in idealized positions and refined as riding to their carrier C atoms, with bond lengths fixed to 0.93 (aromatic CH), 0.96 (methyl CH₃), and 0.98 Å (methine CH). Atom H2 bonded to N2 was found in a difference map and refined freely, although N—H bond length was restrained to 0.91 (1) Å. Isotropic displacement parameters were calculated as $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{carrier atom})$ for the methyl group and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier atom})$ otherwise. The absolute configuration was assigned from the known configuration of the chiral amine used as starting material, and measured Friedel pairs (705) were merged.

Figures

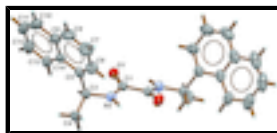


Fig. 1. The title molecule with displacement ellipsoids for non-H atoms shown at the 30% probability level. Non labeled atoms are generated by symmetry operator $x-y, -y, 1-z$.

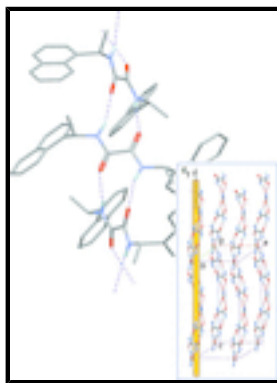


Fig. 2. Hydrogen bonds linking molecules in the [001] direction (dashed bonds). The inset represents Δ helix formed by hydrogen bonds along the screw axis 6_1 . For the sake of clarity, only oxalamide atoms are represented, and one 6_1 axis is shown (yellow backbone).

(-)-(S)-N,N'-Bis[1-(1-naphthyl)ethyl]ethanediamide

Crystal data

$\text{C}_{26}\text{H}_{24}\text{N}_2\text{O}_2$

$M_r = 396.47$

Hexagonal, $P6_122$

Hall symbol: P 61 2 (0 0 -1)

$a = 11.4489$ (11) Å

$c = 28.350$ (4) Å

$V = 3218.2$ (7) Å³

$D_x = 1.227\text{ Mg m}^{-3}$

Melting point: 513 K

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 67 reflections

$\theta = 4.1\text{--}11.9^\circ$

$\mu = 0.08\text{ mm}^{-1}$

$T = 298\text{ K}$

$Z = 6$ Prism, colourless
 $F(000) = 1260$ $0.40 \times 0.22 \times 0.20$ mm

Data collection

Siemens P4 diffractometer $R_{\text{int}} = 0.057$
 Radiation source: fine-focus sealed tube $\theta_{\text{max}} = 25.1^\circ$, $\theta_{\text{min}} = 2.1^\circ$
 graphite $h = -13 \rightarrow 2$
 ω scans $k = -1 \rightarrow 13$
 5314 measured reflections $l = -33 \rightarrow 1$
 1208 independent reflections 3 standard reflections every 97 reflections
 730 reflections with $I > 2\sigma(I)$ intensity decay: 1%

Refinement

Refinement on F^2 Secondary atom site location: difference Fourier map
 Least-squares matrix: full Hydrogen site location: inferred from neighbouring sites
 $R[F^2 > 2\sigma(F^2)] = 0.043$ H atoms treated by a mixture of independent and constrained refinement
 $wR(F^2) = 0.138$ $w = 1/[\sigma^2(F_o^2) + (0.0649P)^2 + 0.2213P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $S = 1.11$ $(\Delta/\sigma)_{\text{max}} < 0.001$
 1208 reflections $\Delta\rho_{\text{max}} = 0.12 \text{ e } \text{\AA}^{-3}$
 141 parameters $\Delta\rho_{\text{min}} = -0.14 \text{ e } \text{\AA}^{-3}$
 1 restraint Extinction correction: *SHELXL97* (Sheldrick, 2008),
 $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
 0 constraints Extinction coefficient: 0.011 (2)
 Primary atom site location: structure-invariant direct methods

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.1760 (3)	0.1496 (2)	0.53227 (7)	0.0718 (8)
C1	0.1517 (3)	0.0760 (3)	0.49767 (11)	0.0539 (8)
N2	0.1898 (3)	0.1213 (3)	0.45411 (9)	0.0594 (8)
H2	0.168 (3)	0.058 (3)	0.4311 (9)	0.071*
C3	0.2678 (3)	0.2653 (3)	0.44315 (11)	0.0589 (9)
H3A	0.3249	0.3110	0.4705	0.071*
C4	0.3604 (4)	0.2880 (4)	0.40144 (13)	0.0852 (13)
H4B	0.4194	0.2535	0.4088	0.128*
H4C	0.4131	0.3828	0.3949	0.128*
H4D	0.3072	0.2420	0.3743	0.128*
C5	0.1787 (4)	0.3254 (4)	0.43491 (11)	0.0632 (10)
C6	0.0662 (4)	0.2582 (5)	0.40749 (15)	0.0878 (12)
H6A	0.0436	0.1736	0.3957	0.105*

