Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Diethyl *N*,*N*′-cyclohexane-1,4-diyldioxalamate

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Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.004 Å
R factor = 0.073
wR factor = 0.177
Data-to-parameter ratio = 15.3

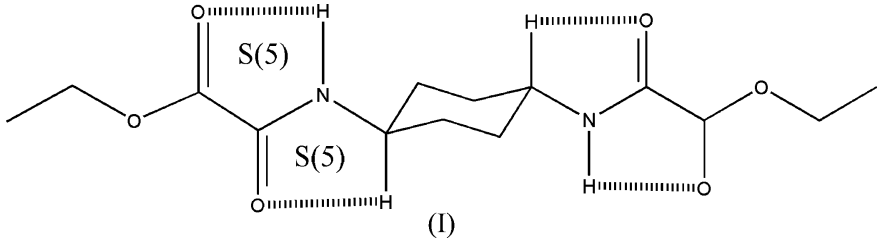
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 10 August 2005
Accepted 12 August 2005
Online 20 August 2005

The title compound, $C_{14}H_{22}N_2O_6$, possesses C_i symmetry and crystallizes with one half-molecule in the aymmetric unit. The structure can be described as cyclohexyldiamide singly bonded to two ethyl carboxylate groups. The supramolecular structure is achieved through intermolecular hard N—H···O hydrogen-bonding interactions involving only the amide group. The full hydrogen-bonding network is described by the $C_2^2(8)[S(5)S(5)C(4)]$ motif that develops along the c-axis direction.

Comment

A limited number of crystalline structures bearing aliphatic oxalamates (also named as oxamates) are known (Cambridge Structural Database, April 2004 Version; Allen, 2002), in spite of the fact that they have also been used in the synthesis of oxalamides (Toda *et al.*, 1986) and oxalic acid derivatives which exhibit inhibitory protein tyrosine phosphatase activity (Andersen *et al.*, 2002). As a continuation of our efforts to use the oxalyl group as a synthon in the design of molecular clefts (Padilla-Martínez *et al.*, 2003, 2005), the crystalline structure of diethyl *N*,*N*′-1,4-cyclohexyldioxalamate, (I), is described. Compound (I) forms monoclinic crystals ($P2_1/c$, Z = 2) with the molecule disposed about a crystallographic centre of symmetry.



(I)

The molecular structure of (I) and atom-numbering scheme are shown in Fig. 1 and a summary of bond lengths and angles is listed in Table 1. The central cyclohexyl group adopts a chair

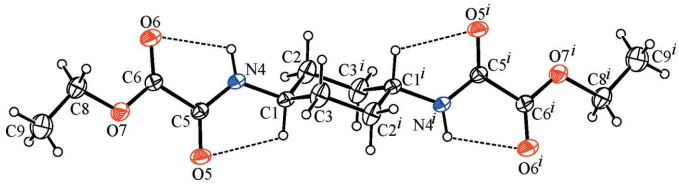


Figure 1
Plot of the molecular structure of the title compound, with displacement ellipsoids drawn at the 30% probability level for non-H atoms, showing intramolecular hydrogen-bonding interactions as dashed lines. [Symmetry code: (i) −*x*, −*y*, −*z*.]

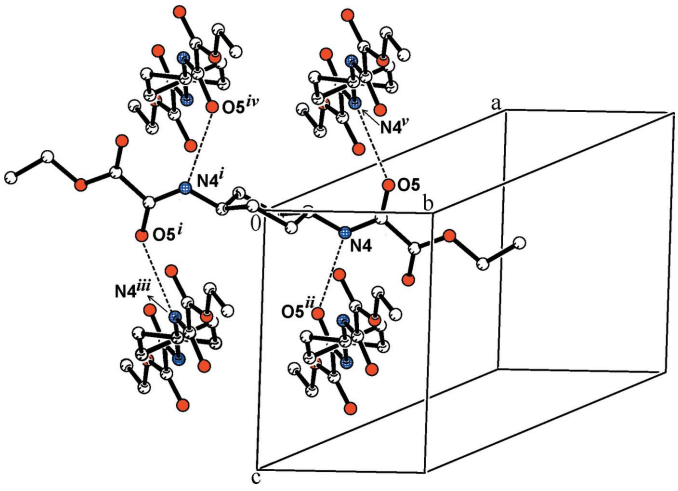


Figure 2
The supramolecular arrangement of the title compound by N4—H4···O5 intermolecular hydrogen-bonding interactions (dashed lines). [Symmetry codes: (i) $-x, -y, -z$; (ii) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (iii) $-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (iv) $-x, -\frac{1}{2}+y, -\frac{1}{2}-z$; (v) $x, \frac{1}{2}-y, -\frac{1}{2}+z$.]