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C7	-0.0158 (6)	0.3123 (7)	0.39661 (18)	0.1117 (17)
H7A	-0.0907	0.2651	0.3773	0.134*
C8	0.0142 (6)	0.4343 (7)	0.4144 (2)	0.1100 (17)
H8B	-0.0420	0.4692	0.4079	0.132*
C9	0.1289 (6)	0.5082 (5)	0.44246 (16)	0.0855 (13)
C10	0.1624 (8)	0.6363 (6)	0.4601 (2)	0.119 (2)
H10B	0.1074	0.6721	0.4529	0.143*
C11	0.2721 (8)	0.7080 (6)	0.4873 (2)	0.126 (2)
H11D	0.2911	0.7913	0.4993	0.151*
C12	0.3575 (6)	0.6564 (5)	0.49739 (19)	0.1110 (17)
H12B	0.4343	0.7068	0.5156	0.133*
C13	0.3293 (5)	0.5332 (4)	0.48084 (13)	0.0781 (12)
H13B	0.3868	0.5003	0.4881	0.094*
C14	0.2145 (4)	0.4552 (4)	0.45291 (12)	0.0660 (10)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0854 (19)	0.0634 (16)	0.0510 (13)	0.0256 (14)	0.0089 (12)	-0.0117 (12)
C1	0.055 (2)	0.0567 (19)	0.0495 (17)	0.0279 (17)	0.0013 (16)	-0.0044 (19)
N2	0.071 (2)	0.0555 (19)	0.0477 (15)	0.0284 (16)	0.0035 (15)	-0.0042 (13)
C3	0.063 (2)	0.056 (2)	0.0540 (18)	0.0272 (19)	0.0031 (17)	-0.0023 (16)
C4	0.088 (3)	0.084 (3)	0.081 (2)	0.041 (3)	0.032 (2)	0.011 (2)
C5	0.068 (3)	0.068 (3)	0.0532 (18)	0.033 (2)	0.0073 (19)	0.0067 (19)
C6	0.087 (3)	0.093 (3)	0.087 (3)	0.048 (3)	-0.015 (3)	-0.001 (3)
C7	0.097 (4)	0.136 (5)	0.113 (4)	0.067 (4)	-0.017 (3)	0.014 (4)
C8	0.108 (4)	0.136 (5)	0.120 (4)	0.087 (4)	0.018 (4)	0.035 (4)
C9	0.104 (4)	0.087 (3)	0.081 (3)	0.060 (3)	0.034 (3)	0.026 (3)
C10	0.175 (7)	0.104 (4)	0.116 (4)	0.098 (5)	0.066 (4)	0.037 (4)
C11	0.178 (7)	0.073 (4)	0.128 (5)	0.065 (4)	0.061 (5)	0.013 (3)
C12	0.129 (5)	0.065 (3)	0.110 (3)	0.027 (3)	0.030 (4)	-0.003 (3)
C13	0.089 (3)	0.058 (3)	0.075 (2)	0.028 (2)	0.015 (2)	-0.002 (2)
C14	0.078 (3)	0.063 (2)	0.0587 (19)	0.036 (2)	0.025 (2)	0.014 (2)

Geometric parameters (\AA , $^\circ$)

O1—C1	1.231 (4)	C7—C8	1.358 (7)
C1—N2	1.326 (4)	C7—H7A	0.9300
C1—C1 ⁱ	1.512 (7)	C8—C9	1.400 (7)
N2—C3	1.463 (4)	C8—H8B	0.9300
N2—H2	0.911 (10)	C9—C10	1.409 (7)
C3—C5	1.506 (5)	C9—C14	1.418 (6)
C3—C4	1.522 (5)	C10—C11	1.348 (8)
C3—H3A	0.9800	C10—H10B	0.9300
C4—H4B	0.9600	C11—C12	1.401 (7)
C4—H4C	0.9600	C11—H11D	0.9300
C4—H4D	0.9600	C12—C13	1.363 (6)
C5—C6	1.366 (5)	C12—H12B	0.9300