conformation bearing the two ethyl oxalyl groups in equatorial position. The N4—C1 bond length is 1.457 (3) Å and the N4—C5 bond length is 1.321 (3) Å, this latter being significantly shorter than the values found in other aliphatic [1.3603 (19) Å; Martínez-Martínez *et al.*, 2004] or even aromatic [1.348 (3) Å; García-Báez *et al.*, 2003] ethyl oxalamates, suggesting a strong electron delocalization from atom N4 to the C5═O5 carbonyl group. This result is supported by the longer bond length exhibited by the amide O5═C5 carbonyl group of 1.221 (3) Å relative to that of the ester O6═C6 carbonyl group of 1.193 (3) Å, which makes the former carbonyl the best hydrogen-bonding acceptor (see below). Both carbonyl groups adopt an antiperiplanar arrangement with the torsion angle O5—C5—C6—O6 equal to −174.9 (3)°, while the oxalyl C5—C6 bond length is 1.538 (4) Å, almost exactly the value for a Csp^3—Csp^3 single bond (Dewar & Schmeizing, 1968). Thus, (I) can be considered as being composed of a cyclohexyldiamide group bonded to two ethyl carboxylate groups, as observed for aromatic ethyl oxalamates (Padilla-Martínez *et al.*, 2001). The oxamide O5═C5 carbonyl group is almost eclipsed with respect to the C1—H1 bond. Furthermore, the C1···O5 distance of 2.849 (3) Å (C1—H1*A*···O5 = 102°) suggests the formation of a weak intermolecular hydrogen-bonding interaction C1—H1*A*···O5 (Desiraju, 1996), while the primary hard interaction N4—H4···O6 [N4···O6 = 2.703 (3) Å and N4—H4···O6 = 109 (2)°] completes the intramolecular hydrogen-bonding scheme as an *S*(5)*S*(5) motif (Bernstein *et al.*, 1995) (Fig. 1), which is characteristic of oxalamates and oxamides derived from primary amines (Nuñez *et al.*, 1988; García-Báez *et al.*, 2003; Padilla-Martínez *et al.*, 2003). Hydrogen-bonding geometries are listed in Table 2. Each molecule interacts with four neighbouring molecules through N4—H4···O5 strong intermolecular hydrogen bonding [N4···O5 = 3.026 (3) Å and N4—H4···O5 = 160°] (Fig. 2), forming antiparallel four-membered chains which develop along the *c*-axis direction.

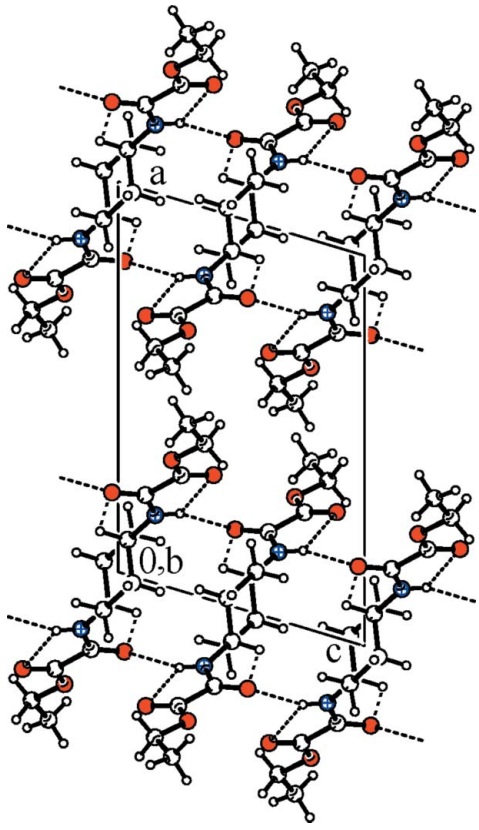


Figure 3
The hydrogen-bonding (dashed lines) network, viewed along the *c* axis. Bifurcated O6···H4···O5 hydrogen-bonding interactions are shown and a $C_2^2(8)[S(5)S(5)C(4)]$ motif is observed.

Amide atom H4 is involved in a bifurcated hydrogen-bonding interaction O6···H4···O5 (Steiner, 2002). The full hydrogen-bonding network is described by the graph-set descriptor $C_2^2(8)[S(5)S(5)C(4)]$ (Fig. 3).

Experimental

The title compound was prepared from *trans*-1,4-diaminocyclohexane (500 mg, 4.4 mmol) and ethyl chlorooxoacetate (0.94 ml, 8.8 mmol), according to reported procedures (Martínez-Martínez *et al.*, 1998), to yield, after crystallization from ethyl acetate, 890 mg (90%) of a white solid (m.p. 478.2 K). IR (KBr, cm^{-1}): 3257 (NH), 1729, 1678 (CO); ^{1}H NMR (300.08 MHz, DMSO-d_6): δ 6.97 (*d*, 1H, ^3J = 8.4 Hz, NH), 4.34 (*q*, 2H, ^3J = 7.2 Hz, OCH_2), 3.78 (*m*, 1H, NCH), 2.08, 1.64 (*a*, 2H each, CH_2 cy), 1.39 (*t*, 3H, ^3J = 7.0 Hz, CH_3); ^{13}C NMR (75.46 MHz, DMSO-d_6): δ 161.0 (COO), 156.0 (CON), 63.6 (OCH_2), 48.2 (NCH), 31.2 (CH_2 cy), 14.0 (CH_3). Crystals suitable for X-ray analysis were obtained after slow crystallization from ethyl acetate.

Crystal data

$C_{14}H_{22}N_2O_6$
M_r = 314.34
Monoclinic, $P2_1/c$
a = 13.145 (3) Å
b = 7.2093 (15) Å
c = 8.6617 (17) Å
β = 106.709 (3)°
V = 786.2 (3) Å^3
Z = 2
D_x = 1.328 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 600 reflections
θ = 20–25°
μ = 0.10 mm^{-1}
T = 100 (2) K
Block, colourless
0.20 × 0.15 × 0.09 mm

Data collection

Bruker SMART area-detector diffractometer	1387 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.030$
Absorption correction: none	$\theta_{max} = 26.0^\circ$
7841 measured reflections	$h = -16 \rightarrow 16$
1546 independent reflections	$k = -8 \rightarrow 8$
	$l = -10 \rightarrow 10$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0721P)^2 + 0.4735P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.073$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.177$	$\Delta\rho_{max} = 0.26$ e Å^{-3}
$S = 1.19$	$\Delta\rho_{min} = -0.17$ e Å^{-3}
1546 reflections	
101 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

O5—C5	1.221 (3)	N4—C1	1.457 (3)
O6—C6	1.193 (3)	N4—C5	1.321 (3)
O7—C6	1.306 (4)	C5—C6	1.538 (4)
C1—N4—C5	123.37 (19)	O5—C5—C6	121.6 (2)
N4—C5—C6	112.4 (2)	O6—C6—C5	122.9 (3)
O5—C5—N4	126.0 (2)		
O5—C5—C6—O6	−174.9 (3)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4···O6	0.88	2.32	2.703 (3)	106
N4—H4···O5^{i}	0.88	2.19	3.026 (3)	160
C1—H1A···O5	1.00	2.48	2.849 (3)	102

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

All H atoms were included in calculated positions, with C—H = 0.98–1.00 Å and N—H = 0.86 Å. They were refined using the riding-model approximation, with $U_{iso} = 1.2U_{eq}$ ($1.5U_{eq}$ for methyl) of the carrier atom.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXL97* (Sheldrick, 1997) and *WinGX2003* (Farrugia, 1999).

This work was supported by CGPI–IPN (Coordinación General de Posgrado e Investigación del Instituto Politécnico Nacional).

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