C5—C14	1.424 (5)	C13—C14	1.406 (6)
C6—C7	1.394 (6)	C13—H13B	0.9300
C6—H6A	0.9300		
O1—C1—N2	123.8 (3)	C8—C7—C6	119.6 (5)
O1—C1—C1 ⁱ	121.4 (4)	C8—C7—H7A	120.2
N2—C1—C1 ⁱ	114.8 (3)	C6—C7—H7A	120.2
C1—N2—C3	122.3 (3)	C7—C8—C9	120.8 (5)
C1—N2—H2	117 (2)	C7—C8—H8B	119.6
C3—N2—H2	121 (2)	C9—C8—H8B	119.6
N2—C3—C5	112.1 (3)	C8—C9—C10	121.0 (6)
N2—C3—C4	109.8 (3)	C8—C9—C14	120.0 (4)
C5—C3—C4	112.0 (3)	C10—C9—C14	119.0 (5)
N2—C3—H3A	107.6	C11—C10—C9	121.5 (6)
C5—C3—H3A	107.6	C11—C10—H10B	119.2
C4—C3—H3A	107.6	C9—C10—H10B	119.2
C3—C4—H4B	109.5	C10—C11—C12	119.6 (6)
C3—C4—H4C	109.5	C10—C11—H11D	120.2
H4B—C4—H4C	109.5	C12—C11—H11D	120.2
C3—C4—H4D	109.5	C13—C12—C11	120.8 (6)
H4B—C4—H4D	109.5	C13—C12—H12B	119.6
H4C—C4—H4D	109.5	C11—C12—H12B	119.6
C6—C5—C14	119.4 (4)	C12—C13—C14	120.9 (5)
C6—C5—C3	119.6 (3)	C12—C13—H13B	119.6
C14—C5—C3	120.9 (3)	C14—C13—H13B	119.6
C5—C6—C7	122.0 (5)	C13—C14—C9	118.2 (4)
C5—C6—H6A	119.0	C13—C14—C5	123.7 (4)
C7—C6—H6A	119.0	C9—C14—C5	118.1 (4)
O1—C1—N2—C3	1.3 (5)	C8—C9—C10—C11	179.7 (5)
O1—C1—C1 ⁱ —O1 ⁱ	164.3 (5)	C14—C9—C10—C11	-1.2 (7)
C1 ⁱ —C1—N2—C3	-178.1 (2)	C9—C10—C11—C12	1.7 (8)
C1—N2—C3—C5	-86.9 (4)	C10—C11—C12—C13	-1.4 (8)
C1—N2—C3—C4	148.0 (3)	C11—C12—C13—C14	0.5 (7)
N2—C3—C5—C6	-44.7 (4)	C12—C13—C14—C9	0.0 (5)
N2—C1—C1 ⁱ —N2 ⁱ	163.2 (5)	C12—C13—C14—C5	-179.4 (4)
C4—C3—C5—C6	79.2 (4)	C8—C9—C14—C13	179.4 (4)
N2—C3—C5—C14	139.2 (3)	C10—C9—C14—C13	0.3 (5)
C4—C3—C5—C14	-96.9 (4)	C8—C9—C14—C5	-1.2 (5)
C14—C5—C6—C7	-0.3 (6)	C10—C9—C14—C5	179.8 (4)
C3—C5—C6—C7	-176.5 (4)	C6—C5—C14—C13	-179.0 (3)
C5—C6—C7—C8	-1.5 (8)	C3—C5—C14—C13	-2.9 (5)
C6—C7—C8—C9	1.9 (8)	C6—C5—C14—C9	1.6 (5)
C7—C8—C9—C10	178.5 (5)	C3—C5—C14—C9	177.7 (3)
C7—C8—C9—C14	-0.6 (7)		

Symmetry codes: (i) $x-y, -y, -z+1$.

Hydrogen-bond geometry (Å, °)

D—H \cdots A	D—H	H \cdots A	D \cdots A	D—H \cdots A
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N2—H2 \cdots O1ⁱⁱ

0.91 (1)

2.06 (2)

2.931 (3)

161 (3)

Symmetry codes: (ii) $y, -x+y, z-1/6$.

Fig. 1

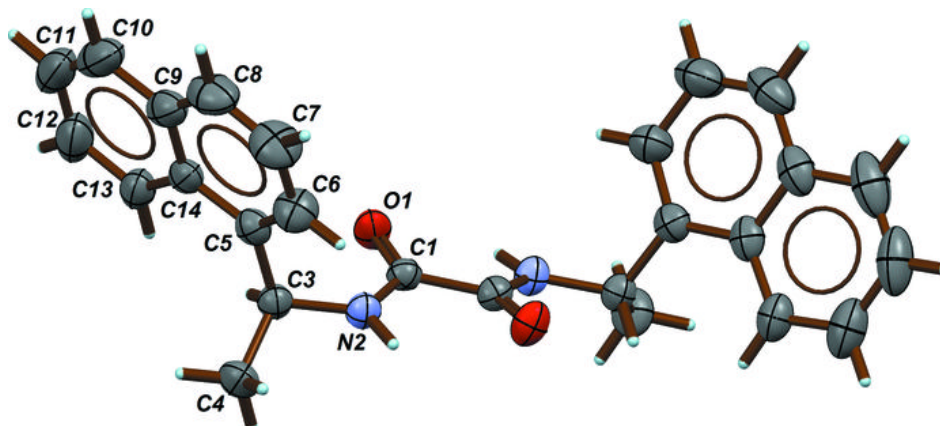


Fig. 2

